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Meta-Analysis of Biochar as an Amendment for Arsenic Mitigation in Paddy Soils

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Abstract

Purpose of Review The purpose of this review is to evaluate the effectiveness of biochar in immobilizing arsenic (As) in contaminated paddy soils and its impact on As availability and bioaccumulation in rice, as well as rice plant biomass.

Recent Findings Recent studies have focused on managing As contamination in agricultural fields, with a particular focus on South and Southeast Asia, where rice, a primary food source and As accumulator, is of significant concern. Biochar, a product of biomass pyrolysis, has emerged as a viable solution for environmental remediation due to its effectiveness in immobilizing metal(loid)s in water and soil. The successful implementation of biochar as a soil amendment strategy has led to growing interest in its use as an effective means of reducing the bioaccumulation and availability of metal(loid)s, including As.

Summary A meta-analysis of 25 studies revealed that biochar generated from maize and sewage sludge successfully reduced As availability and bioaccumulation in rice grains. In addition, the use of biochar led to higher biomass and yield of rice crops compared to control groups. Modified biochar was more effective in decreasing As availability, likely due to interactions with iron and calcium phases or complexes occurring in or on the biochars. Nevertheless, at elevated biochar dosages, As mobilization was noted in field conditions which warrants further investigation.

Keywords Arsenic · Contamination · Biochar · Meta-analysis · Rice · Soil

Introduction

Arsenic (As) contamination of terrestrial and aquatic systems is a persistent global problem, particularly in south and Southeast Asia, and Latin America [1]. Arsenic contamination in groundwater and its associated human health risks have been recorded in at least 20 countries around the world, including Argentina, Chile, Finland, Hungary, Mexico, Nepal, Republic of China, Bangladesh, and India [2•]. While drinking water is considered a significant source of As exposure, food is an equally important exposure route, especially in the South and Southeast Asian countries [3–6]. Irrigation water has been shown to greatly contribute to the accumulation of As in soils, especially paddy soils in Asian countries [7••]. This is because paddy fields are frequently irrigated with As-contaminated groundwater, especially during the dry season [6]. Data analytics have been employed to more than 50,000 aggregated data sets globally of observed groundwater As concentrations [8••]. The authors created a global map of groundwater As exceeding 10 μg L^{-1} and predicted areas with future As problems. It was estimated that approximately 94 to 220 million people globally, the vast majority (94%) of which reside in Asia, could be exposed to high levels of As in groundwater through drinking water and food sources. Rice is the primary food source for half of the world's population, especially in Asian, African, and Latin American countries and for a large population in Asia, notably for the 560 million people who live in poverty [7••]. Asia produces and consumes 90% of the

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world's rice, a significant proportion of which is produced in As-contaminated areas [7••].

An overview of the total As concentrations in rice grains, soils, and irrigation waters in Asian countries [8••] shows that the mean total As content in rice grains ranged from 18 to 1560 mg kg^{-1} with a mean of 420 mg kg^{-1}, which is higher than the Codex Alimentarius Commission's maximum level for inorganic As (i-As) in husked rice (350 mg kg^{-1}) and in polished rice (200 mg kg^{-1}) [8••]. The As concentration in irrigation water ranged from quantification limits to 1014 mg L^{-1} and in soils, it ranged from 0.06 to 112 mg kg^{-1} with a mean of 11.74 mg kg^{-1} [8••]. The authors also reported a significant ($p < 0.05$) positive correlation was found between As concentrations in rice grains, soils ($r = 0.65$), and irrigation waters ($r = 0.46$).

Management solutions that are effective, efficient, and feasible (especially under local and regional conditions) are needed for the remediation of As-contaminated soil to reduce human health risks from the soil-crop-food transfer. Both phytoremediation and bioremediation have been used to remediate As-contaminated sites [9–12]. Site remediation options for As include inorganic amendments such as phosphorus [12], silicon [13], iron [14], and selenium [15], and organic amendments such as sugarcane bagasse [16, 17] and vermicompost [18, 19]. One of the limitations of organic amendments, however, is that they need to be applied in large quantities. Biochars have proven to be effective organic amendments in contaminated soils for reducing the availability and bioaccumulation of metal(loid)s, such as As [20, 21, 21–23]. Biochar is produced by subjecting organic matter to pyrolysis at high temperatures ranging from 300 to 1000 °C in an oxygen-deprived environment [24]. The biochar's surface functional groups, including hydroxyls (OH), carbonyls (CO), and carboxyls (COOH), when ionized, act as binding sites for metal(loid)s [24]. The negatively charged OH groups bind to positively charged metals, C=O groups form bonds by contributing lone pairs of electrons from the C atom to metals, and COOH forms coordinate covalent bonds through carboxylate anions (COO^{-}). Moreover, the electron-rich aromatic surface of biochar can attract electron-deficient metal cations through donor–acceptor interactions [25]. The promising outcomes from various studies demonstrating the effectiveness of biochar in sequestering contaminants have generated significant interest in its potential as a soil amendment for environmental remediation [21]. Pristine biochar poorly adsorbs both inorganic and organic As, the two most common forms of As in paddy porewater [22]. Moreover, pristine biochar has limited effects on As immobilization as reported for palm fibers [26•], rice straw [27•], and corn stem [28•]; hence, there is a need for modification of the biochar to ensure adsorption of As.

At present, most biochar research has focused on its use from a technical or economic perspective in relation to soil quality and the remediation of surface-, ground-, and waste-waters [29–31]. There has been little systematic, integrated research undertaken on the main properties/mechanisms of biochars that can be utilized to effectively prevent the availability and bioaccumulation of As from contaminated soils for the protection of human and animal health. Meta-analysis is increasingly being used in contaminant science to systematically synthesize the findings from single independent studies with a similar question to derive conclusions about the larger body of research. A meta-analysis approach can also help in resolving conflicting results obtained from different studies by providing a quantitative estimate of the overall effect size. This is particularly useful when the results of individual studies are inconclusive or when the sample size of a single study is not large enough to detect a statistically significant effect. Meta-analysis has been used to address a range of contaminant-related issues, including the effects of pesticides and fertilizers on soil and aquatic fauna, the toxicity of pesticides in aquatic ecosystems, the challenge of micropollutants in aquatic systems, the effects of insecticides on freshwater ecosystems, and heavy metal pollution in urban soils [32, 33].

