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Impact of Chemically Engineered Biochar on Stabilization of Arsenic in an Acid Soil

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ABSTRACT

The study was conducted during June, 2024–August, 2025 at the division of Soil Science and Agricultural Chemistry ICAR-IARI, New Delhi, India to investigate the efficacy of chemically engineered biochars for remediating arsenic (As)-contaminated soils and reducing its uptake by rice. Engineered biochars were produced from rice straw (RBC), sugarcane bagasse (SBC), and jute stalk (JBC) by chemical modifications with $FeCl_3$, goethite (FeOOH), and magnetic iron oxides. Initial screening in an As-spiked acidic Inceptisol from Assam demonstrated a strong dose-dependent immobilization effect. The $FeCl_3$-modified biochars, particularly those from rice straw (RBC-$FeCl_3$) and sugarcane bagasse (SBC-$FeCl_3$), achieved the highest arsenic immobilization efficiencies, up to 81.0%, at an application rate of 6.70 g kg^{-1} soil. Detailed sorption-desorption studies revealed that SBC-$FeCl_3$ exhibited the maximum adsorption capacity and strongest binding affinity for As, characterized by high Freundlich adsorption intensity and significant positive hysteresis (Desorption Index>1), indicating stable, long-term retention. Superior performance was attributed to the formation of reactive iron oxide phases (akaganéite and hematite) on the biochar surface, as confirmed by XRD and FTIR analyses. A net house pot experiment with rice (*Oryza sativa* L., cv. Ranjit) showed that SBC-$FeCl_3$ application (6.67 g kg^{-1}) significantly reduced extractable soil As by 46% and lowered As concentration in rice straw by 64% compared to the control. The study concluded that $FeCl_3$-engineered biochar, especially SBC-$FeCl_3$, was a highly effective, dual-benefit strategy for immobilizing arsenic in acidic soils and mitigating its transfer into the food chain.

KEYWORDS: Arsenic immobilization, acid soil, engineered biochar, rice

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1. INTRODUCTION

According to the data presented in the House Assembly of Assam, total of 1,247 habitations in 12 districts are affected by arsenic contamination. The highest is in Nalbari district, followed by Baksa and then Barpeta district reported by the Rattan Lal Kataria, the Minister of State for Jal Shakti in 2021 (Anonymous, 2021). The Himalayan Mountain region serves as the primary source of arsenic (As) within the Ganga-Brahmaputra-Meghna (GBM) river system, throughout Northeast India specifically in the states of Assam, Manipur, Arunachal Pradesh, Nagaland, and Tripura groundwater where arsenic levels have reached critical levels, surpassing the World Health Organization's safety threshold of 10 μg l^{-1} (Kumar et al., 2022). In Assam, this contamination was identified across twenty districts including Nalbari, Jorhat, Barpeta, Dhemaji, and Dibrugarh, among others (Sathe et al., 2021). The contamination of arsenic in soil is through polluted ground water through irrigation (Sinha and Bhattacharya, 2014; Kumar et al., 2016), which is taken up by plants and consequently enter the food chain. Elevated concentration of As in rice is a developing issue that is now acknowledged as a recent calamity in Southeast Asia (Meharg and Rahman, 2003). Ohno et al. (2007) have determined that, on an average, rice contributes significantly more to As intake than drinking water, at 56% and 13%, respectively, giving it the opportunity to enter the human food chain (Lee et al., 2008; Mondal and Polya, 2008; Rahman et al., 2008). Developing sustainable remediation strategies is essential to mitigate arsenic (As) contamination. While phytoextraction is recognized as a low-input, eco-friendly method for cleaning metal-contaminated soils (Purakayastha et al., 2008, Mandal et al., 2014), its practical use is often restricted by slow processing times and the complexities of disposing of contaminated plant biomass. Consequently, the chemical stabilization of arsenic using reactive solid substances has emerged as a viable alternative (Kumpiene et al., 2006). This stabilization is achieved through soil amendments rich in iron (Fe) and aluminum (Al), such as red mud, steel slag, or Fe-oxyhydroxides like hematite and goethite, which facilitate arsenic adsorption and oxidation (Lin and Puls, 2000; Raza et al., 2024). Furthermore, biochar has gained prominence for its ability to stabilize metalloids (Ahmad et al., 2014). As a highly stable, porous carbonaceous material produced through the thermal decomposition of organic waste in oxygen-limited environments (Purakayastha et al., 2015; El-Ramady et al., 2020), biochar possesses functional groups that enhance ion exchange. This increases nutrient retention and effectively immobilizes arsenic in light-textured soils (Lehmann and Rondon, 2005; Li et al., 2018) and its translocation to the rice (Raza et al., 2025). Chemical treatments, specifically iron-coating, significantly enhance biochar's anion exchange capacity (AEC) to better stabilize soil arsenic. Methods include acid pre-treatment or pH-adjusted iron salts (Li et al., 2016; Zhang et al., 2021) and magnetic treatments (Chen et al., 2021). Recently, complex treatments using ozone or mixed acids have shown dramatic improvements in both cation exchange capacity (CEC) and anion exchange capacity (AEC) (Dey et al., 2023). Despite existing research, no studies have examined chemically engineered biochar for immobilizing arsenic and reducing its transfer to rice in Assam's spiked soil. This study aims to fill that gap based on two hypotheses: first, that iron-based agents (like FeOOH) increase biochar's positive surface charge and AEC, facilitating arsenic capture via electrostatic attraction and ligand exchange; and second, that these engineered biochars will effectively arrest arsenic translocation from soil to rice plants. To address these, the following objectives were established to screen these engineered biochars based on their arsenic adsorption capacity in soil and evaluate the impact of the most effective biochars on arsenic immobilization in soil in a controlled experiment tested in rice.

