

REVIEW

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Modified biochar for remediation of potentially toxic elements in soils: a systematic review of modification approaches, novel mechanisms and field-scale applications

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Abstract

Modified biochar based remediation has emerged as a promising strategy for addressing potentially toxic elements (PTE) in soils, owing to its diverse physicochemical properties and environmental compatibility. Most prior reviews focus on pristine biochar for wastewater treatment, overlooking the enhanced potential of modified biochars in soil based PTE remediation. This review establishes a clear linkage between the pristine biochar modification methods to surface chemistry changes and novel immobilization mechanisms, while also evaluating field applicability and long-term risks. A bibliometric analysis of 1170 publications from 2010 to 2024 was conducted to map international collaborations, thematic evolution, and knowledge hotspots. Results showed that research themes clustered around bioremediation processes, metal adsorption/immobilization mechanisms, and biochar based pollution control. The analysis revealed a shift from foundational studies to application-driven research, with a surge in interest toward modified biochars and complex contaminant interactions after 2021. Biochar production parameters and post-synthesis modifications critically shape its functional properties, which in turn govern key immobilization mechanisms. However, field efficacy of modified biochar is influenced by environmental factors. Additionally, aging processes and potential metal remobilization pose long-term sustainability concerns. Modified biochars offer a context-dependent but promising tool for sustainable soil remediation, contingent on addressing their environmental trade-offs and implementation challenges.

Keywords Modified biochar, Soil remediation, Bibliometric analysis, Functional properties, Environmental sustainability

1 Introduction

Potentially toxic element (PTE) in soils poses a significant threat to environmental health, agricultural productivity, and food safety worldwide. The PTEs such as cadmium (Cd), lead (Pb), chromium (Cr), mercury (Hg), arsenic (As), copper (Cu), and zinc (Zn) are introduced into soils through various anthropogenic sources, including industrial



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emissions, mining, smelting, wastewater irrigation, excessive fertilizer and pesticide application, and improper waste disposal [13, 75]. Once deposited in the soil, these elements persist for long periods due to their non-biodegradable nature and strong affinity for soil components [36]. As a result, they accumulate in the soil matrix, leading to long-term contamination [98]. Elevated PTE concentrations disrupt soil microbial activity, impair nutrient cycling, and inhibit plant growth by interfering with water and nutrient uptake [87]. Over time, these toxic elements may enter the food chain via plant uptake and bioaccumulation, posing serious health risks to animals and humans, including carcinogenic, neurotoxic, and mutagenic effects [182].

Given the environmental and health concerns associated with PTE contamination, sustainable and cost-effective remediation strategies are critical. Among these, biochar has emerged as a versatile amendment with strong potential for PTE immobilization in contaminated soils [91, 122]. Biochar is a stable, carbon-rich product obtained through pyrolysis, a thermochemical conversion of organic biomass such as crop residues, wood waste, manure, or sewage sludge under oxygen-limited conditions, typically below 1000 °C. Its high porosity, large specific surface area (10–400 m² g⁻¹), and alkaline pH (8–11) make it particularly effective for metal sorption and soil amelioration [104]. In addition to improving soil structure and aeration, biochar enhances nutrient retention, increases water-holding capacity, and moderates soil acidity [11, 195]. More importantly, it reduces the bioavailability and leaching of toxic metals by adsorbing or precipitating them through various chemical and physical mechanisms [93, 209]. These advantages position biochar as a promising tool for sustainable land management and ecological restoration.

The remediation capacity of biochar stems from its complex surface chemistry and structural features. Its surface is enriched with functional groups such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (–C=O), which participate in surface complexation and coordination with metal ions [23, 117, 217]. Additionally, biochar exhibits high cation exchange capacity (CEC) (8.2–27.5 cmol(+) kg⁻¹), enabling effective competition among soil solution cations for metal binding [14, 88, 185]. It also facilitates redox mediated reactions, such as the reduction of Cr(VI) to less mobile and less toxic Cr(III), which can then be retained via electrostatic attraction or co-precipitation [162]. Chen et al. [32] reported that biochar reduced extractable Cd by 52%, Pb by 46%, Cu by 29%, and Zn by 36%. Similarly, Lu et al. [116] demonstrated that 3–5% (w w⁻¹) rice straw or bamboo biochar consistently decreased PTE mobility in soils. Biochar's negative surface charge and high surface area collectively contribute to decreased metal solubility and uptake by plants [33, 187].

