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Stabilization and Remediation of Arsenic-Contaminated Soil: Fly Ash-Based Technology for Industrial Site Restoration

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Abstract: Arsenic contamination of various environmental components poses a serious threat to human and animal health. Soil As contamination is particularly hazardous, as soil is a vital pathway to the food chain. We conducted experiments on soil from a typical pharmaceutical and chemical industry relocation site in Hubei Province, focusing on modification using fly ash through mechanical and chemical mechanisms. We subjected varying proportions of lime, ferrous sulfate, and fly ash to mechanical ball milling and used these mixtures to perform remediation of arsenic-contaminated soil and site restoration. Our findings are as follows: in soil culture experiments, the As stabilization efficiency reached 90% within 90 days with ferrous salt-modified fly ash. In actual site restoration, As-stabilization efficiency exceeded 95% across different soil depths within 30 days, demonstrating significant stabilization effects. Optimal modified dosages were determined as 2% ferrous sulfate and 2% fly ash. After stabilization, As in the soil primarily existed in amorphous iron-aluminum oxide-bound (F3) and crystalline iron-aluminum oxide-bound (F3 + F4) and residual (F5) states. Fluctuations in the moisture content and pH mainly activated F3 and F4, transitioning them into exchangeable (F1) and surface-adsorbed (F2) states. Arsenic leaching was predominantly associated with the F1 form. Fly ash-based restoration technology demonstrates promising capabilities in waste treatment and pollution control, offering significant potential for widespread application.

Keywords: fly ash; soil remediation; stabilization; soil arsenic morphology; site restoration

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Citation: Yu, J.; Bao, J.; Su, Q.; Zhang, W.; Ye, B.; Zhou, X.; Li, H.; Li, X. Stabilization and Remediation of Arsenic-Contaminated Soil: Fly Ash-Based Technology for Industrial Site Restoration. *Sustainability* **2024**, *16*, 8132. https://doi.org/10.3390/su16188132

Academic Editor: Mariusz Gusiatin

Received: 12 June 2024
Revised: 2 September 2024
Accepted: 3 September 2024
Published: 18 September 2024

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1. Introduction

The rapid urbanization and industrial modernization in China have led to the transformation of traditional industrial enterprises, resulting in the abandonment of numerous pollution sites in urban and surrounding areas. According to incomplete statistics from the Ministry of Ecology and Environment, there are more than 500,000 contaminated sites, with a single area larger than 10,000 m^2 in China [1]. The 2014 National Soil Pollution Status Survey Bulletin highlighted significant soil environmental issues in abandoned industrial and mining sites, with 34.9% of these sites exceeding the permissible pollution limits due to industrial waste and 2.7% of the soil samples indicating As contamination [2]. Research reveals that the area of soil and groundwater in China with As concentrations exceeding 10 $\mu g \cdot L^{-1}$ has expanded to 580,000 km^2, with approximately 20 million residents inhabiting high-risk areas of soil As pollution. These regions include the Tarim Basin in Xinjiang, Inner Mongolia, Heihe in Gansu, Henan, and Shandong [3].

Soil pollution risk mitigation can be achieved through various methods, including reducing pollutant concentrations, controlling the migration and diffusion of pollutants, and minimizing exposure to environmentally sensitive receptors. Among these methods, soil stabilization technology offers advantages such as minimal secondary pollution,

economic feasibility, short implementation time, and consistent restoration effects. Consequently, it has gained significant attention and widespread application in the field of soil remediation. In 2018, stabilization and solidification methods were utilized in 48.5% of cases of engineering application [4–7]. Previous studies have highlighted the critical role of components such as activated carbon, red mud, iron, aluminum, and manganese in immobilizing heavy metals in soil [8–10]. Fly ash, a byproduct of coal-fired power plants, possesses characteristics conducive to effective soil stabilization. Its components, including Al and Si, react with magnetic iron minerals at high temperatures to form a glass-phase magnetic bead structure characterized by uniform particle size, high porosity, and large specific surface area. With appropriate treatment, fly ash shows promising potential for resource utilization [8–10]. Furthermore, the reactivity of silicate components such as silicon dioxide and alumina in fly ash can be enhanced through mechanical grinding and alkali (e.g., with lime), acid, and salt activations. This leads to hydration reactions upon contact with water, resulting in the formation of various crystalline products such as hydrated calcium silicate or hydrated aluminum silicate [11]. Through the stimulation of the surface reactivity of fly ash, heavy metal ions can be immobilized within new crystal structures, thereby reducing their likelihood of remigrating into the environment and significantly enhancing the stabilization capacity of heavy metals [12–15].

Previous studies have primarily focused on applying stabilization technology to address soil heavy metal pollution at industrial sites, neglecting the investigation of alterations in the heavy metal distribution, concentration, and form following soil stabilization. Additionally, assessing the leaching potential for different forms of stabilized heavy metals has been overlooked. Understanding the changes in the concentrations of diverse heavy metal forms and their environmental processes, along with investigating leaching mechanisms of distinct forms of As in soil, is crucial for achieving long-term stability in soil pollution remediation efforts [4,12,16–18].

In this study, lime and ferrous sulfate were added to the fly ash during the mechanical grinding process using a ball mill, resulting in the development of the iron + fly ash co-modification treatment system. The efficiency of stabilization was assessed through soil processes. The optimization of the modification combination was achieved through experiments on fly ash stimulation factors. Alterations in the distribution and concentration of As chemical forms were monitored during the soil stabilization and oscillating leaching processes, enabling the investigation of stabilization and reactivation processes, as well as the leaching potential of different As forms. The feasibility of employing fly ash as an eco-friendly remediation agent was confirmed through the structural and compositional characterization of fly ash. Implementation of the remediation system at real-world As pollution sites provided valuable experience and technical support for long-term stability research on soil As pollution remediation.

2. Materials and Methods

2.1. Experimental Materials

Soil samples were collected from a vacated pharmaceutical chemical site in Hubei Province, China (115°59′50.31″ E, 29°54′7.49″ N). A preliminary investigation [19], assessing contamination severity using the Muller index [20], identified 30 kg of heavily contaminated fresh soil at a depth of 0–20 cm. These samples were carefully collected and stored in nylon bags. After natural air drying, the soil was crushed using a hammer mill, sieved through a 100-mesh screen, and homogenized using a planetary mixer at 50 r·min^{-1} for 15 min. This process yielded a homogeneous polluted soil sample for further testing. The soil's basic physicochemical properties and the As concentration of the soil are detailed in Table 1.