The aim of the present study was to conduct a meta-analysis of independent biochar amendment studies and evaluate the potential efficacy of biochar application as an effective amendment to prevent the availability of As in contaminated paddy soils and its bioaccumulation into rice grain. This meta-analysis provides key information on the design and use of biochars to amend As-contaminated soils.

Materials and Methods

A systematic review was undertaken of published articles reporting the use of biochar to amend As-contaminated paddy soils. Boolean operators (e.g., "OR" and "AND") were used to develop search terms from the keywords—"arsenic," AND "soil," AND "biochar," AND ("rice" OR "paddy"). Searching ISI Web of Science and PubMed with these terms identified relevant research papers published in English from 2006, when the term "biochar" was first formally used [34]. The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) flowchart is presented in Fig. 1. Studies were only included in the meta-analysis if (1) the research was carried out using rice as the test crop; (2) information regarding the characteristics of the biochar was reported; (3) As concentrations in the soil and paired rice grain were reported; and (4) details of the analytical method(s) and quality assurance procedures were reported. Based on the criteria above, out of 52 studies initially identified, 25 studies (published between 2013 and 2023) were used for meta-analysis. The studies provided data on parameters such as sample size and mean values of As concentrations in rice and soil, agronomic parameters (tiller

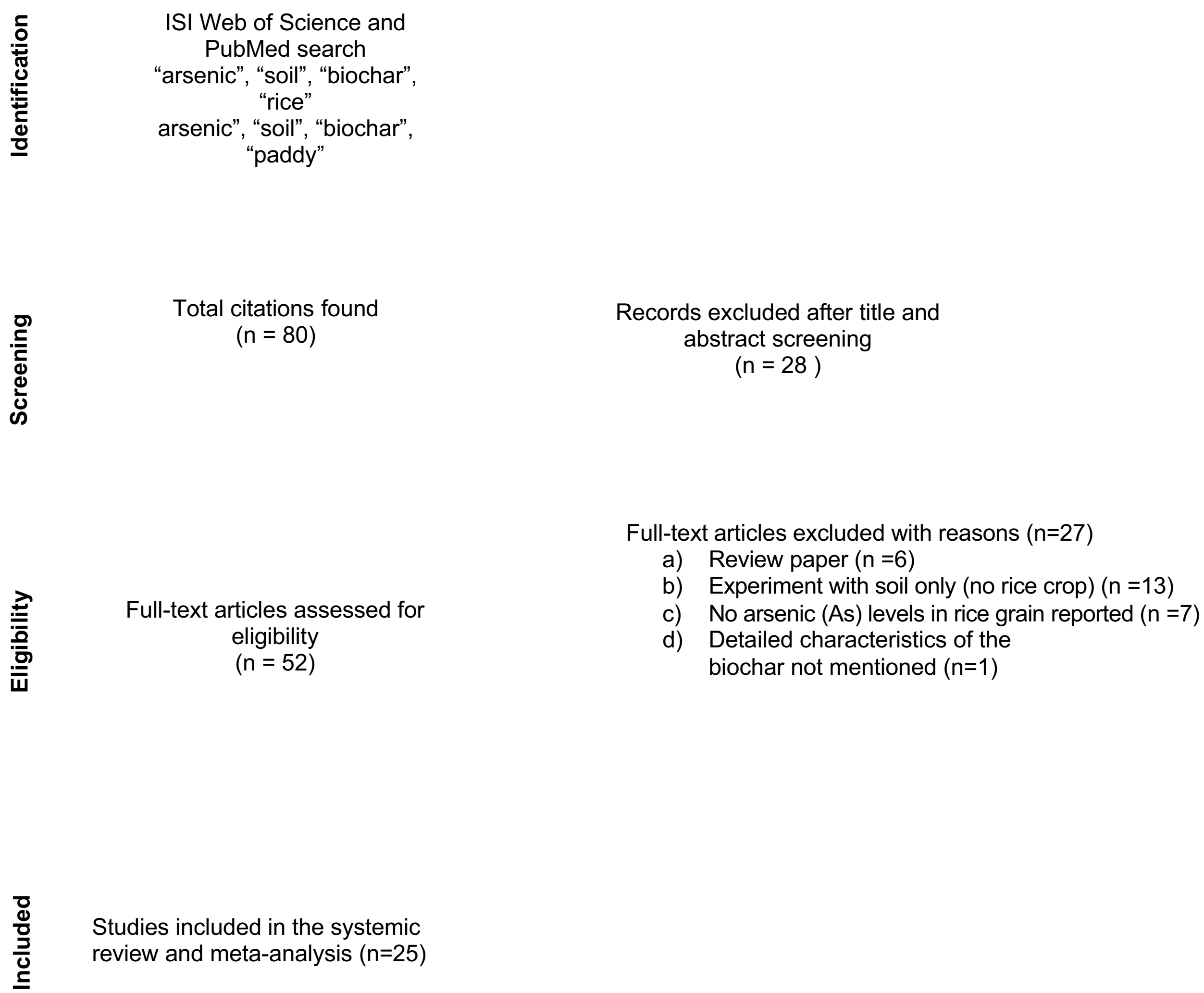

Fig. 1 PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) flowchart showing the selection of studies eligible for a meta-analysis

number, plant height, leaf, grain, shoot and root biomass), biochar (type, pyrolysis conditions, modification), and soil condition (type, physiochemical properties). Where the data were presented only in the form of figure, the data were extracted manually from the figures using WebPlotDigitizer version 4.6 [35].

A “random-effects” (RE) model was used for the meta-analysis presented here as it allows for variation in effect sizes between studies, beyond what would be expected by chance. This variation is due to differences in study design, sample size, population characteristics, or other factors that can affect the outcome being measured [36]. The RE model is a statistical method used in meta-analysis to combine data from multiple studies with a common research question [36]. It accounts for both within- and between-study variation in estimating the overall effect size. In a RE model, it is assumed that the true effect size varies across studies, and the observed effect sizes are drawn from a normal distribution with a mean equal to the true effect size and a variance that includes both within- and between-study variation [36]. This means that each study has its own true effect size, but these true effect sizes are not identical across studies, and the variation in true effect sizes is assumed to follow a normal distribution [37]. Observed study estimates vary not only due to random sampling error but also due to inherent differences in the way studies have been designed and conducted [38].