In addition to reducing metal toxicity, biochar offers co-benefits such as enhanced carbon sequestration, improved soil health, and the recycling of organic waste materials [47, 126, 127]. However, despite its many advantages, unmodified biochar may exhibit limitations such as reduced mechanical strength, loss of active functional groups during pyrolysis, and suboptimal performance for specific metal ions [92, 156]. Consequently, researchers have focused on developing engineered or modified biochars with enhanced sorption capacity and functional performance. Modification techniques include surface oxidation, mineral impregnation, sulfur or iron doping, and surfactant treatment [105, 130]. These modifications aim to increase reactive surface sites, improve selectivity for target metals, and enhance stability in various soil environments [96, 211]. As a result,

modified biochars offer a more robust and tailored approach to addressing the complexity of soil contamination.

Numerous studies highlight the improved performance of modified biochars in remediating specific PTEs. Sulfur-modified biochar has demonstrated a high affinity for Hg, reducing its bioavailable concentration in soil to below $200 \mu\text{g L}^{-1}$ [147]. Surfactant-modified maize straw biochar using hexadecyl trimethyl ammonium bromide consistently reduced As uptake by plants by over 80% compared to unmodified biochar [134]. These findings suggest that tailored biochars can target specific pollutants more effectively than general-purpose amendments [53]. Furthermore, modification expands the range of suitable applications, including remediation of soils co-contaminated with organic and inorganic PTEs [63, 101]. While scaling up remains a challenge, continued advances in feedstock selection, production optimization, and field validation are paving the way for the adoption of biochar based technologies in large-scale environmental remediation projects. Overall, biochar, especially in its modified forms represents a promising and adaptable tool for the sustainable management of heavy-metal-contaminated soils.

Despite the growing interest in the multifunctionality of biochar, remediation of PTEs in soils, particularly through the use of modified biochars remains insufficiently synthesized from a mechanistic and application-oriented perspective. While numerous reviews have addressed biochar based remediation in soils, much of the existing literature predominantly emphasizes pristine biochar, focusing on general adsorption behavior, contaminant-specific performance, or improvements in soil physicochemical properties. Reviews that consider modified biochars often treat modification approaches descriptively or in isolation, without systematically linking modification-induced changes in surface chemistry and composition to distinct immobilization mechanisms operating in soils. Moreover, although soil applications are well represented in the literature, mechanistic insights derived from controlled systems, frequently extrapolated from batch or short-term studies continue to dominate, whereas field-scale validation, long-term stability, and soil–plant–microbe interactions remain comparatively underexplored. Market evidence further suggests that biochar adoption is still largely driven by fertility-related functions rather than contaminant mitigation, with only a small proportion of agricultural users applying biochar specifically for nutrient or contaminant reduction [60].

To address these gaps, we conducted a systematic review of modified biochar based remediation of PTE contaminated soils from 2010 to 2024, integrating quantitative bibliometric mapping with qualitative thematic synthesis. This approach enabled us to chart global collaboration networks and thematic evolutions, pinpoint knowledge hotspots and underexplored regions, and uncover shifts in research trends. By critical synthesis of literature, we evaluated how production parameters, post-synthesis modifications, and environmental variables influence biochar's functional properties, immobilization mechanisms, and long-term stability. Specifically, we address the following key research questions:

1. What are the prevailing research trends, international collaborations, institutional contributions, and geographic patterns in the global scientific landscape of modified biochar based PTE remediation?

2. How do different production techniques and surface modification strategies influence the physicochemical properties of biochar relevant to PTE immobilization?
3. Which mechanisms predominantly contribute to the immobilization of specific PTEs by modified biochars?
4. How do environmental and operational factors affect the efficacy of biochar in remediating heavy-metal-contaminated soils?
5. What are the potential agronomic benefits and environmental trade-offs associated with the field-scale application of modified biochar, and what are the long-term challenges or risks related to its stability, metal remobilization, and impact on soil ecosystems?

Through this critical synthesis, we aim to offer a unified overview of global research trends, key modified biochar characteristics, and the mechanisms underlying PTE remediation. By doing so, this review serves as a valuable resource for the scientific community, helping to inform future research directions and support the development of more effective and sustainable modified biochar based remediation strategies.