Analytical-grade calcium carbonate ($CaCO_3$) and iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from commercial sources. The fly ash, meeting the specifications outlined in "Fly Ash for Cement and Concrete" (GB/T 664—2011) [21], was a weakly magnetic powder with a pH of 10.19.

Table 1. Physical and chemical properties of soil.

Soil Type	Natural Moisture Content (%)	Soil Organic Matter ($g \cdot kg^{-1}$)	pH	Total Arsenic ($mg \cdot kg^{-1}$)	Hexachlorocyclohexane ($mg \cdot kg^{-1}$)	Dichloro-Diphenyl-Trichloroethane ($mg \cdot kg^{-1}$)
Clay	31.4	15.6	6.16	2749	0.002	0.014

2.2. Structure and Phase Morphology of Fly Ash

The surface structure of the material was examined using an SU-8010 field-emission scanning electron microscope (SEM, Hitachi, Tokyo, Japan). Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS) configured in the SEM. Phase composition and crystalline structure were analyzed using a D8 Advance X-ray diffractometer (XRD; Bruker AXS, Karlsruhe, Germany). The specific conditions for the XRD analysis were as follows: CuKα radiation, testing voltage of 40 kV, testing current of 40 mA, scanning angle range of 5° to 85°, wavelength of 0.02°, and scanning speed of $1° \cdot min^{-1}$.

2.3. Influence of Varying Activation Conditions of Fly Ash on Arsenic Stabilization

Fly ash was activated using a combination of mechanical milling and various chemical stimuli, including alkali (lime), salt (ferrous sulfate), and a combination of both. A control group without fly ash was subjected to similar treatments. The experimental design included five distinct groups: (1) untreated dry control (CK) and control subjected solely to moisture content (MC) treatment (CW), (2) lime and ferrous sulfate activation (AB), (3) ferrous sulfate and fly ash activation (BC), (4) lime and fly ash activation (AC), and (5) lime, ferrous sulfate, and fly ash activation (ABC). Each experiment was replicated three times. Based on previous experimental results and the literature [22–27], the mass of the soil is 600 g, the quantity of each component added to the experimental groups was standardized to 2% (w/w) of the soil mass.

Experimental procedure: The experimental groups underwent mechanical mixing using a mini planetary ball mill (PM400, RETSCH, Haan, Germany). The grinding ball-to-material ratio was maintained at 10:1, with a revolution speed of 120 $r \cdot min^{-1}$ and a milling time of 15 min. Subsequently, the homogenized soil (600 g) was placed in a 1 L beaker. After the addition of the designed reagents, the beaker was sealed with HDPE film and placed on a magnetic stirrer for gentle stirring to ensure thorough mixing of the soil and reagents. To maintain a stable MC, small holes were evenly punctured on the sealed film to facilitate periodic leaching using sterile water.

2.4. Fly Ash Activation Using Various Concentrations of Ferrous Sulfate for Arsenic Stabilization

The fly ash addition was kept constant at 2% (w/w) for various concentrations of ferrous sulfate to enhance its activation. Ten experimental groups were established with a gradient of ferrous sulfate concentrations of 0, 0.5, 0.8, 1.0, 1.5, 1.8, 2.0, 2.2, 2.4, and 2.6% (w/w). The specific experimental procedures were the same as those described in Section 2.3, and the stabilization period was 60 days.

2.5. Analysis and Testing

The As concentration in the soil leachate was determined according to the "Solid Waste Leaching Toxicity Leaching Method Sulfuric Acid Nitric Acid Method" (HJ/T299-2007) [28]. A mixture of concentrated sulfuric and nitric acids in a mass ratio of 2:1 was added dropwise into ultrapure water (~2 drops of the mixed solution per 1 L of water) to achieve a pH of 3.20 ± 0.05 as extractant and was set aside for later use. A quantity of 20 g of contaminated soil was placed in an extraction bottle. A quantity of 200 mL of extractant was added with a liquid-to-solid ratio of 10:1 (v/w), and the bottle was tightly capped and placed in a shaking incubator at 30 $r \cdot min^{-1}$ at 22 °C for 18 h. The sample was taken out and allowed to settle into layers; then, the supernatant liquid was filtered using a 0.45 μm filter, collected into a 10 mL centrifuge tube, and stored at 4 °C for testing.

The determination of soil As forms followed the continuous extraction method proposed by Wenzel et al. [29], using 0.05 mol·L^{-1} of $(NH_4)_2SO_4$, $NH_4H_2PO_4$, ammonium oxalate, ascorbic acid, etc. to extract exchangeable As (F1), surface-adsorbed As (F2), amorphous iron-aluminum oxide-bound As (F3), crystalline iron-aluminum oxide-bound As (F4), and residual As (F5). The extraction liquids were stored at 4 °C for testing. The determination of soil pH was based on the "Determination of Soil pH Value Potentiometric Method" (HJ 962-2018) [30]. The determination of As was based on the "Determination of 12 Metal Elements in Soil and Sediment Nitric Acid Digestion-Inductively Coupled Plasma Mass Spectrometry Method" (HJ803-2016) [31].

2.6. Quality Assurance and Quality Control

All the samples were placed in a low-temperature incubator with blue ice and transported to the laboratory for analysis. Before processing each batch of samples, parallel samples with batch numbers were prepared, comprising 10% of the total samples. Calibration curves and standard substances (GBW07930 and GBW07938) were used to check the stability of the instrument.

2.7. Evaluation of Remediation Effectiveness

For an easy comparison of the As-stabilization ability of fly ash under varying activation combinations, the stabilizing efficiency (%) and degree of activation (%) of the remediation agent on soil As were defined as follows:

$$\text{Stabilization efficiency} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$\text{Activation level} = \frac{C_b - C_a}{C_0} \times 100\% \quad (2)$$

where C_0, C_e, C_a, and C_b represent the As concentration in the leachates from the control soil with the same MC, at the end of the remediation process, in the soil after adding the remediation agent on day a, and in the soil after adding the remediation agent on day b in mg·kg^{-1}, respectively. Here, $0 < a < b$.