Briefly, a forest plot was developed using the data from individual studies in the meta-analysis to give a visual indication of the degree of heterogeneity. The absence of difference between the study group and the marginal level, also known as the “no effect” or “zero effect” line (the mean difference was zero at this point), is shown by a vertical line in the plot’s center. In the plots, the squares represent the mean difference values for each study, and the size of the squares indicates the effect of the estimate and the weight of the studies. Each horizontal segment's succeeding endpoints showed 95% confidence intervals (CI) that were symmetrical about the mean. When the 95% CI did not include zero, the mean effect size was considered statistically significant. If the CIs were 95% overlapping, then there is no statistically significant difference between the two groups [38, 39]. When all the independent studies were combined and averaged, the diamond represents the point estimate and CIs. The blue diamond symbol on plots represents the summary effect estimate, which is a combined estimate of the effect sizes of all the studies included in the meta-analysis. The summary effect estimated in the study was calculated using a weighted average of the individual effect sizes, where the weight of each study is determined by its sample size or precision [38]. The point estimate of the summary effect was represented by the center of the blue diamond, while the width of the diamond represents the precision of the estimate (CI). If the blue diamond does not cross the vertical line of no effect (zero), this suggests the summary effect estimate is statistically significant, indicating that there is evidence of a difference between the treatment and control groups. On the other hand, if the blue diamond crosses the line of no effect, it suggests that the summary effect estimate is not statistically significant, indicating that there is no evidence of a difference between the treatment and control groups. The data analysis was performed in R-Studio (version 1.3.1093 2.3.1) using the "*metafor*" package (version 3.8–1) [40•].

Results

Collated Study Data

The details of biochar (pristine and modified) used for the amendment of the As-contaminated paddy soils are summarized in Table 1. Of the 25 studies selected, twenty studies were undertaken in China, two in Australia, and one in Thailand. Twenty-three studies were pot experiments, whereas two [26, 27^{-1}, with a mean value of 54.17 ± 40.33 g kg^{-1}. The cation exchange capacity (CEC) ranged from 11.5 to 73.0 cmol kg^{-1} with a mean value of 31.04 ± 15.97 cmol kg^{-1}. The mean specific surface area ranged from 2.76 to 276.24 m^2 g^{-1} with a mean of 97.41 ± 87.64 m^2 g^{-1}. The mean pore volume and diameter were 0.1506 ± 0.00784 mL g^{-1} (0.0144 to 0.2026 mL g^{-1}) and 5.68 ± 2.76 mm (4.02 to 10.6 mm), respectively. From the histogram of the dose of biochar (Figure S1, A), it was observed that in most of the cases the biochar dose used was < 2% with a mean of 1.93%. The histogram of total As content (Figure S1, B) of the experimental soil of the studies revealed the presence of very high As with a mean value of 84.22 mg kg^{-1}. The water management strategies followed during experimentation as reported in the different studies have been depicted in Table S1. It was observed that to simulate rice growing conditions that are closer to actual rice soil environments, the biochar-amended soil in the pots were flooded for a week before transplanting of rice seedlings. Generally, throughout rice growth, a 1–2 cm water layer was maintained, increasing to 3 cm and then 6 cm in specific intervals. For continuously flooded condition, the pots were irrigated daily until the soil moisture reached near saturation, and then were continuously flooded until 10 days before the harvest. In case of alternately wet and dry and intermittently flooded condition, the pots were allowed to dry until small, surface cracks were present, at which point the soils were reflooded (with a 2–3 cm water level on the soil surface).

Effect of Biochar Amendment on as Concentrations in Rice

The RE model revealed a significant ($p < 0.001$) weighted mean CI value of − 567.78 mg kg^{-1} (95% CI, − 800.92 to − 334.64) (Fig. 2). An overall negative effect size implies a shift to the left on a scale going from increasing to decreasing As concentrations in rice grains due to the biochar amendment in contaminated paddy soils in comparison to controls [37]. The biochars prepared from sewage sludge (pristine and modified) and maize straw (irrespective of the dose) were found to reduce the As concentrations in rice grains (CIs did not overlap the zero-effect line) (Fig. 2). Pristine biochar prepared from bean stalks and rice straw in field experiments was not effective in reducing the As concentration in rice grains. The inconsistency index of 99.98% indicated significant heterogeneity ($p < 0.001$).

Effect of Biochar Amendment on Rice Agronomic Parameters

The application of biochar in contaminated paddy soils was found to increase rice plant height by a weighted mean value of 7.51 cm (95% CI, 3.39 to 11.63) (Figure S2a). Significant heterogeneity (98.91%; $p < 0.001$) was observed in the data. The sewage sludge, wheat straw (pristine and modified), and rice hull (modified) biochar significantly increased plant height (Figure S2a). A significant effect of biochar amendment was found on rice tiller number ($p < 0.001$) (Figure S2b), with sewage sludge biochar significantly increasing tiller numbers irrespective of the doses. The amendment of contaminated paddy soils with biochar was also found to increase the biomass of rice root (weighted mean value, 0.78 g; 95% CI, 0.59 to 0.98) and shoot (weighted mean value, 2.15 g; 95% CI, 1.30 to 2.99) (Figure S3, a and b). Significant heterogeneity ($p < 0.001$) was observed at 94.69% and 97.56% CI, respectively. Wheat straw (pristine and modified), maize straw (modified), and oil palm fiber (modified) biochars significantly increased the biomass of both the root and shoot of rice plants.