2 Methodology

2.1 Collection of the data

2.1.1 Search strategy

The bibliometric analysis was conducted using the SCOPUS database. The search was performed using a combination of specific keywords and Boolean operators to identify relevant research publications related to the application of biochar for the remediation of PTE-contaminated soils, with a focus on soil health, structure, and sorption mechanisms. The search query included the following combination of keywords: (“Biochar”) AND (“Heavy metal” OR “metalloid” OR “lead” OR “cadmium” OR “chromium” OR “mercury” OR “arsenic”) AND (“soil structure” OR “soil texture” OR “soil remediation” OR “soil health” OR “soil quality” OR “soil aggregation” OR “soil porosity” OR “soil amendment” OR “environmental sustainability” OR “soil reclamation” OR “soil microbe”) AND (“sorption” OR “adsorption” OR “transformation” OR “immobilization” OR “cation exchange” OR “precipitation” OR “surface complexation” OR “electrostatic attraction” OR “pore filling” OR “chelation” OR “redox potential” OR “van der waals” OR “zeta potential”).

Although the term “potentially toxic element (PTE)” has gained recognition in recent years for its inclusiveness, the terminology “heavy metal” remains widely used across the global scientific community, including in many recent high-impact publications. Importantly, SCOPUS continue to index the majority of relevant studies under “heavy metal,” and many researchers use the term as a primary keyword for retrieval and citation visibility. Therefore, in order to ensure a comprehensive and unbiased bibliometric analysis, we adopted “heavy metal” as a core search term while also including individual elements (Pb, Cd, Cr, As, Hg) and the broader category of “metalloid”. This approach not only maximized the retrieval of relevant literature but also ensured alignment with the dominant terminology still prevalent in the indexed databases.

2.1.2 Inclusion and exclusion criteria

To refine the dataset, publications were filtered by year, restricting the range to 2010–2024, resulting in 1501 articles. Further filtering by subject area narrowed the dataset to

1465 articles, with major disciplines including Environmental Science (n = 1232), Agricultural and Biological Sciences (n = 226), Chemistry (n = 195), Earth and Planetary Sciences (n = 113), Chemical Engineering (n = 97), Energy (n = 83), and Materials Science (n = 39). Finally, only original research articles were considered by excluding other document types such as reviews, conference proceedings, editorials, book chapters, and notes, which refined the dataset to 1235 relevant research articles. To ensure consistency and accessibility in the analysis, the dataset was further refined by filtering articles based on English language, reducing the total number of articles to 1181. Subsequently, to eliminate duplicates and maintain a high-quality dataset, non-redundant articles were identified, resulting in a final count of 1170 unique research articles. The PRISMA flow diagram was used to systematically depict the study selection process, clearly outlining the inclusion and exclusion criteria applied at each stage of screening and eligibility assessment (Fig. 1).