2.8. Remediation of the Actual Site

Heavily contaminated soil was selected for stabilization and remediation based on the comprehensive experimental results and actual conditions of the site. An area of 200 m^2 of contaminated land was excavated to a depth of 2 m for the experiments. The volume of the treated contaminated soil was approximately 400 m^3. The average concentration of As in the soil was 1205.88 mg·kg^{-1}. The soil pH was maintained between 6.5 and 6.8 during the 30-day stabilization treatment period. The average organic matter concentration was 16.3 mg·kg^{-1}, and the overall MC ranged from 25 to 31%. The vertical (Kv) and horizontal (Kh) average permeability coefficients were 1.64×10^{-7} cm·s^{-1} and 2.69×10^{-7} cm·s^{-1}, respectively.

The experimental procedure was implemented according to the following steps: (1) Excavation of the contaminated soil within the remediation area, followed by mixing and storage in a pretreatment area. One group was used for the pilot remediation experiment, and the other served as a control. The contaminated soil was initially screened using an Allu (Finland) screening and crushing bucket to remove large rocks and debris. (2) Addition of fly ash-based stabilizers. The contaminated soil was leveled and spread on the surface, and a stabilizer was evenly applied. Subsequently, the soil and the agent were finely screened and mixed using Allu screening equipment and finally backfilled in situ within the remediation area. (3) Soil watering and regular monitoring. The soil was evaluated for its remediation effectiveness through layered assessment at depths of 0–0.5 m and 0.5–1.0 m. Soil samples were collected at 0, 1, 7, 14, 25, and 30 days after As-stabilization treatment, along with control soil samples, to monitor the changes in As concentration in the soil leachate in the remediation area.

3. Results and Discussion

3.1. Analysis of Fly Ash Phase

The fly ash consisted of relatively regular spherical-shaped particles (Figure 1a) with irregular protrusions on the surface and dense, fine striations (Figure 1b). The sizes of the spheres varied (Figure 1c), and agglomerated crystalline substances were attached to their surfaces (Figure 1d). Geldart suggests that when the particle size of fly ash is <20 μm, the interparticle forces outweigh gravity, resulting in a certain degree of aggregation and adhesion [32]. Davidovits found that fly ash undergoes partial dissolution–aggregation hydration reactions under high air humidity conditions. The resulting inorganic silico-aluminate gel material consists of three-dimensional network structures composed of tetrahedral silicon–oxygen and aluminum–oxygen units, which is consistent with the SEM results (Figure 1d) [33,34]. The XRD results indicated that the main crystal phases in the fly ash were mullite ($Al_6Si_{20}O_{13}$) and quartz (SiO_2) (Figure 1e). The presence of elevated peaks in the 20–35° range and the higher background in the diffraction pattern suggest the existence of a glassy phase, unburned carbon particles, and other uncrystallized oxides in the fly ash [35]. The EDS results showed that the major elements in the fly ash were Al, Si, K, Ca, and Na, primarily in the form of oxides, and no toxic element was detected.

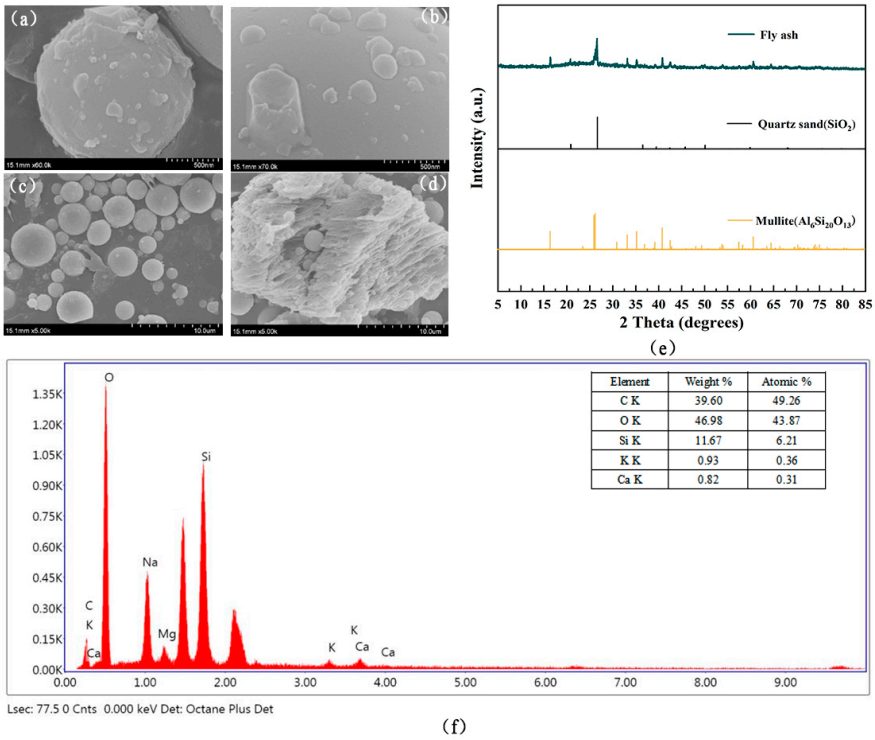


Figure 1. Results of fly ash characterization: (**a**) SEM: 500 nm, (**b**) SEM: 500 nm, (**c**) SEM: 10 μm, (**d**) SEM: 10 μm, (**e**) XRD, and (**f**) EDS.

3.2. Fly Ash Activation Factors

Figure 2 illustrates the experimental results of As stabilization in soils treated using different activation factors. Notably, the treatment involving ferrous salt activation of fly ash (BC) demonstrates significant stabilization effects, with ferrous salt emerging as the optimal activation factor. Both domestic and international research has frequently employed Fe-based substances and other high-specific-surface-area and high-porosity substrate materials as modifiers to enhance the As retention capacity of fly ash [36]. Ferrous salt (B) is commonly used as a chemical stabilizer for heavy metals. It can be easily oxidized to iron and its oxides during the stabilization process, and it possesses advantages such as a high surface charge, strong adsorption capacity, and good ion-exchange capability [4,26,27]. Kim et al. [37] and Seidel et al. [38] corroborate the role of ferrous sulfate in promoting

the stabilization of As during the treatment of As-contaminated areas in gold, silver, lead, zinc, tin, and tungsten tailings. This stabilization process facilitates the formation of iron oxides on the surface of the fly ash matrix, thereby enhancing particle surface magnetism, dispersibility, and adsorption efficiency.