Table 1 Details of the biochar used for amendment of arsenic-contaminated paddy soils

Reference	Country	Raw material	Temperature (°C)	Biochar modification	**Biochar name	Biochar pH	C (g kg^{-1})	CEC (cmol kg^{-1})	***SSA (m^2 g^{-1})	Pore volume (mL g^{-1})	Pore diameter (nm)
[42•]	China	Rice straw	500	Hydroxyapatite, zeolite	Biochar	6.13	57.63	28.93	49.57	---	---
					HZB	7.27	21.24	73.0	---	---	---
[66•]	China	Rice husk	700	Silicon, nano-montmorillonite	RHBC	9.98	55.03	---	187.7	0.1968	4.317
					Si-RHBC	10.41	53.65	---	182.3	0.1968	4.317
					NM-RHBC	9.94	39.86	---	189.6	0.1972	4.159
[63•]	China	Wheat straw	600	Goethite	Biochar	7.45	---	---	44.97	---	---
					GB	7.99	---	---	276.24	---	---
[83•]	China	Wheat straw	600	Goethite	Biochar	7.45	---	---	44.97	---	---
					GB	7.99	---	---	276.24	---	---
[49•]	China	Egg shell, corn cobs	450	Mixing (1:1)	EB	9.58	13.1	---	6.5	---	---
					CB	9.83	81.6	---	75.2	---	---
					ECB	9.66	49.35	---	40.9	---	---
[50•]	China	Egg shell, corn cobs	450	Iron	FCB	8.71	62.6	---	205.8	---	---
					FEB	8.65	7.8	---	25.3	---	---
					FCEB	8.67	35.3	---	115.5	---	---
[84•]	China	Rice husk, codgrass	600	---	RBC	11.3	---	—	---	---	---
					SBC	10.5	---	---	---	---	---
[47•]	China	Sewage sludge	550	---	SSBC	7.22	28.0	-	5.50	0.0144	10.5
					SSBC5%	4.86	14.40	---	---	---	---
					SSBC10%	5.39	20.20	---	---	---	---
[76•]	China	Sewage sludge	600	---	SSBC	7.18	27.8	-	5.57	0.015	10.6
					SSBC5%	5.66	30.5	---	---	---	---
					SSBC10%	5.83	51.5	---	---	---	---
[67•]	Australia	Rice hulls	600	Iron	RBC	9.81	---	---	201.39	0.2026	4.024
					Fe-RBC	5.33	---	---	142.6	0.1650	4.6285
[68•]	Australia	Rice hulls	600	Iron	RBC	9.81	---	---	201.39	0.2026	4.024
					Fe-RBC	5.33	---	---	142.6	0.1650	4.6285
[85•]	Thailand	Rice husk	750	Ash, acid wash	RHB	7.3	37.92	26	---	—	---
					RHA	9.3	31.03	29	---	—	---
					AWB	3.2	31.03	---	---	—	---
[86•]	China	Corn straw	600	Iron, manganese, cerium	BC	8.91	84.92	38.4	60.16	—	---
					FMCBC1	9.41	63.25	43.28	27.16	—	---
					FMCBC2	9.64	56.27	43.86	36.21	—	---
					FMCBC3	9.72	43.48	44.52	46.87	—	---
[87•]	China	Corn straw	600	Iron, manganese	BC	8.93	75.5	---	61	—	---
					FMBC1	9.60	67.3	---	208	—	---
					FMBC2	3.17	53.8	---	7.53	—	---

Table 1 (continued)

Reference	Country	Raw material	Temperature (°C)	Biochar modification	**Biochar name	Biochar pH	C (g kg^{-1})	CEC (cmol kg^{-1})	***SSA (m^2 g^{-1})	Pore volume (mL g^{-1})	Pore diameter (nm)
[28•]	China	Corn stem	600	Iron, manganese, lanthanum	BC	8.93	75.5	---	61	---	---
					FMLBC1	6.96	62.3	---	2.76	---	---
					FMLBC2	6.83	54.8	---	12.2	---	---
					FMLBC3	6.9	47.1	---	30.6	---	---
[88•]	China	Palm shell	500	Nano zero-valent iron	---	---	296	---	244	---	---
[69•]	China	Rice straw, corn straw, bamboo	600	---	RSBC	11	47.1	---	175.5	---	---
					CSBC	10.5	60.3	---	3.6	---	---
					BABC	9.6	87.3	---	9.2	---	---
[26•]	China	Palm fibers	800	Iron	Fe-BC	6.0	60	---	---	---	---
[75•]	China	Palm fibers	700	Zero-valent iron different levels	Biochar	9.3	86.7	11.5	241.6	---	---
[20•]	China	Oriental plane	650	Iron	RawBC	9.25	69.34	21.59	110.7	---	---
					FeBC	4.41	59.91	16.70	74.5	---	---
[41•]	China	Rice straw	450	Iron	Biochar	10.7	---	15.1	---	---	---
					Fe-Biochar	4.87	---	14.2	---	---	---
[61•]	China	Corn straw	600	Manganese oxide	BC	10.4	85.3	---	60.9	---	---
					MBC	10.8	73	---	3.18	---	---
[27•]	China	Bean stalk, rice straw	500	---	BBC	9.2	44.5	27.5	---	---	---
					RBC	10.5	27.4	32.1	---	---	---
[48•]	China	Rice husk, pig carcass	650	Silicon, iron, phosphorus	SiBC	9.0	43.7	---	237.3	---	---
					PBC	10.6	30.8	---	18.4	---	---
					Fe-Si-BC	3.1	38.8	---	69.3	---	---
					Fe–P-BC	3.6	40.4	---	43.6	---	---
[82•]	China	Rice husk, pig carcass	650	Iron, phosphorus	PBC	10.6	30.8	---	18.4	---	---
					FePBC	3.6	40.4	---	43.6	---	---
Mean ± SD			590.74 ± 92.33	---	---	8.06 ± 2.28	54.17 ± 40.33	31.04 ± 15.97	97.41 ± 87.64	0.1506 ± 0.0784	5.68 ± 2.76
Range (minimum–maximum)			450–800	---	---	3.10–11.3	7.8–296.0	11.5–73.0	2.76–276.24	0.0144–0.2026	4.02–10.6

*Indicates field experiment

**Biochar name: *HZB* hydroxyapatite zeolite biochar, *RHBC* rice husk biochar, *Si-RHBC* silicon-RHBC, *NM-RHBC* nano-montmorillonite-RHBC, *GB* goethite biochar, *EB* egg shell biochar, *CB* corn cob biochar, *FCB* iron-CB, *ECB* iron-CB, *SSBC* sewage sludge biochar, *RHA* rice husk acid wash, *FMBC* iron-manganese-cerium biochar, *FMLBC* iron-manganese-lanthanum biochar, *BBC* bean stalk biochar, *RBC* rice straw biochar