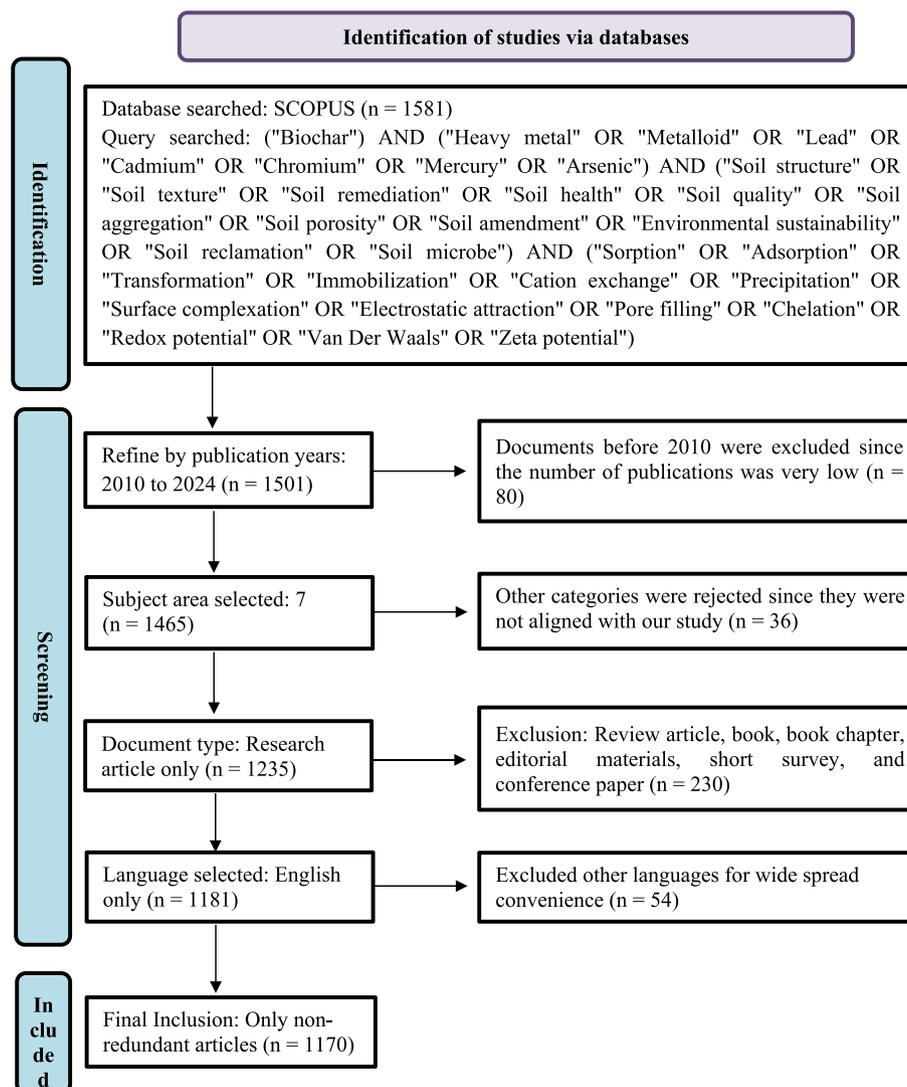


Fig. 1 PRISMA flow diagram of bibliometric data selection with process of data inclusion and exclusion criteria for PTEs remediation using biochar

2.2 Quality assessment

To ensure methodological rigor and transparency, the quality assessment followed Joanna Briggs Institute critical appraisal checklist (<http://joannabriggs.org/research/critical-appraisal-tools.html>). Each included study was systematically evaluated for relevance, credibility, and potential sources of bias, with particular attention to issues such as selective reporting and conflicts of interest. Studies exhibiting significant bias, especially those influenced by commercial interests, were excluded. Screening was conducted independently by two reviewers, with disagreements resolved through consensus or, when necessary, adjudication by a third reviewer to ensure inter-reviewer reliability. This structured evaluation process enhanced the validity and consistency of the review. Additionally, thematic analysis was employed to identify recurring patterns and key conceptual themes, ensuring alignment with the study's objectives.

2.3 Software tools used for bibliometric analysis

A comprehensive bibliometric analysis was conducted using the bibliometrix R-package [17] to assess the research landscape on biochar-mediated remediation of PTE-contaminated soils. The bibliometric data were curated and organized using Microsoft Excel 2021. For network based visualizations, including keyword co-occurrence, author collaboration, and cluster analysis, VOSviewer was employed to explore thematic structures and interconnections within the research domain [184]. Additionally, R programming was utilized to generate figure visualizations and temporal trend maps, enabling the presentation of key insights in a structured and visually interpretable format.

3 Findings and discussion

3.1 Bibliometric analysis

3.1.1 Key insights and global trends

The bibliometric analysis of research on biochar-mediated remediation of PTE contaminated soils over the period 2010–2024 revealed a rapidly growing and dynamic research domain. A total of 1170 non-redundant research articles were analyzed, published across 181 scientific sources. The field involved contributions from 3238 unique authors, indicating a high level of global scholarly engagement. The average number of co-authors per document was 6.62, reflecting a strong trend toward collaborative research. Furthermore, international co-authorship accounted for 41.88% of the publications, emphasizing the global relevance and transnational nature of the research. The dataset included 2598 distinct author keywords, highlighting the diversity of topics and sub-themes addressed within the scope of biochar applications in soil remediation. The average age of the documents was 4.38 years, signifying the recency and relevance of the literature. The field has demonstrated a notable annual growth rate of 39.76%, underlining its emerging importance and increasing research interest. Additionally, the average citation per document stood at 55.22, suggesting a significant academic impact and widespread recognition of the published work within the scientific community. The annual publication trend from 2010 to 2024 shows a steady rise in research output, starting with 2 articles in 2010 and reaching a cumulative total of 1170 articles by 2024, with notable yearly contributions including 150 in 2020, 169 in 2022, and a peak of 217 in 2024 (Fig. 2a). The most frequently occurring terms in the analyzed literature highlight key themes such as charcoal and biochar, soil contamination and pollution, specific PTEs like cadmium