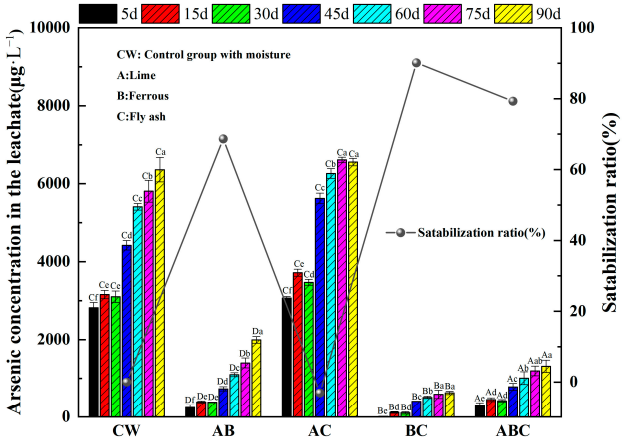


Figure 2. As concentrations in the soil leachates for varying treatment combinations and periods.

The adsorption and stabilization of pollutants precipitate changes in soil physicochemical properties, with the variation in pH serving as an important indicator of dissolution–precipitation and other chemical reactions within the soil. Notably, the presence of ferrous sulfate (B) in stabilizing agents substantially reduces soil pH. Conventional engineering techniques often incorporate lime (A) to buffer soil pH [37,38]. The pH values of stabilized soils across different groups were as follows: CK (6.78), CW (6.97), AB (7.15), AC (7.80), BC (6.06), and ABC (7.10). The application of lime and ferrous sulfate (AB) resulted in excessively high pH values, rendering the soil alkaline. As the concentration of OH^- ions increases in the environment, the competition for anion adsorption becomes more significant, leading to a diminished fixation of effective As forms, namely, arsenate and arsenite [36–38], thus affecting soil As stabilization. Conversely, the ferrous sulfate–fly ash (BC) treatment group exhibited favorable pH buffering. Therefore, in the optimization of the activation factor (BC), it is necessary to further evaluate changes in factors such as pH, MC, and As forms at different stages throughout the stabilization process and to elucidate the factors influencing soil As stabilization.

3.3. Optimization and Evaluation of Optimal Activation Factor

Figure 3 shows the experimental results of the effects of different concentrations of the activation factor on the stabilization of soil As. The results indicate that a concentration of 2% (w/w) was the optimal dosage with an Fe^{2+} concentration of 0.4% (w/w), yielding the best stabilization efficiency. Figure 3a shows the 3D mapping surface plot. In the ferrous fly ash treatment group with a total As concentration of 2884.47 $mg \cdot kg^{-1}$, as the concentration of ferrous salt increased, the stabilization efficiency gradually increased and eventually stabilized. At a dosage of 2% (w/w), the stabilization efficiency reached a maximum of 90.43% and remained above 90% throughout the curing period, indicating that this dosage meets the requirement for stabilizing As in soil. Figure 3b is a contour plot. When moving along the x-axis to the right, under the condition of a fixed fly ash matrix quantity, the stabilization efficiency improves as the concentration of the activation factor increases. The activation factor with a dosage of 0.5% (w/w) exhibited the highest rate of increase in stabilization efficiency, achieving an improvement of 201.93% in the efficiency of fly ash stabilization of As. At this dosage, the Fe/As ratio was 5:2, which is consistent with the findings of Moore [39], and the stabilization efficiency remained above 75% throughout the curing period. When moving upward along the y-axis, the stabilization period gradually

extends; however, there was a slight decrease in the stabilization efficiency, with the most significant fluctuation occurring on the day 45.

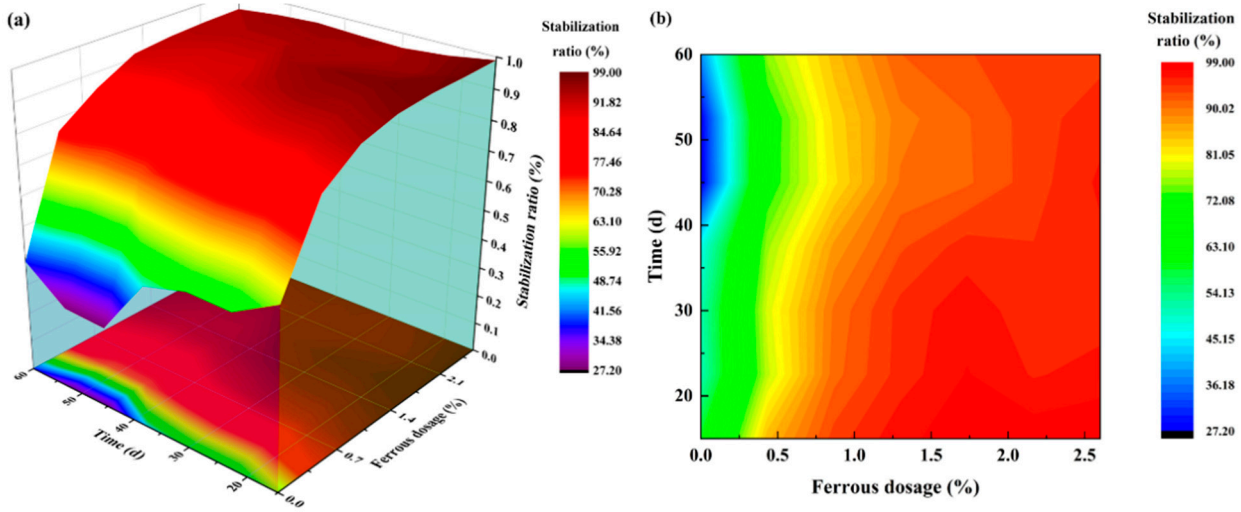


Figure 3. Changes in stabilization efficiency with various concentrations of ferrous modified fly ash: (**a**) 3D mapped surfaces; (**b**) contour map.