****SSA* specific surface area

• Papers of importance

•• Papers of major importance

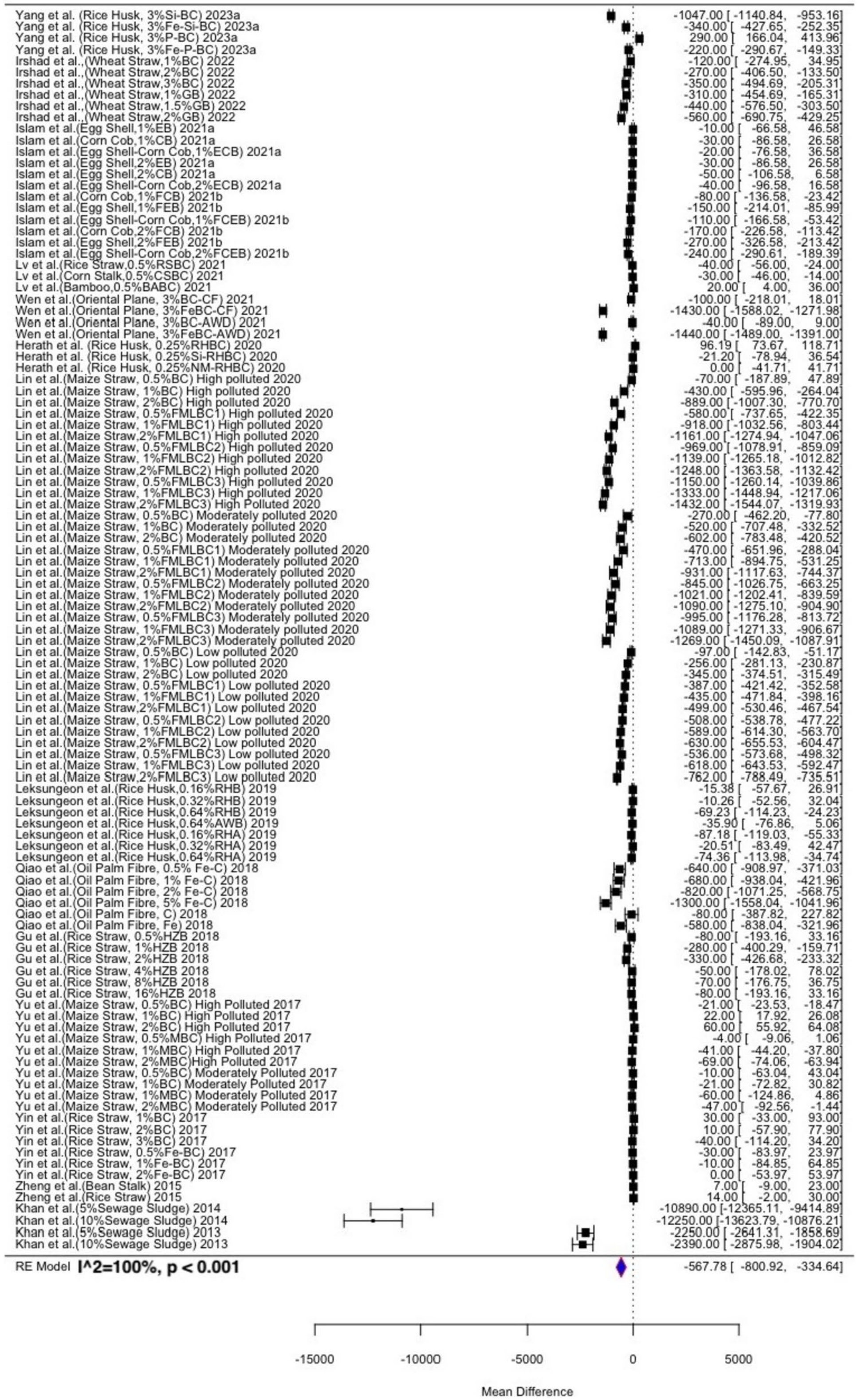

Fig. 2 Forest plot showing the effect of biochar on the weighted mean difference of arsenic concentration in rice grain (mg kg.$^{-1}$) between the different studies with their respective confidence intervals and weight in the meta-analysis together with the heterogeneity statistics. Si-BC, silicon-enriched biochar; BC, biochar; MBC, manganese oxide biochar composites; BC:Fe:Mn:La at different weight ratios: (FMLBC1) 25:4:1:1, (FMLBC2) 25:4:1:3, and (FMLBC3) 25:4:1:5. The number of studies considered was 15

The effect of biochar amendment in contaminated paddy soils on the biomass of leaf and grain is presented in Figure S4. Biochar application increased the biomass of leaf (weighted mean value, 1.54 g; 95% CI, 0.95 to 2.12) and grain yield (weighted mean value, 3.44 g; 95% CI, 2.52 to 4.36) (Figure S4 a and b). The maize straw (pristine and modified) biochar significantly increased the rice plant leaf biomass, whereas the sewage sludge (pristine), maize straw (pristine and modified), and oil palm fiber (modified) biochar significantly increased the grain biomass. Again, significant heterogeneity of 97.04% and 99.31% ($p < 0.001$) was observed in the leaf and grain biomass data, respectively.

Effect of Biochar Amendment on Exchangeable as Concentrations in Paddy Soils

The effect of biochar amendment on the exchangeable As concentrations in the contaminated rice paddy soils is presented in Figure S5a. The application of biochar was found to reduce the exchangeable As concentrations in soils (weighted mean value = – 0.04 mg kg^{-1}; 95% CI, – 0.06 to – 0.02). Significant heterogeneity of 99.96% was observed in the data. Maize (pristine and modified) and rice straw (pristine and modified) biochar amendment was found to significantly reduce ($p < 0.001$) the exchangeable As concentration in paddy soils (Figure S5a). The extraction of exchangeable As was done by shaking soil for 4 h at 20 °C using a neutral salt like 0.05 M $(NH_4)_2SO_4$ as an extracting agent [28• and 41•] whereas 1 M NH_4Cl has also been used as the extracting agent [42•].