2. MATERIALS AND METHODS

The study was conducted during June, 2024-August, 2025 at the Division of Soil Science and Agricultural Chemistry ICAR-Indian Agricultural Research Institute, New Delhi, India.

2.1. Preparation of the biochar

Biochar was produced from sun-dried rice straw (RBC), sugarcane bagasse (SBC), and jute stalk (JBC) in the division of Soil Science and Agricultural Chemistry, IARI, New Delhi. The biomass was chopped into 30–50 mm fragments and processed in a temperature-controlled steel chamber at 500 °C under a continuous nitrogen flow (1.5 l min^{-1}) to ensure an oxygen-free environment. Following the protocol by Purakayastha et al. (2015), the temperature was increased at 2°C min^{-1} and maintained for two hours. After cooling overnight, the resulting biochar was recovered, pulverized using a mixer grinder, and passed through a 0.70 mm sieve.

2.1.2. Methodology for preparation of chemically engineered biochar

Pristine biochars were chemically engineered using three distinct methods to enhance their AEC through iron impregnation. For $FeCl_3$-HCl treatment following Li et al. (2016), biochar was first activated in 6 M HCl for one hour, rinsed to a neutral pH, and dried at 75°C. This activated material was then mixed with 1 mol l^{-1} $FeCl_3.6H_2O$ (maintaining a 0.70 iron-to-biochar mass ratio). The suspension was neutralized using 3 M KOH, settled, washed, and dried. FeOOH treatment based on Zhang et

al. (2021), biochar was dispersed in distilled water (1:40) and stirred with $Fe(NO_3)_3.9H_2O$ (2 g g^{-1} of biochar). The pH was adjusted to 12 using 1.0 M NaOH to precipitate iron oxyhydroxides. After a 12 h incubation and extensive filtration with deionized water, the composite was dried at 60°C. Magnetic treatment was done according to Chen et al. (2021), 10 g of pristine biochar and 10 g of $FeCl_3$ were stirred in 200 ml of water. After partial evaporation in a water bath and oven, the mixture underwent a second pyrolysis cycle under original production conditions. This thermal process integrated iron into the carbon matrix, resulting in a magnetic, Fe-modified biochar.

2.2. Screening of engineered biochar based on As adsorption capacity

2.2.1. Soil properties

Soil sample was collected from, Titabar, Jorhat (Assam), latitude 26.724231°N and longitude 94.193211°E, and this sample was spiked with 50 ppm of As (mg Kg^{-1}) and kept for 30 days at 50% of the water holding capacity for homogenization. Water holding capacity (WHC) was measured by the Keen box. The soil had pH 4.33, EC 0.003 dS m^{-1} (Jackson, 1973), sandy clay loam in texture, CEC 8.4 cmol (p+) kg^{-1}, total organic C (TOC) 0.64% (Walkley and Black, 1934), and available N 158 kg ha^{-1} (Subbiah and Asija, 1956), available P 59.7 kg ha^{-1} (Olsen et al., 1954). The soil had total arsenic 3.4 mg kg^{-1} and 0.34 mg kg^{-1} total and available As (Olsen et al., 1954), respectively.

2.2.2. Biochar adsorption capacity

An incubation study was conducted in soil to know the effective dose of biochar to reduce arsenic (As) availability. Biochar was mixed into soil at five different amounts: 0, 1.12, 2.23, 4.46, and 6.70 g kg^{-1}. The moisture content in soil+biochar mixture was adjusted to field capacity and maintained for three days. After this period, extractable As was estimated using a 0.5 M $NaHCO_3$. The As content in this extract was measured with an Inductively Coupled Plasma Mass Spectroscopy (ICP MS, PerkinElmer, NexION 300X) (Raza et al., 2024). The reduction in available As due to biochar addition was expressed as

$$\text{As immobilization efficiency} = (As_{initial} - As_{final}) \times 100/As_{initial}$$

where,

$As_{initial}$-Initial extractable As content in soil

As_{final}-Final extractable As content in soil

2.2.3. Adsorption and desorption behaviour of arsenic

The three modified biochar types showing the highest reduction in available As-RBC-$FeCl_3$, SBC-$FeCl_3$, and JBC-$FeCl_3$-were chosen for further study. 200 g soil sample were treated with these biochars, brought to a moisture level of 70% water-holding capacity, and kept at a constant temperature for one month. Untreated soil was used for comparison. The aged samples were then air-dried for subsequent adsorption and desorption tests.