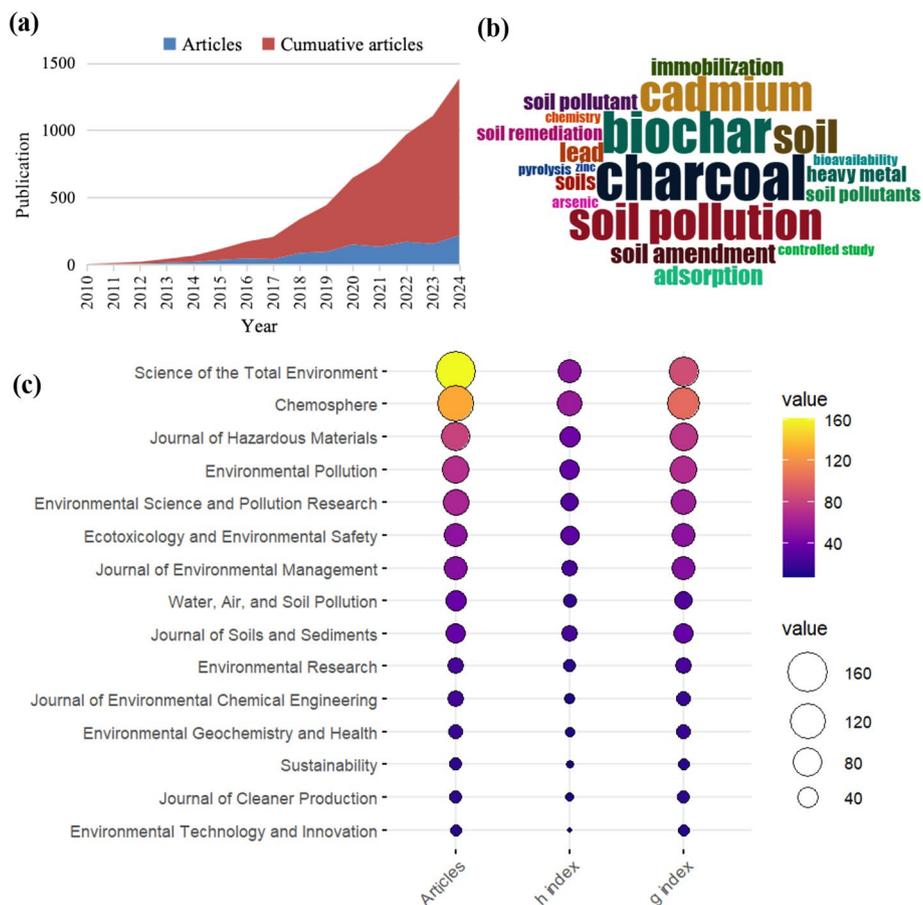


Fig. 2 Key research trends in bibliometric analysis with **a** publication volume, **b** keywords occurrence, **c** leading journals with scholarly impact in global recognition

and lead, soil properties and amendments, adsorption and immobilization processes, pollutant dynamics, remediation strategies, bioavailability, pyrolysis techniques, and relevant chemical aspects, reflecting the core focus areas in the field (Fig. 2b). The analysis of publication sources revealed that *Science of the Total Environment* leads with 161 articles, an h-index of 52, and a g-index of 87, followed closely by *Chemosphere* with 131 articles, the highest h-index of 57, and a g-index of 102 (Fig. 2c). Other prominent journals include *Journal of Hazardous Materials* (81 articles, h-index 40, g-index 74), *Environmental Pollution* (71 articles, h-index 35), and *Environmental Science and Pollution Research* (65 articles, h-index 28, g-index 69). These journals collectively represent the core platforms for high-impact research in biochar and soil remediation, with varying degrees of productivity and citation influence across the field. Based on the total citations of the top 15 most influential publications, along with their countries of origin and normalized total citation scores (Table 1), the analysis highlights a concentration of highly impactful studies originating predominantly from leading research-intensive countries. Hence, future research should move beyond rapid publication growth toward a mechanistic understanding, long-term field-scale validation, and standardized assessment of biochar performance across various soil types and PTEs. Greater integration of interdisciplinary approaches, advanced analytics, and globally coordinated collaborations will be essential to translate high-impact research into scalable, policy-relevant remediation solutions.