The effect of biochar amendment on the Fe- and Ca-bound As fractions in the rice paddy soil is presented in Figure S6 (a and b). Both Fe-bound (weighted mean value, 1.40 mg kg^{-1}; 95% CI, 0.74 to 2.05) and Ca-bound (weighted mean value, 1.69 mg kg^{-1}; 95% CI, 1.13 to 2.26) As increased significantly ($p < 0.001$) with the addition of biochars. Significant heterogeneity of 95.24% and 99.21%, respectively, was observed in the data. The Fe-bound As was extracted by shaking the soil for 4 h at 20 °C in the dark using 0.2 M NH_4-oxalate buffer at pH 3.25 (amorphous Fe) and 0.2 M NH_4-oxalate buffer + 0.1 M ascorbic acid at pH 3.25 (crystalline Fe). The Ca-bound As was extracted by microwave-assisted digestion of soil with acids like H_2SO_4 and HNO_3. The rice straw (pristine and modified) and maize straw (pristine and modified) biochars increased the Ca-bound fraction of As in soils. Maize straw (pristine and modified) biochar was the only biochar that significantly increased the Fe-bound As fraction in amended soils.

Discussion

Biochar as an Amendment for As-Contaminated Paddy Soils

Twenty-three experiments were conducted as pot trials, with only two under field conditions. The soils used for the pot experiments were mine-impacted soils rather than the soils that were geogenically contaminated with As, like the soils of south and Southeast Asia (contamination due to the use of contaminated irrigation water). The meta-analysis revealed that the application of biochar (pristine and modified) in As-contaminated rice paddy soils was not only effective in reducing As concentrations in rice grains but also in improving grain and plant agronomic parameters (plant height and biomass of root, shoot, leaf, and grain). Consequently, the utilization of biochar led to an increase in rice yield. This indicated that biochar has the potential to serve as a dual-purpose amendment, enhancing soil fertility and mitigating As contamination simultaneously. The increase in rice biomass is likely due to the reduced effect of contamination in soils and access to readily accessible nutrients (e.g., macronutrients such as nitrogen (N), phosphorus, and potassium (K) from mineralization of organic matter [43–46]).

It is important to note that the efficiency of biochar in immobilizing As varies depending on factors, such as the properties of the biochar itself (e.g., feedstock, production conditions), the characteristics of the soil or water system, and the specific form of As present. In all the studies considered in the meta-analysis, the biochar used were prepared at high temperature, resulting in high pH of the biochar in most of the cases. The pH of the medium (i.e., soil solution) can affect the charge characteristics of the biochar surface as well as As speciation, but not the pH of biochar. The pH of the medium does not affect the pH of biochar. The pH of biochar is determined by the pH of the solution in which it is formed. Once biochar is formed, its pH is relatively stable and does not change with the pH of the medium [25]. For example, depending on the solution pH, various functional groups, such as amine, alcohols, and carboxylic, on the surface of biochar tend to be protonated, hence altering the surface charge of biochar [25]. From the meta-analysis, it was observed that pristine biochar prepared from sewage sludge [47•] and modified biochar with Fe, Mn, and La from maize straw [28•] were effective in reducing the As content in rice grain. The meta-analysis further revealed that rice husk biochar, specifically modified with Fe and Si, demonstrated effective reduction in grain arsenic (As) content [48•]. However, biochar derived from eggshell and corn cob did not effectively reduce grain As content [49•, 50•]. On the other hand, biochar derived from oriental plane and modified with Fe exhibited a reduction in grain As content [51•]. However, maize straw biochar modified with MnO was not effective in reducing the As content. The detailed mechanism of As adsorption and immobilization has been discussed in subsequent sections.

Maize straw biochar application reduced the concentration of As in soil solution by adsorbing As onto biochar solid phase surfaces, effectively immobilizing As in the soils and reducing its uptake by rice plants [52]. The study also suggested that the effectiveness of biochar in immobilizing As depended on the type and dosage of biochar applied. In a greenhouse study, corn straw biochar increased soil pH and reduced the availability of As in soil by changing its chemical speciation and solid phase binding in soils [53]. A field study reported that Fe-modified palm fiber biochar was effective in reducing the availability of As in a contaminated soil [27•]. Conversely, the availability of As increased in contaminated soils due to rice straw and bean stalk biochar amendment, likely due to solid phase surface competition between phosphate released from biochars and arsenate on the surface of solid phases [43].

From the meta-analysis, it was observed that biochar application alters soil pH [28, 45, 54], and it may also have an indirect impact on how plants receive nutrients [55]. Different soil and biochar mixtures may have various pH buffering capabilities [56]. Numerous studies have demonstrated that adding biochar to soil can greatly increase its nutritional content [57] and [58]. This is due in part to the direct supply of nutrients, like N, P, and K, as well as a decrease in runoff and leaching [59]. Previous findings demonstrated that utilizing soil amendments increased nutrient concentrations in brown rice and improved the soil CEC and organic matter content due to retained and reduced leaching of nutrients [60]. The improvements in soil physical properties resulting from the addition of pristine or modified biochar can primarily be attributed to the observed increase in root weight, grain weight, and overall biomass, as indicated by the meta-analysis. Functionalized biochars have, to a certain extent, resulted in adjustments to soil pH, improvements in soil fertility status, mitigation of potentially toxic element availability, and stimulation of enzymatic activities in the soil. These effects contribute to creating enhanced soil conditions and a more environmentally friendly setting for rice cultivation. This phenomenon occurs because the incorporation of biochar into the soil effectively reduces the bulk density of the topsoil, thereby facilitating the growth of roots deeper into the soil profile. Consequently, this enhanced root growth promotes a greater bioavailability of nutrients for rice plants, leading to increased grain weight and overall biomass. However, it is noteworthy that the growth of roots, rice grains, and biomass did not exhibit a proportional increase with higher biochar doses. This suggests that an excessive amount of biochar might not necessarily lead to a corresponding increase in biomass. It is important to maintain an optimal level of biochar [61•].

Mechanism of as Immobilization in Paddy Soils by Amendment with Biochars (Pristine and Modified)

The type of biochar used, preparation approach, and modifications affect the mechanisms of As immobilization in soils. Surface functional groups are important determinants of biochar adsorption capacity for metals and metalloids, and the amount and type of functional groups vary depending on the feedstock and pyrolytic temperature [62]. The presence of numerous functional groups, like alcoholic, phenolic, and carboxylic groups associated with the biochar, can play the role of electron donors regulating the reduction of As(V) to As(III) [53]. Carboxylic and phenolic functional groups on the surface of biochar particles have been suggested to be strong adsorption/complexation sites for As in soils [63•].