For each soil-biochar mixture, 3 g soil was placed in a oak ridge centrifuge tubes with a solution of 20 ml of a background solution (0.01 M KNO_3) spiked with graded arsenic concentrations (0, 5, 10, 20, 50, and 80 mg l^{-1}), and prepared from sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$). The tubes were shaken for 24 h to allow the soil to adsorb arsenic from the solution. The tubes were centrifuged at 5000 rpm for 10 min. A 10 ml aliquot of the supernatant was then filtered through Whatman No. 42 filter paper into a polypropylene tube and stored for subsequent arsenic analysis by ICP-MS (PerkinElmer, NexION 300X) (Raza et al., 2024).

Adsorbed As (q_e) was computed as follows: $q\{e\}=(C_o - C_e * V)/w$

Sorption data were summarized with the help of Langmuir.

$q_e=q_{max}C_eK_l/1+K_lC_e$

Which is linearized to $C_e/q_e=C_e/q_m+1/K_lq_m$

Freundlich sorption isotherm $q_e=K_fCe^{1/n}$ which was linearized to $\log q_e=\log K_f+1/n \log C_e$

C_o and C_e were the initial As (V) concentration (mg l^{-1}) and equilibrium As concentration (mg l^{-1}), respectively; V was the volume of solution taken; and w denoted the weight of adsorbent taken; q_{max} (mg kg^{-1}) represented the maximum adsorption capacity, K_l (l mg^{-1}) stands for the Langmuir constant. K_f was the Freundlich constant (l kg^{-1}), and 1/n denoted the adsorption intensity (1<n<10).

Arsenic desorption was performed in the same centrifuge tubes used for the sorption experiment. To each tube, 10 ml of 0.01 M KNO_3 background solution was added, maintaining the original 3:20 (g:ml) soil-to-solution ratio. The tubes were then placed in an environmental shaker at 25°C and subjected to an intermittent shaking schedule-6 h of shaking followed by 6 h of rest-over a total period of 72 h. After this equilibration, the tubes were centrifuged at 5000 rpm for 10 min. The resulting supernatant was filtered and collected in a polypropylene tube for the determination of arsenic concentration by ICP-MS (PerkinElmer, NexION 300X) (Raza et al., 2024).

The amount of arsenic desorbed (q_d, mg kg^{-1}) was calculated using the following equation:

$q_d=[(C_d - C_e * df) * V]/w$

where:

C_d=Arsenic concentration at desorption equilibrium (mg l^{-1})

Ce=Arsenic concentration at sorption equilibrium (mg l^{-1})

df=Dilution factor

V=Volume of the desorption solution (L)

w=Mass of the soil/biochar adsorbent (g)

The reversibility of arsenic sorption was evaluated using a Desorption Index (DI), calculated from the linearized Freundlich isotherm parameters:

DI=n_sor / n_des

where:

n_sor=Freundlich exponent (1/n) derived from the adsorption isotherm

n_des=Freundlich exponent (1/n) derived from the desorption isotherm

2.3. Screening engineered biochar for As release behaviour in water

Different doses of the engineered biochar (150, 200, and 250 mg l^{-1}) were screened in the 5 ppm of sodium arsenate ($Na_2HAsO4.7H_2O$) solution. For this, 6, 8, and 10 mg of the different engineered and untreated biochar were taken in 50 ml centrifuge tube, and to this 40 ml of a 5 ppm (mg l^{-1}) solution of sodium arsenate ($Na_2HAsO_4.7H_2O$) was added to it. It will be kept for 24 h, shaken in an orbital shaking incubator for 24 h, and then filtered with Whatman No. 42, and then 0.5 M $NaHCO_3$ extractable As concentration in soil was measured by ICP- MS (PerkinElmer, NexION 300X) (Raza et al., 2024).