3.3.1. Degree of Activation

The degree of As activation was low when the ferrous iron concentration was between 2.0 and 2.6% (*w*/*w*). Based on the experimental results at days 15 and 45 (a = 15 and b = 45), the formula for the degree of activation was used to evaluate the fluctuation in the stabilization efficiency. The results are shown in Figure 4. As the concentration of ferrous salt increased, a consistent decrease was observed within the range of 0–1.8% (*w*/*w*), followed by a gradual increase beyond 1.8% (*w*/*w*). This suggests that the influence of the degree of activation was mainly concentrated within 0–1.8% (*w*/*w*). The higher the concentration within this range, the greater the degree of activation.

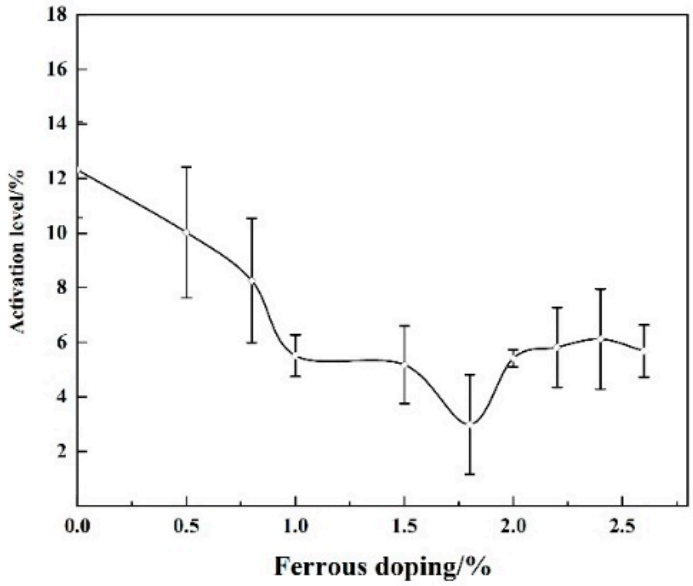


Figure 4. Degree of activation of fly ash treated with different ferrous iron dosages.

3.3.2. Soil pH

Soil pH is an important environmental factor that affects heavy metal activation. The addition of 2.0% (*w*/*w*) ferrous salt had a minimal impact on pH change, stabilization

efficiency, and the degree of activation. Based on the experimental results, regression analysis was conducted using SPSS 26 and Origin 2021 to investigate the correlation between ferrous salt concentration and soil pH changes. These results conformed to the ExpDec1 model. The p value of the model was <0.05, indicating significance. The R2 value of the model was 0.9931, indicating that 99.31% of the variation in the ferrous salt factor data could be explained by this model, thus exhibiting high reliability. The curve fitting illustrated in Figure 4 shows a good linear correlation between the ferrous salt concentration and pH. As the ferrous salt concentration increased, the pH gradually converged. After reaching a concentration of 1.8% (w/w), the rate of pH change remained below 4.18%. This suggests that within the range of 1.8 to 2.6% (w/w) of ferrous salt dosage, the effect of its concentration variation on pH was low, consequently exhibiting a minor impact on stabilization efficiency, which is consistent with the evaluation results of the degree of activation.

3.3.3. Moisture Content

A lower variation in the MC was more conducive to maintaining the stability of soil As. The As concentration in the leachate from the dry sample control group (CK) showed no significant change during the stabilization period, indicating that the pollutants were relatively stable in the dry soil and less prone to migration and leaching. The variation in the MC in the optimal treatment system is shown in Figure 5. The MC of the soil was increased by 10–12% on day 45 to simulate water stress conditions in the soil. A comparison of pre- and post-day-45 results indicates that the change was <4% during days 0–45 and <2% during days 60–90. These findings suggest that the impact of increased moisture on MC is minimal over time. Analysis of pH levels in both the control group with moisture (CW) and the optimally treated group shows a slight increase after 45 days, followed by a gradual decrease toward a stable and neutral state. This suggests that higher moisture levels accelerate the reaction of H^+ ions in the soil and facilitate ion exchange, albeit with negligible effects on pH stability. The variation in MC affects the distribution of As forms in the soil environment, thereby increasing the leachable form of As through chemical reactions during the stabilization/activation process.

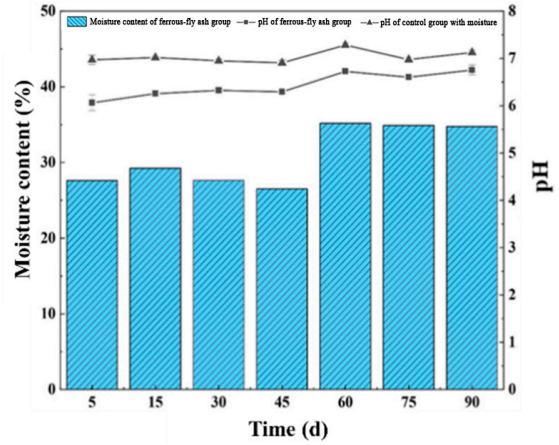


Figure 5. Variations in soil moisture content and pH of the optimal treatment system.

3.4. Analysis of Arsenic Forms and Leaching Capacity during the Stabilization Process

Following stabilization, As predominantly existed mainly in iron oxide-bound (F3 + F4) and residual (F5) states. The changes in the concentration and distribution of As forms during the stabilization process are shown in Figure 6. Overall, there was a slight decrease in total soil As during stabilization. Notably, the concentration of each form showed a significant variation within the first 45 days, gradually stabilizing thereafter by day 60. This suggests that chemical reactions predominantly occurred during the initial 45-day stabilization period, leading to substantial transformations in various As forms. By

day 60, equilibrium was reached, signifying soil stabilization. The concentrations of F1 and F2 decreased with reduction rates of 91.3 and 50.84%, respectively, whereas those of F3, F4, and F5 increased. Specifically, the distribution of the F3 + F4 As forms significantly increased during the initial 0–30 days of stabilization, experienced a slight decrease from days 45 to 60, and continued to rise until stability was achieved, with an overall increase of 15.65%. Within the first 30 days of stabilization, the proportion of the F3 As form significantly increased, with a growth rate of 102.11%, whereas the proportion of the F4 As form increased significantly from 0 to 5 days, with a growth rate of 65.44%.