A high (> 450 °C) pyrolysis temperature has been used to prepare pristine biochar in all the studies considered in the meta-analysis. The yield and surface characteristics of biochar are based on thermochemical methods, operating conditions, and feedstock. It is widely known that low-temperature-generated biochars from slow pyrolysis have low hydrophobicity and aromaticity but significant surface acidity and polarity. Volatile chemicals in the biomass tend to be eliminated from the medium as the pyrolytic temperature rises. This increases surface area and ash content while reducing surface functional groups and exchange sites [20•]. As the pyrolytic temperature rises, aliphatic C species are transformed into aromatic rings, generating a graphene-like arrangement that enhances the pore volume, pore distribution, and surface area of the pristine biochar [20•]. Biochars with a high concentration of C in condensed aromatic rings have few functional groups. High-temperature pyrolysis carbonization is appropriate for forestry and agricultural wastes with higher levels of lignin, cellulose, and hemicellulose [64••].

All the studies included in the meta-analysis have consistently utilized a high pyrolytic temperature (> 450 °C) for the production of biochar. According to Lehmann et al. [44], the impact of low-temperature pyrolysis (≤ 450 °C) on pristine biochars did not influence the mobility of As in soil. However, it was noted that pristine biochars produced through high-temperature pyrolysis (> 450 °C) significantly increased the mobility of soil-bound As. Biochars created through higher pyrolysis temperatures exhibit greater efficacy in immobilizing As compared to those generated at lower temperatures. This enhanced immobilization potential can be attributed to their heightened aromaticity, porous structure, and the presence of mineral phases (such as $CaHPO_4$, $Ca_3(PO_4)_2$, $CaCO_3$) [65••]. The escalation in pyrolysis temperature is believed to enhance the breakdown of lignin and cellulose in the source materials while eliminating functional groups containing hydrogen and oxygen. As a result, the surface area of the biochar increases [30]. Notably, in the studies analyzed for this meta-analysis, pristine biochars produced from rice biomass [66•, 67•,68•, 69•] at elevated temperatures demonstrated a greater surface area, which has the potential to 330 enhance the adsorption of As. Moreover, biochars derived from rice husk [66•] and rice hulls [67•, 68•] exhibited pore diameters within the 1-10 nm range, proving to be particularly effective in immobilizing As in soil.

Modification of biochar may be a solution to enhance the adsorption of As by biochar, reducing its mobility/availability as observed from the results of meta-analysis. Rice straw biochar modified with hydroxyapatite and zeolite increased the amount of Ca in soil which sequesters As from the exchangeable fraction, likely into insoluble Ca-bound As [42•]. The presence of a larger surface area and pore density in biochars modified with zeolite likely further increased their ability to remove As from the exchangeable fraction in soils. Additionally, modified biochar having higher amounts of oxygen-containing functional groups [70] may covalently link to As [71] and remove it from the soil available fraction for crop uptake. Modification of wheat straw biochar with goethite likely removed As from the exchangeable fraction in soils due to adsorption reactions on Fe solid phases. The addition of Fe and Mn oxide phases to soils has been shown to reduce As mobility and bioavailability [61, 72]. The addition of Fe-amended biochars in soils may also decrease As uptake by rice through an Fe plaque formation and As adsorption on roots [51, 61, 66, 71, 73], potentially by limiting the dissolution of Fe minerals [68•]. The silicate groups present in biochar can oxidize Fe(II) ions on the biochar surface to Fe(III) at near-neutral pH levels. Iron(III) rapidly forms a Si-based ferrihydrite complex on the surface of the biochar by complexing with hydroxyl ions found in the soil-porewater [68•]. Silicon exhibits greater mobility than As, which means that it can compete with As for uptake by the plant. This competition for uptake may also be influenced by the expression of silicon transporters [71]. Depending on the soil pH, As(III) likely present under reducing paddy soil conditions can bind to ferrihydrite through, for example, As(III) inner-sphere complexes through bidentate interactions [74]. The combination of ZVI with oil palm fiber biochar resulted in a significant decrease in As bioavailability in rice paddy soils [75•]. Oxic-suboxic conditions in paddy soils can result in the oxidation of the highly reactive ZVI, converting the released soluble Fe into amorphous iron oxyhydroxides phases (e.g., amorphous iron oxyhydroxides, such as ferrihydrite). Soluble Fe^{2+} can be oxidized by biotic (iron-oxidizing bacteria, FeOBs) or abiotic processes [75•]. The meta-analysis revealed that the application of maize straw biochar, modified with manganese oxide, resulted in a reduction of available As in paddy soils. As a result, the bioaccumulation of As in rice was also decreased. The availability of As in paddy soils is significantly influenced by redox conditions, which in turn affect the way As is chemically structured in soil solutions and its interaction with surfaces through modifications in the surface charge of iron (Fe), manganese (Mn), and aluminum (Al) oxides and hydroxides [61•].

Some studies have reported that adding biochar to the soil throughout rice cultivation increased the amount of dissolved As in soil pore water, mainly due to the release of As from amorphous and crystalline Fe-oxide fractions as observed in pot experiments [49, 76, 77]. The authors, in microcosm-based anaerobic incubation studies, found As concentrations in soil solutions treated with biochar significantly increased by 2.8–6.6 times, with the increase in biochar doses (0.5–5%, w/w), especially at higher concentrations (3–5%, w/w). Iron and As were shown to be significantly positively correlated during rice culture ($r^2 = 0.73$, $p < 0.001$), suggesting that the microbially mediated reductive dissolution of Fe (oxyhydr-) oxides may be the primary cause of the release of As during rice cultivation [78, 79]. Increased activity of *Geobacter* and *Desulfosporosinus* (As(V)-/Fe(III)-reducing bacteria) triggered by an excessive biochar dose was likely responsible for the increase of As in pore waters under anaerobic settings [80, 81]. These studies suggest that elevated application rates for some biochars could increase the As concentrations in soil solutions and hence the fraction available to rice plants, increasing the accumulation of As in rice [61, 79]. Higher doses of biochar (1–5%) have also been shown to increase the As in soil pore water under anoxic conditions [70]. Therefore, the dose of biochar can significantly modify As mobility in soil and needs to be optimized.