2.4. Net house experiment with rice

The engineered biochars treated with $FeCl_3$-produced from rice straw, sugarcane bagasse, and jute stalk-along with their corresponding pristine biochars were chosen for a net house study based on initial screening results. Soil for the experiment (Inceptisol) was collected from a depth of 0–15 cm in Titabar, Assam, and the popular local rice cultivar, Ranjit, was selected. Fertilizer was applied at the recommended dose for this cultivar in Assam Inceptisol: 26.8 mg N, 17.9 mg P_2O_5, and 17.9 mg K_2O per kilogram soil basis. Rice plants were harvested at the maximum vegetative stage. For arsenic analysis in rice straw, an aliquot of 0.5 g sample was digested using a hot plate. The sample was placed in a conical flask with 5 ml of concentrated HNO_3 and left overnight. The next day, the flask was heated at 60°C for 2 h with a funnel placed over its mouth. Afterwards, 2 ml of perchloric acid was added, and digestion continued at 160°C for 4–5 h. After cooling, the digest was diluted to 50 ml with distilled water and filtered through Whatman No. 42 filter paper (Rahman et al., 2008). Post-harvest soil analysis included measurement of pH and electrical conductivity (EC) at a 1:2.5 soil-to-water ratio (Jackson, 1973), soil organic carbon (SOC) content determined by the wet oxidation potassium dichromate method (Walkley and Black, 1934), and extractable arsenic extracted with 0.5 M $NaHCO_3$ (pH 8.5) (Olsen et al., 1954). Arsenic concentrations in the extracts were measured by ICP-MS (PerkinElmer, NexION 300X) (Raza et al., 2024). For total arsenic in soil, 0.5 g of soil was digested on a hot plate with 5 ml concentrated HNO_3 overnight, followed by heating at 60°C for 2 h. Subsequently, 2 ml $HClO_4$ and 3 ml H_2SO_4 were added, and digestion proceeded at 160°C for 4–5 h (Rahman et al., 2008).

2.5. Statistical analysis

The data collected from all experiments were examined using analysis of variance. For experiments with multiple treatment factors, a factorial design was applied. When the statistical analysis showed that treatment effects were significant, the averages of different treatments were compared using the Least Significant Difference method to identify which treatments were distinct from each other.

3. RESULTS AND DISCUSSION

3.1. Screening of engineered biochar based on its arsenic adsorption capacity in soil

The screening test revealed a strong dose-dependent increase in arsenic (As) immobilization efficiency for all engineered biochars (Table 1, 2 and 3). At the highest application rate (6.70 g kg^{-1}), $FeCl_3$-modified biochars consistently performed best. RBC-$FeCl_3$ achieved the maximum efficiency of 81.0%, while SBC-$FeCl_3$ and JBC-$FeCl_3$ also showed superior results. In contrast, pristine biochars and goethite-modified variants demonstrated significantly lower effectiveness. In the acidic Assam soil, $FeCl_3$-modified biochars, particularly RBC-$FeCl_3$ (mean 67.2% efficiency), outperformed magnetic and goethite variants. This superior performance was attributed to the formation of specific

Table 1: Arsenic (As) immobilisation efficiency of pristine and engineered rice straw biochar (RBC) applied in Inceptisol of Assam

Treatment	RBC	RBC-goethite	RBC-magnetic	RBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
1.12	$18.4l^{¶}$	13.3^{m}	51.6^{g}	58.0^{f}	$35.3^{D§}$
2.23	25.0^{k}	15.8^{n}	57.7^{f}	63.3^{e}	40.5^{C}
4.46	26.7^{j}	28.3^{i}	68.4^{c}	66.6^{d}	47.5^{B}
6.70	27.6^{i}	38.8^{h}	76.4^{b}	81.0^{a}	55.9^{A}
Mean	$24.4^{C\$}$	24.0^{C}	63.5^{B}	67.2^{A}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC×D, respectively and are significant according to least significant difference (LSD) at p=0.05

Table 2: Arsenic (As) immobilisation efficiency of pristine and engineered sugarcane bagasse biochar (SBC) applied in Inceptisol of Assam

Treatment	SBC	SBC-goethite	SBC-magnetic	SBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
1.12	$24.4^{n¶}$	44.5^{i}	44.9^{i}	52.2^{d}	$41.5^{C§}$
2.23	26.5^{m}	47.7^{g}	46.7^{h}	61.9^{c}	45.7^{B}
4.46	30.0^{l}	48.9^{f}	51.0^{e}	70.0^{b}	49.9^{A}
6.70	31.9^{k}	51.1^{e}	37.6^{j}	78.9^{a}	50.0^{A}
Mean	$28.2^{D\$}$	48.0^{B}	45.0^{C}	65.7^{A}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC×D, respectively and are significant according to least significant difference (LSD) at p=0.05

Table 3 Screening of the pristine and engineered jute biochar (JBC) applied in Inceptisol of West Bengal

Treatment	JBC	JBC-goethite	JBC-magnetic	JBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
1.12	$25^{m¶}$	47^{h}	22.3^{n}	61^{c}	$38.8^{B§}$
2.23	28.3l	51.3^{f}	34^{k}	65.3^{b}	44.73^{AB}
4.46	32.6^{j}	53.9^{e}	48.5^{g}	69.3^{a}	51.0^{A}
6.70	37.5^{i}	55.3^{d}	55.4^{d}	55.1^{d}	50.8^{A}
Mean	$30.8^{C\$}$	51.88^{AB}	40.05^{BC}	62.6^{A}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC x D, respectively and are significant according to least significant difference (LSD) at p=0.05

iron oxide phases, akaganéite (β-FeOOH) and hematite (α-Fe_2O_3), identified via XRD. Akaganéite's tunnel structure provides a high affinity for As anions in acidic conditions. Successful loading of these oxides was confirmed by FTIR analysis, which showed distinct Fe–O stretching vibrations. The results demonstrated that $FeCl_3$ modification, by creating these reactive iron phases, was the most effective strategy for enhancing biochar's As immobilization capacity in acidic soils.