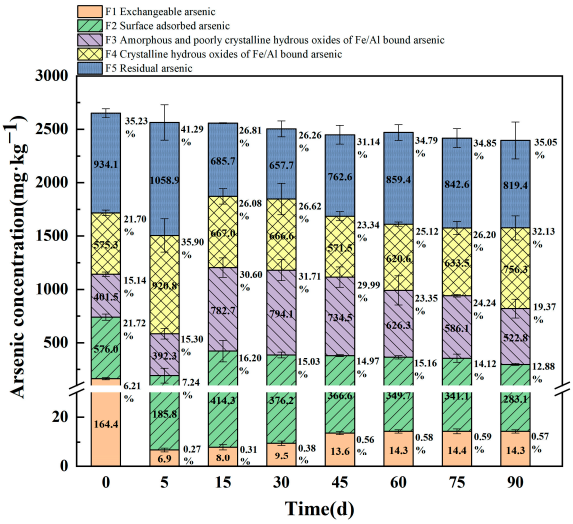


Figure 6. Morphological changes in soil arsenic occurrence following stabilization with the optimal treatment.

At day 45, the distributions of the F3 and F4 forms decreased due to an 8% increase in the MC. During the 45–90-day stabilization period, the proportions of F2 and F3 slightly decreased over time, while those of F1 and F4 gradually increased. The total distribution of the Fe–As-bound state (F3 + F4) increased by 15.65% before stabilizing, indicating that the optimal system gradually immobilizes the F1 and F2 forms of As in F3 and F4 through iron oxide adsorption, with primary release and transformation occurring between F2 and F3. This underscores that the stabilization of As pollution is achieved through chemical treatment, and the Fe–As-bound state is the major form after chemical processing, aligning with previous research [14,15].

During the stabilization period, concentrations of the exchangeable (F1) and surface adsorption (F2) forms significantly decreased and then gradually recovered and stabilized. This suggests that F1 and F2 are the primary forms that influence the As concentration in the soil leachate after activation by the optimal system.

The concentration of the exchangeable As form (F1) was the primary factor affecting the leaching of As in the soil and it was positively correlated with the concentration in the leachate. Based on the experimental results, a regression analysis was performed using SPSS 26 and Origin 2021 to analyze the reduction rate of the F1 form and the stabilization efficiency at different stabilization times. The results conform to the Asymptotic1 model. The *p* values of the models were all <0.05, indicating statistical significance. According to the variance results of the models, the R^2 values for the reduction rate of F1 and the stabilization efficiency were 0.93293 and 0.93218, respectively, indicating that >93% of the data could be explained by the same model, showing a strong correlation and high reliability. The curve-fitting results are shown in Figure 7, where the trends of the stabilization efficiency and F1 reduction rate are consistent with the progression of the stabilization time (x). This indicates that the exchangeable form (F1) primarily affected the leaching of As from the soil and had a significant impact on the As concentration in the soil leachate. The greater the distribution of F1, the higher the As concentration in the soil leachate.

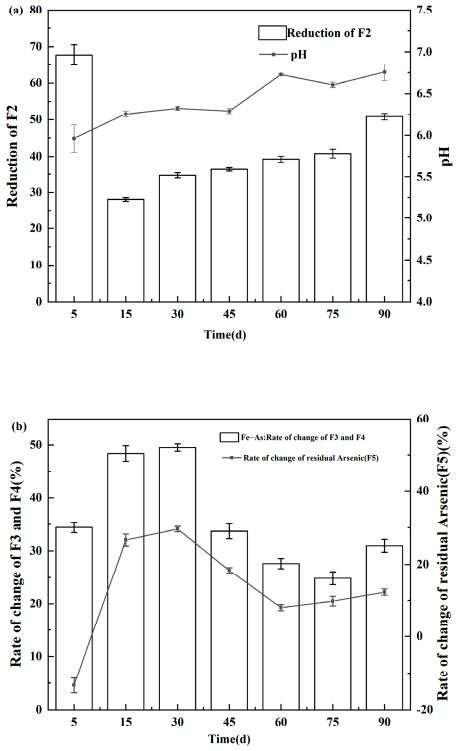


Figure 7. Rate of change in morphology of soil As. (**a**) Reduction rate of F2. (**b**) Rates of change in F3 + F4 and F5.

Surface-adsorbed As in the form of F2 was most easily desorbed when the soil pH was between 6 and 7. The pH is the main factor that activates this process. The reduction rate of F2 is shown in Figure 8a. Within the first five days of stabilization, F2 significantly decreased due to the addition of stabilizers. By day 15 of stabilization, the soil pH reached 6–7, resulting in a significant decrease in the reduction rate of F2. As the stabilization progressed, both the reduction rate of F2 and the soil pH gradually increased, indicating substantial desorption of F2 near pH 6 and a gradual decrease in its desorption capacity as the pH increased. These results were consistent with the findings of Goh et al. [40] and Chen et al. [41]. At pH 6–7, surface-adsorbed As (F2) was the most prone to desorption, while at pH > 7, the desorption of As did not show a clear correlation with pH, indicating a stable remediation effect [40,41].

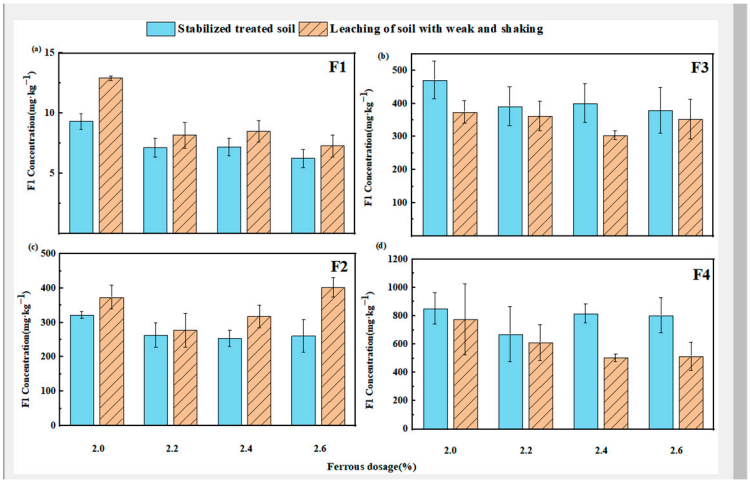


Figure 8. Results of soil As concentration after leaching with weak acid and shaking treatment. (**a**) F1; (**b**) F2; (**c**) F3; (**d**) F4.