It is widely acknowledged that soil enzyme activities serve as important indicators for assessing the impact of contaminations on soil quality, soil management, and agricultural practices [48•]. In this study, the results of redundancy analysis revealed a significant contribution (3.3%, $p = 0.006$) of available As to the variability observed in enzyme activities from application of Si- and Fe-modified biochar. Moreover, all enzymes, with the exception of acid phosphatase, exhibited a positive correlation ($p < 0.01$) with available As in the soil. It is attributed to the enhanced coordination between the active sites of enzymes and substrates in the soil [48•]. Regarding As, its behavior is intricately linked to microbiological activities and Fe chemistry under different redox conditions [82•]. Under intermittent flooding conditions along with the application of Fe-enriched biochar, where oxygen levels experience temporary interruptions, As interactions involve the participation of Fe-oxidizing bacteria like *Acidovorax*. These conditions lead to the incorporation and/or co-precipitation of As by Fe oxides, with *Acidovorax* showing relatively high abundance due to the intermittent oxygen availability [82•]. In order to enhance the safety of rice production, it is crucial to not only implement water management strategies for paddy fields but also to dedicate further endeavors towards the utilization of modified biochar for the sustainable remediation of soils contaminated with As. This entails tasks such as refining application rates, adjusting the proportion of additive materials, optimizing modification methods, and developing novel modified biochars.

Conclusion and Future Directions

Overall, the meta-analysis suggests that biochar has the potential to immobilize As in paddy soils, reduce its mobility and bioavailability, and improve soil properties, which can indirectly affect As contamination in rice crops. The effectiveness of biochar as an amendment for As-contaminated paddy soils is influenced by various physical and chemical properties and further research is needed to better understand the mechanisms and optimize the use of biochar in this context.

The surface area, pore volume, functional groups, and organic/inorganic makeup of biochar surfaces, as well as their adsorption capacity, differed substantially (e.g., contents of C, O, inorganic elements, ash, mobile matter). These crucial characteristics are influenced by several factors, including the feedstock used in the production of biochar, the machinery used (drum pyrolizers, rotary kilns, fixed bed reactors), the pyrolysis temperature, and duration, heating rate and post- and pre-treatments (drying, crushing, sieving, activation, impregnation). The maize straw and sewage sludge pristine biochars were most effective in reducing the As content in rice grain in terms of the type of feedstock used to produce biochar. The modified biochars were most effective in the immobilization of As in soil and hence reducing As bioavailability. The rice straw biochar modified with hydroxyapatite, zeolite, and Fe, and maize straw biochar modified with Fe and Mn effectively increased the Fe- and Ca-bound As fractions in the soil, which resulted in the reduced bioavailability of As. Following the addition of modified biochars to paddy soils, As may accumulate less in rice tissues due to a variety of processes and mechanisms, such as the chemi- and physisorption of As species onto biochars, sequestration of As on Fe plaque and decreased As uptake by rice roots due to the competitive uptake with silicate ions. Further, the addition of biochar leads to a decrease in the number of Fe(III)-reducing bacteria, which, in turn, reduces the mobility and bioavailability of inorganic As species in the rice rhizosphere. A low dose of biochar 0.5–2% (w/w) was effective in reducing the As content in rice grain even in highly polluted soils. However, reports of As mobilization due to the application of biochar at higher doses was also observed. One of the benefits of using biochar as an amendment is that it is required in much smaller quantities compared to organic amendments, such as vermicompost or farmyard manure, which need to be applied in large quantities.

While meta-analysis is a powerful tool for critically analyzing research findings, it also has certain limitations. Firstly, the included studies exhibited considerable heterogeneity in terms of study design, participant characteristics, and outcome measures, which might influence the pooled effect estimates, which are considered by the RE model. Furthermore, variations in study quality and the availability of data, as well as the inherent limitations of relying on aggregated data rather than individual-level data, may have impacted the precision and generalizability of the results. Finally, it should be noted that the meta-analysis provides summary estimates based on group-level data and may not fully capture individual-level nuances or subgroups within the data. Despite these limitations, this meta-analysis provides valuable insights into the overall trends and patterns in the available literature on the potential use of biochar as an amendment for As-contaminated paddy soil.

Future studies should consider using biochar-based sorbents for the remediation of As in rice soils and address the following research gaps:

- Competitive sorption of As on the surface of biochar in the presence of different anions and cations should be studied, as these may be present concurrently with As in the real environment. The competing ions may include phosphates, sulphates, silicates, metal(loid)s, pesticides, and per- and poly-fluoroalkyl substances.
- In paddy fields, the pH and redox condition of soil fluctuate drastically during the crop cultivation period due to flood irrigation after a dry spell. Further research is required to assess the efficacy of biochars in reducing As availability under varying pH and redox conditions.
- Further research is needed to understand the longevity of biochar's efficiency to keep the grain As content low and the frequency of biochar application to keep As in rice grains below the recommended safe levels.
- The influence of biochar addition to soils (physicochemical properties) on the soluble As speciation in pore waters and solid phase partitioning needs to be understood.
- Most pot experiments on As and biochar undertaken to date have used soil contaminated with As by mining activities. Further research is needed in soils that are geogenically contaminated with As or receive As-contaminated wastewater, mirroring the soils of South and Southeast Asia.
- The efficacy of biochars in reducing As in rice grain needs to be assessed under field conditions (where water sources for irrigation are contaminated with As). The amount of irrigation water used, As concentration in irrigation water, the use of fertilizers, and the cropping sequence are likely to affect the efficacy of biochar in As immobilization/mobilization.
- Research on novel thiol-functionalized biochars, biochar/nano-ZVI composites, and nano-particle-impregnated (e.g., mackinawite) biochars is needed. Although little research has concentrated on these features, modification with amide functional groups on biochar's surface may significantly aid in sequestering As.

- A cost–benefit analysis of modified biochar production and its application in field conditions is needed to assess its viability for local and regional use. Pristine biochars are easier to manufacture and are also effective in immobilizing As in the soil.
- From a pragmatic standpoint for use in regions such as South Asia, methods for low-tech production of biochar that can be used by farmers are required to facilitate the adoption and implementation of biochar use for the remediation of As-contaminated paddy soils.

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Declarations

Conflict of Interest The authors declare no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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Papers of particular interest, published recently, have been highlighted as: The rationale for the importance level assigned to an article is explained in bold text at the end of the reference.

- • Of importance
- •• Of major importance

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