3.2. Screening of engineered biochar for arsenic release behaviour in water

The arsenic (As) immobilization efficiency of pristine and modified rice biochar (RBC) showed significant variation (p<0.05) depending on both treatment type and application dose. Among the treatments, RBC-$FeCl_3$ demonstrated the highest mean As immobilization efficiency (47.0%), followed by RBC-Magnetic (27.8%) and pristine RBC (26.6%), while RBC-Goethite showed the lowest efficiency (14.4%) (Table 4). Among the treatments, SBC-Magnetic exhibited the highest mean As immobilization efficiency (98.9%), followed closely by SBC-$FeCl_3$ (93.7%), while SBC-Goethite (47.7%) and pristine SBC (19.5%) showed considerably lower efficiencies (Table 5). JBC and JBC-Magnetic exhibited the highest mean As immobilization efficiency (61.7%), followed by JBC-$FeCl_3$ (56.8%), while JBC-Goethite showed the lowest efficiency (39.9%) (Table 6). Increasing the biochar dose from 150 to 250 mg l^{-1} significantly enhanced As immobilization, with the highest efficiency (72.7%) observed at the 250 mg l^{-1} dose. This phenomenal performance was a direct function of the material's properties: the XRD-confirmed magnetite/maghemite phases, the Fe-O bonds visible in FTIR, and the homogeneous layer of nanoparticles observed via SEM that creates an immense number of accessible sorption sites.

3.3. Sorption of arsenic in soils as affected by the screened engineered biochar

The sorption-desorption characteristics of arsenic (As) in the contaminated Inceptisols from Assam was profoundly altered by the application of engineered biochars, with the $FeCl_3$-modified variants demonstrated superior

Table 4: Screening of the pristine and engineered rice biochar (RBC) in water containing 5 mg l^{-1} As

Treatment	RBC	RBC-Magnetic	RBC-Goethite	RBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
150	$20.6^{i¶}$	23.2^{h}	9.4^{k}	37.1^{c}	$22.6^{C§}$
200	27.6^{f}	26.0^{g}	12.2^{j}	49.2^{b}	28.8^{B}
250	31.8^{e}	34.1^{d}	21.5^{i}	54.4^{a}	35.5^{A}
Mean	$26.6^{B\$}$	27.8^{C}	14.4^{D}	47.0^{A}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC×D, respectively and are significant according to least significant difference (LSD) at p=0.05

Table 5: Arsenic (As) immobilisation efficiency of pristine and engineered sugarcane bagasse biochar (SBC) tested in water

Treatment	SBC	SBC-magnetic	SBC-goethite	SBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
150	$14.6^{k¶}$	97.8^{c}	42.2^{h}	87.8^{e}	$60.6^{C§}$
200	18.7^{j}	99.05^{b}	44.7^{g}	94.9^{d}	64.3^{B}
250	25.0^{i}	99.7^{a}	56.3^{f}	98.3^{c}	69.9^{A}
Mean	$19.5^{D\$}$	98.9^{A}	47.7^{C}	93.7^{B}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC×D, respectively and are significant according to least significant difference (LSD) at p=0.05

Table 6: Arsenic (As) immobilisation efficiency of pristine and engineered jute stalk biochar (JBC) tested in water

Treatment	JBC	JBC-magnetic	JBC-goethite	JBC-$FeCl_3$	Mean
Doses of biochar (g kg^{-1})	As immobilisation efficiency (%)				
150	$45.9^{d¶}$	45.9^{d}	36.8^{f}	36.2^{f}	$41.2^{C§}$
200	57.9^{c}	57.9^{c}	40.3^{e}	48.4^{d}	51.1^{B}
250	81.2^{b}	81.2^{b}	42.5^{e}	85.8^{a}	72.7^{A}
Mean	$61.7^{A\$}$	61.7^{A}	39.9^{C}	56.8^{B}	

The data followed by different upper case letters in the column (§) and row ($) and data followed by different lowercase letters in column or row (¶) are representing main effect of biochar (BC), dose (D), and interaction effect of BC×D, respectively and are significant according to least significant difference (LSD) at p=0.05

performance. The adsorption isotherms (Figure 1) clearly established that all amendments enhanced As retention compared to the unamended control, with sugarcane-$FeCl_3$ biochar (SBC-$FeCl_3$) consistently exhibited the highest adsorption capacity across the entire equilibrium concentration range in the soil. This was directly attributable to the successful loading of specific iron oxide phases, such as akaganéite (β-FeOOH) and hematite (α-Fe_2O_3), as confirmed by XRD analysis, which provided the abundant surfaces for arsenate binding through ligand exchange (Mamindy-Pajany et al., 2011; Mercado-Borrayo et al., 2016). The FTIR data, showed strong Fe-O stretching vibrations (~587 cm^{-1}), provided further evidence of this