Iron oxides (F3 + F4) and their residual forms (F5) were more susceptible to desorption under water-induced stress, with the increase in MC being the main activating factor. The changes in the reduction rates of F3 + F4 and F5 are shown in Figure 8b. Overall, F3 + F4 and F5 showed an increasing trend, indicating that they primarily transformed As in stabilized soil. During the initial 45 days of stabilization, F3 + F4 and F5 increased significantly. After 45 days, the rate of change decreased and then rebounded, suggesting that the disturbance in MC led to the desorption of As associated with iron oxides and some residual forms, resulting in the activation of F3, F4, and a portion of F5. These findings are consistent with those of Lu et al. [42], who found that when As was stabilized in soil using $FeSO_4$ and CaO, the predominant binding form of As shifted toward F3, increasing from 22.3 to 57.1%. Studies have shown [43–45] that Fe^{2+} stabilizers are easily oxidized to Fe^{3+} under acidic or neutral conditions with a high MC. Fe^{3+} oxidizes As^{3+} to As^{5+} in the environment and reacts with soluble AsO_4^{3-}, AsO_3^{3-}, and AsO_2^{-} to form iron arsenate and pentahydrated sub-arsenic acid iron precipitates, resulting in a decrease in exchangeable (F1) and surface-adsorbed (F2) As and an increase in iron oxide-bound (F3 + F4) and residual (F5) As.

3.5. Leaching Process and Mechanisms of Stabilization/Activation for Various Arsenic Forms in Soil

Moisture content and the stability of pH influence As stabilization. The stabilized soils were subjected to simulated leaching under acidic flooding conditions to assess their resilience. Figure 8 presents the classification of As forms in the leached soil residues. Notably, concentrations of F1 and F2 increased in all soil groups, whereas those of F3 and F4 decreased. These findings suggest that fluctuations in MC and pH primarily cause the activation of iron oxides, leading to the desorption of fixed As (F3 and F4) and an increase in the quantities of freely exchangeable forms of Fe and As (F1 and F2) in the soil. This, in turn, enhances their capacity for diffusion from the soil to the solution interface. Furthermore, it was observed that the migration and diffusion abilities of F1 were higher than those of F2, indicating that F1 was the predominant leachable form.

Figure 9 illustrates the soil stabilization/activation process, highlighting the primary occurrence of iron oxide transformation. Notably, pH and MC emerge as the principal influencers in this process. Previous research has emphasized the impacts of soil physicochemical properties, parent material, and land use on the risk posed by heavy metals in soil. Among these factors, pH (acidity/alkalinity) is a critical determinant of heavy metal bioavailability and mobility in soil. The use of ferrous salts for chemical stabilization poses a potential risk of soil acidification. Traditional approaches often involve the application of lime to adjust pH levels, which may inadvertently lead to an increase in soil salinity and cause new environmental challenges [44–47].

In cohesive soils, MC is typically considered damp at approximately 30% and saturated at 50%, beyond which waterlogging occurs. Waterlogging is a common occurrence during rice cultivation. Irrigation promotes the activation of iron oxides, leading to the conversion of crystalline iron to amorphous and ionic forms. Conversely, drainage or drought conditions induce the transformation of ionic and amorphous iron oxides in the soil back to crystalline iron [48–50].

Excessive moisture or water logging can cause the decomposition of iron oxides, resulting in a decrease in the content of Fe–As complexes (F3 and F4) and an increase in exchangeable (F1) and adsorbed (F2) forms of As. Therefore, the application of fly ash with ferrous salts not only enhances stabilization efficiency but also regulates soil pH and improves water retention. This aids in slowing down the downward migration and diffusion of soil moisture, effectively storing water within the applied fly ash and meeting the water absorption needs of the corresponding soil depth [46,47]. Consequently, this facilitates the stable distribution of soil moisture and reduces the activation of soil heavy metals.