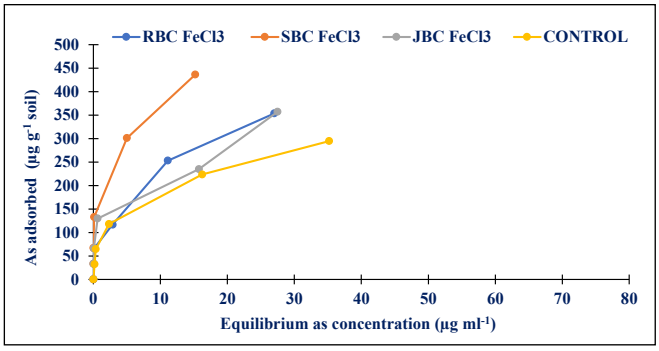

Figure 1: Adsorption isotherms at different as concentrations as affected by screened engineered biochar in inceptisol of Assam

successful functionalization, creating the high-density sorption sites responsible for the enhanced immobilization.

The modeling of adsorption data revealed critical insights into the governing mechanisms. The Freundlich model demonstrated a superior fit (higher R^2 values) for most treatments compared to the Langmuir model (Table 7), indicating that As adsorption in these amended soils was best described by a multilayer, heterogeneous process (Zhang and Selim, 2005; Kumar et al., 2016). The Langmuir model assumes a monolayer adsorption onto a homogeneous surface, whereas the Freundlich model was based on a multilayer and heterogeneous adsorption mechanism (Mead, 1981; Musah et al., 2022). This heterogeneity aligns with the SEM observations of a non-uniform nanoparticle coating on the biochar surface, creating a variety of energy sites for As binding. The Freundlich parameters (Table 7) further elaborated on this: the lower 1/n values for amended soils (e.g., 0.229 for SBC-$FeCl_3$ in Inceptisol from Assam) compared to the control (0.382) confirm a more heterogeneous surface with a wider distribution of binding sites. Concurrently, the significantly higher 'log a' values for the amendments (e.g., 2.35 for SBC-$FeCl_3$ vs. 1.895 for control in Inceptisol from Assam) quantify the dramatic increase in adsorption capacity, representing a 24% increase in effective sorption sites. This combination-increased site heterogeneity and greater capacity-was a hallmark of an effective amendment.

The Langmuir parameters provided a quantitative measure of performance (Table 7). The maximum adsorption capacity (b) for As was highest for SBC-$FeCl_3$ in the Inceptisol from Assam (429 mg kg^{-1}), representing a 44.5% increase over their control. More strikingly, the bonding strength constant (k) for As in SBC-$FeCl_3$ was an order of magnitude higher 475% (2.90 l mg^{-1} in Inceptisol from Assam) than the control, indicating an immensely stronger affinity for As and explaining its steep initial adsorption slope. This translated into an enormously enhanced maximum As buffering capacity (MAsBC), with SBC-$FeCl_3$ showing a 733% increase in Inceptisols from Assam. This suggested

Table 7: Arsenic adsorption equations for different engineered biochars applied in Inceptisol of Assam

Treatment	Langmuir equation c/x=c/b+1/kb	R^2	b (mg kg^{-1})	K (l mg^{-1})	MAsBC (l kg^{-1})	Freundlich equation log x=log a+1/n log c	R^2	1/n	log a
West Bengal									
RBC- $FeCl_3$	c/x=0.0028c+0.0057	0.94	$361^{b\S}$	$0.48^{c\S}$	$174^{c\S}$	log x=0.6909 log c+1.6785	0.66	0.320^{b}	2.039^{c}
SBC-$FeCl_3$	c/x=0.0022c+0.0008	0.97	429^{a}	2.90^{a}	1247^{a}	log x=0.2289 log c+2.3516	0.99	0.229^{c}	2.350^{a}
JBC-$FeCl_3$	c/x=0.0029c+0.0024	0.94	329^{c}	1.20^{b}	398^{b}	log x=0.2404 log c+2.156	0.97	0.240^{c}	2.149^{b}
Control	c/x=0.0034c+0.0066	0.98	297^{d}	0.50^{c}	149^{c}	log x=0.3827 log c+1.8952	0.97	0.382^{a}	1.895^{d}
LSD (p=0.05)			16	0.199	102			0.036	0.0307

RBC-rice straw biochar, SBC-sugarcane bagasse biochar, JBC- jute stalk biochar, b -maximum adsorption capacity, bonding strength constant (k), and maximum arsenic buffering capacity (MAsBC), adsorption intensity (1/n) and adsorption capacity (log a). §The values followed by different lowercase letters in a particular column are significant according to LSD (p=0.05)

that the SBC-$FeCl_3$ amendment not only holds more As but does so much more tightly, drastically increasing the soil's resilience against As leaching.

The desorption studies (Figure 2) were crucial for assessing the long-term stability of immobilized As. SBC-$FeCl_3$ consistently showed the lowest As desorption percentages across all steps, indicating the strongest and most stable retention. This was reinforced by the Langmuir desorption parameters (Table 8), where SBC-$FeCl_3$ had the highest bonding strength (k) in soil (58.5 l mg^{-1} in Inceptisol from Assam) confirming the formation of strong inner-sphere complexes that resisted release. The desorption index (DI) values, which were significantly higher for allthe amendments than the control (Table 7), indicated positive hysteresis-the adsorbed As was not easily desorbed (Elrashidi and O'Connor, 1982). This hysteresis was a definitive indicator of specific adsorption and potential precipitation, crucial for ensuring the immobilized As did not become bioavailable again. In conclusion, the $FeCl_3$-engineered biochars, particularly those derived from sugarcane bagasse,

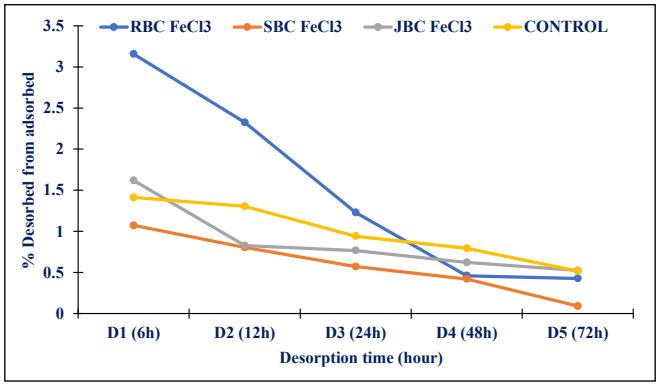

Figure 2: Stepwise desorption curves of arsenic (80 mg kg^{-1}) concentration as affected by different treatments of the screened biochar in Inceptisol of Assam

fundamentally transformed the As sorption-desorption dynamics in acidic soil. They introduced a high capacity of heterogeneous, high-affinity binding sites, primarily through iron oxide-mediated ligand exchange, leading to strong, hysteretic retention of As. This proved their immense potential as sustainable and highly effective amendments for the long-term stabilization and remediation of arsenic-contaminated soils, thereby mitigating the threat to human and ecosystem health.

3.4. Effect of screened and respective pristine biochar on the postharvest parameter of soil and the rice plant

The application of engineered biochars significantly altered the physicochemical properties, which directly influenced arsenic (As) bioavailability and subsequent plant uptake. In the acidic Inceptisol from Assam, $FeCl_3$ engineered biochar generally caused a slight decrease in pH (e.g., SBC-$FeCl_3$: 5.78) compared to their pristine counterparts (SBC: 6.11) (Table 9). This mild acidification was likely as a result of the hydrolysis of Fe^{3+} ions from the $FeCl_3$ treatment, which might have released H^+ into the soil solution. This acidic environment might have enhanced the protonation of iron oxyhydroxide surfaces, increasing their positive charge and thereby strengthening their affinity for arsenate anions ($HAsO_4^{2-}$) through ligand exchange, a process well-documented for iron oxides (Mamindy-Pajany et al., 2011). The most striking change was in EC, where JBC-$FeCl_3$ and SBC-$FeCl_3$ drastically reduced the EC to 0.01 and 0.08 dS m^{-1}, respectively, from much higher values in the control (0.49 dS m^{-1}) and pristine biochars (Table 9). This indicated that these amendments effectively adsorbed or precipitated soluble salts and ions, a property that likely extended to arsenate ions, reducing their mobility and bioavailability. This was confirmed by the extractable As data, where SBC-$FeCl_3$ and JBC-$FeCl_3$ were the most effective treatments, reducing extractable As to 3.33 and 4.81 mg

Table 8: Arsenic desorption equations and Langmuir and Freundlich parameters for different screened biochar applied in Inceptisol of Assam

Treatment	Langmuir equation c/x=c/RAs+1/kRAs	R^2	RAs (mg kg^{-1})	k (l mg^{-1})	Desorption ratio	Freundlich equation log x=log a+1/n log c	R^2	1/n	log a	DI
Inceptisol (West Bengal)										
RBC- $FeCl_3$	c/x=c0.0028+0.0005	0.99	$355^{b\S}$	$6.09^{b\S}$	$98.1^{c\S}$	log x=2.49+0.04 log c	0.93	$0.03^{b\S}$	$2.60^{a\S}$	$10.5^{ab\S}$
SBC-$FeCl_3$	c/x=c0.0023+0.00004	0.99	441^{a}	58.6^{a}	102^{b}	log x=2.63+0.01 log c	0.85	0.02^{b}	2.67^{a}	12.6^{b}
JBC-$FeCl_3$	c/x=c0.0028+0.0001	1.0	357^{b}	21.8^{b}	108^{a}	log x=2.53+0.02 log c	0.82	0.03^{b}	2.58^{a}	8.17^{ab}
Control	c/x=c0.0034+0.0003	0.99	295^{c}	13.4^{b}	99.3^{c}	log x=0.382 log c+1.89	0.74	0.10^{a}	2.14^{b}	2.53^{b}
LSD			13.5	18.1	2.49			0.07	0.26	9.59