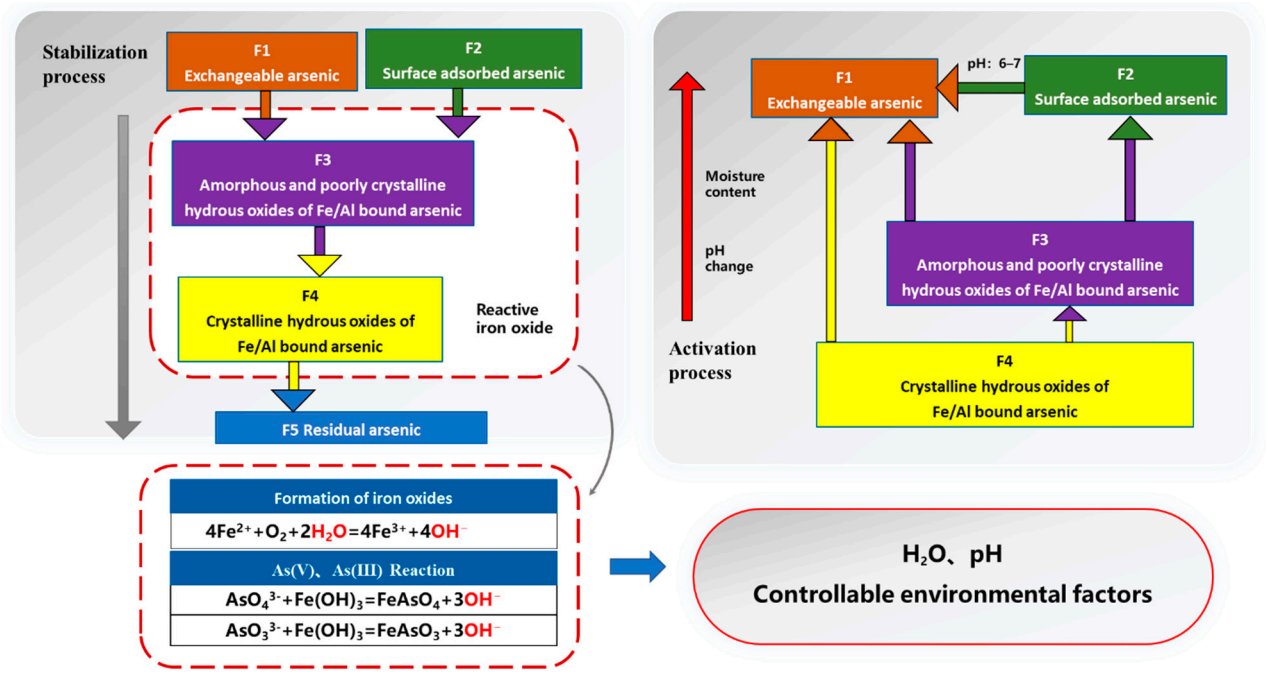


Figure 9. Stabilization/activation processes of various forms of arsenic in soil.

3.6. Results of Actual Field Remediation

In a 30-day trial in the field, the stabilization efficiency of surface soil (0–0.5 m) for As was 97.41%, maintaining a stable leachate concentration of 2.8 μg·L^{-1}. Similarly, for deeper soil (0.5–1.0 m), the stabilization efficiency for As was 95.37%, with a stable leachate concentration of 5.8 μg·L^{-1}. These results are presented in Figure 10. Throughout the 30-day field remediation process, the stabilization efficiency for As across different soil depths was consistently >95%. Notably, the As concentrations in the soil leachates at all depths met the standards for surface water quality (GB 3838-2002) [51] and groundwater quality (GB/T 14848-2017) [52], which specify Class III limits for As at 0.05 and 0.01 mg·L^{-1}, respectively. These results indicate the efficacy of the remediation process.

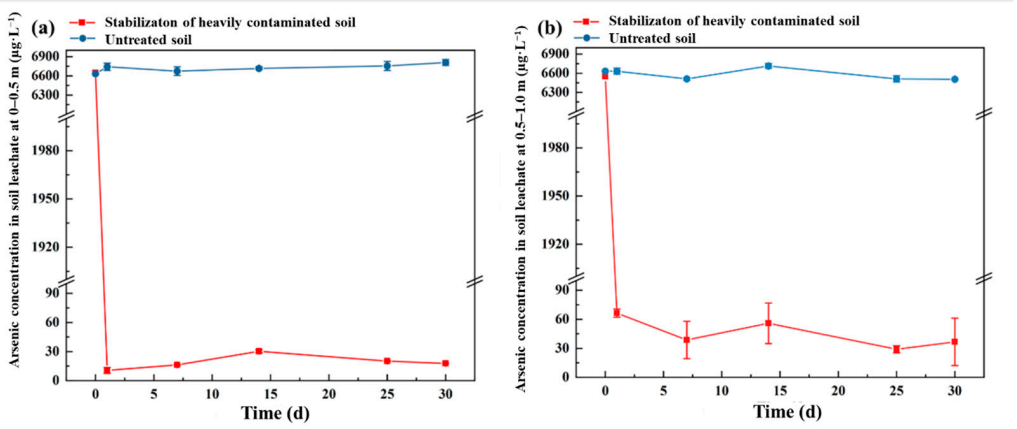


Figure 10. Arsenic concentrations in soil leachates at different depths: (**a**): As concentration in soil leachate at 0–0.5 m (μg·L^{-1}); (**b**) As concentration in soil leachate at 0.5–1.0 m (μg·L^{-1}).

4. Conclusions

When modified by ferrous sulfate, fly ash emerges as a potent soil stabilizer, effectively mitigating the activation of heavy metals within the soil matrix. The optimal treatment formulation, comprising 2% (*w*/*w*) ferrous sulfate and 2% (*w*/*w*) fly ash, showcased remarkable efficacy in stabilizing soil As pollution. Under the optimum condition of 2%

(*w*/*w*) ferrous sulfate admixture, the Fe^{2+} composition of 0.4%, which has a lesser effect on pH change, is the most efficient in stabilizing arsenic in the soil. The lower the change in water content, the more beneficial it is to maintain soil arsenic stabilization.

In a soil cultivation experiment, the ferrous fly ash treatment group (BC) demonstrated a total As concentration of 2884.47 mg·kg^{-1}, with a commendable stabilization efficiency of 90.43% over a 90-day period.

The stabilization process primarily involved the immobilization of exchangeable As (F1) and adsorbed As (F2) into iron oxide-bound As (F3 + F4) and residual As (F5), with the order of stability being F5 > F4 > F3. After stabilization, notable reductions of 50.84% in the F2 concentration and 91.3% in the F1 concentration were observed. Notably, variations in the F1 concentration of the soil were positively correlated with the As concentration of the leachate, highlighting F1 as the principal form influencing the As concentration of the soil leachate, with MC and pH crucially affecting stabilization/activation dynamics. Increased moisture facilitated the desorption and activation of iron oxide-bound As (F3 + F4), whereas a pH range of 6 to 7 caused the activation of adsorbed As (F2). The optimal treatment induced a 12% decrease in soil pH, gradually restoring neutral levels after stabilization. The activation process involved the transformation of F3 and F4 into F1 and F2, respectively.

Remarkable remediation effects were evidenced in field trials. For heavily polluted soil with a total As concentration of 1205.88 mg·kg^{-1}, the stabilization efficiency of surface soil (0–0.5 m) reached 97.41%, whereas for deep soil (0.5–1.0 m), it was 95.37%. The As concentration in the soil leachate met the remediation requirements, demonstrating promising application potential.

Author Contributions: Conceptualization, J.B.; methodology, J.Y. and Q.S.; and formal analysis, J.Y.; investigation, Q.S.; resources, Q.S.; data curation, J.Y., B.Y., X.L. and X.Z.; writing—original draft preparation, J.Y.; writing—review and editing, W.Z., B.Y. and H.L.; funding acquisition, J.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "National Key Research and Development Program of China, grant number 2023YFC370988" and "The Environmental Protection Scientific Research Project of Hubei Province and Knowledge Innovation Program of Wuhan—Basic Research, grant number 2022020801010384".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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