RBC: Rice straw biochar; SBC: Sugarcane bagasse biochar, JBC: Jute stalk biochar; Maximum As retention after desorption (RAs); K: bonding strength, bonding energy (1/n) and sorption sites (log a) DI (desorption index). The values followed by different lowercase letters in a particular column are significant according to LSD (p=0.05)

Table 9: Effect of screened and respective pristine biochar on the pH, EC and carbon contents in Inceptisol of Assam

Treatment	pH	EC (dS m^{-1})	SOC (%)	Extractable As (mg kg^{-1})	TC (%)	Straw yield (g pot^{-1})	Plant As (mg kg^{-1})	Plant uptake (g pot^{-1})
RBC	6.05^{bc}	0.33^{c}	0.63^{de}	5.96^{ab}	0.75^{d}	47.4^{ab}	4.98^{b}	236^{a}
RBC- $FeCl_3$	5.97^{cd}	0.34^{c}	0.70^{cd}	5.11^{c}	0.90^{cd}	43.0^{bc}	4.30^{d}	184^{d}
SBC	6.11^{b}	0.50^{b}	0.64^{de}	5.78^{b}	1.03^{c}	38.7^{c}	4.62^{c}	178^{d}
SBC-$FeCl_3$	5.78^{e}	0.08^{c}	0.82^{a}	3.33^{e}	0.85^{cd}	41.4^{bc}	2.22^{f}	91.9^{f}
JBC	5.93^{e}	0.04^{c}	0.73^{bc}	5.31^{c}	1.32^{b}	51.2^{a}	4.22^{d}	216^{b}
JBC-$FeCl_3$	6.23^{a}	0.01^{a}	0.78^{ab}	4.81^{d}	1.81^{a}	46.5^{ab}	3.11^{e}	144^{e}
Control	5.99^{cd}	0.49^{b}	0.61^{e}	6.16^{a}	0.73^{d}	38.0^{c}	5.39^{a}	204^{c}
LSD (p=0.05)	0.09	0.04	0.07	0.20	0.28	7.40	0.25	10.4

EC: Electrical conductivity; SOC (Easily oxidizable organic carbon) and TC (Total carbon). The values followed by different lowercase letters in a particular column are significant according to LSD (p=0.05)

kg^{-1}, respectively, compared to 6.16 mg kg^{-1} in the control. The increase in SOC for $FeCl_3$-treated biochars, particularly SBC-$FeCl_3$ (0.82) and JBC-$FeCl_3$ (0.78), suggested that the modification process did not destroy the organic carbon matrix (Table 9). This enhanced SOC, combined with the iron oxides, could have provided additional binding sites for As through complexation (Sinha et al., 2011).

Plant response directly reflected the changes in soil extractable As, confirming the well-established positive relationship between bioavailable As and plant uptake (Giri et al., 2011; Das et al., 2013). The amendments that reduced extractable As the most also resulted in the lowest As content in rice straw. SBC-$FeCl_3$ (most reduced extractable As) led to the lowest As content (2.22 mg kg^{-1}) (Table 9). It was well-established that amendments rich in Fe could promote the formation of iron plaque on rice roots (Awasthi et al., 2017). The modified biochar's iron-containing complexes probably prevented arsenic movement from roots to shoots, by plaque formation which decreased the plant's overall arsenic build-up (Li et al., 2018).

The impact of screened biochar treatments on straw yield was more complex and soil-specific. Several amendments (RBC, JBC, JBC-$FeCl_3$) increased yield as compared to the control, likely by improving soil health and nutrient supply (Adekiya et al., 2020). The application of engineered biochars significantly increased the total carbon ((TC) content compared to their respective control (Assam control: 0.73%) (Table 9). Notably, JBC-$FeCl_3$ caused the largest increase in TC content (1.81%). The organic carbon matrix itself provided functional groups (e.g., carboxyl, phenolic) that could bind As through mechanisms like complexation and cation bridging, adding to the overall immobilization capacity of the soil (Arco-Lázaro et al., 2016). The organic carbon from the biochar might influence microbial activity in the rhizosphere, further modifying As speciation and bioavailability (Huang et al., 2019).

The recalcitrant nature of pristine and engineered biochar might have enhanced TC content in soil (Purakayastha et al., 2015).

4. CONCLUSION

Engineered biochar prepared from sugarcane bagasse with $FeCl_3$ with an application rate of 6.70 g kg^{-1} emerged as the best management strategy to stabilize arsenic in Inceptisol of Assam and further arrested its transfer from soil to rice plant. The amendments that reduced extractable As the most also resulted in the lowest As content in rice straw i.e. SBC-$FeCl_3$ led to the lowest As content. The results of the greenhouse experiment were indicative only which need to be further reconfirmed through field experimentation.

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