Table 1 Highly cited studies on biochar based remediation of potentially toxic elements: bibliometric impact, geographic distribution, and key findings

References	Journal name	Corresponding author's country	Normalized total citation	Key finding
Beesley et al. [24]	Environmental Pollution	United Kingdom	1.4	Biochar reduced Cd, Zn, and PAH bioavailability and phytotoxicity but increased Cu and As mobility, revealing element-specific trade-offs
Park et al. [136]	Plant and Soil	Australia	2.17	Chicken manure- and green waste-derived biochars immobilized Cd, Cu, and Pb, reduced plant metal uptake, and markedly enhanced plant biomass by shifting metals to less bioavailable soil fractions
Zhang et al. [220]	Environmental Science and Pollution Research	China	2.8	Biochar reduces the bioavailability and mobility of heavy metals and organic pollutants in soils, offering a promising amendment for contaminated soil remediation
Uchimiya et al. [181]	Journal of Agricultural and Food Chemistry	United States	1.55	Heavy metal sequestration by biochar is governed primarily by surface functional groups and pH _{pzc} , making biochar selection highly case-specific to feedstock, pyrolysis temperature, soil properties, and target metals
Houben et al. [71]	Chemosphere	Belgium	2.49	Biochar reduced Cd, Zn, and Pb extractability and plant uptake mainly via pH increase and aging effects, enhancing long-term immobilization if soil pH is maintained
Zhao et al. [223]	Journal of Cleaner Production	China	7.15	Pyrolysis temperature is the dominant factor controlling rapeseed stem biochar properties, with higher temperatures producing more alkaline, microporous, high-surface-area biochars suitable for environmental remediation
Jindo et al. [81]	Biogeosciences	Spain	3.22	Biochar properties are strongly governed by feedstock and pyrolysis temperature, with high-temperature biochars (600–800 °C) exhibiting higher carbon content, surface area, and adsorption capacity, while low-temperature biochars retain more labile components
Bian et al. [27]	Journal of Hazardous Materials	China	2.93	A single application of wheat straw biochar sustainably reduced soil Cd and Pb bioavailability and rice Cd uptake over three years through pH increase and mineral-biochar binding mechanisms
Agrafioti et al. [6]	Journal of Analytical and Applied Pyrolysis	Greece	2.01	Sewage sludge-derived biochar, especially non-impregnated forms, effectively reduced heavy metal leaching and preferentially adsorbed cationic metals (Cr ³⁺) over anions (As(V)), with pyrolysis temperature strongly controlling yield and surface area
Jien and Wang [79]	CATENA	Taiwan	1.9	Biochar amendment markedly improved soil fertility, aggregation, and microbial activity while reducing soil erosion by up to 64% in highly weathered acidic Ultisols
Jiang et al. [80]	Journal of Hazardous Materials	China	2.5	Rice straw biochar increased soil pH and negative surface charge, consistently immobilizing Cu and Pb by shifting them to reducible and oxidizable fractions, while Cd showed comparatively weaker stabilization
Yang et al. [212]	Environmental Science and Pollution Research	China	4.14	Rice straw biochar, especially at higher rates and finer particle size, more effectively reduced heavy metal extractability and enhanced soil enzyme activity than bamboo biochar over one year

Table 1 (continued)

References	Journal name	Corresponding author's country	Normalized total citation	Key finding
Uchimiya et al. [179]	Chemosphere	United States	0.6	Biochar aging via oxidation and interaction with organic matter can mobilize Cu, while low-temperature, base-treated broiler litter biochar enhanced immobilization of multiple heavy metals
Abbas et al. [1]	Ecotoxicology and Environmental Safety	Pakistan	3.5	Rice straw biochar dose-dependently immobilized Cd, reduced wheat grain Cd by up to 57%, and improved growth and physiological performance in Cd-contaminated soil
Alhashimi and Aktas [10]	Resources, Conservation and Recycling	USA	3.32	Compared with activated carbon, biochar offers lower environmental impacts and comparable or lower costs for heavy metal adsorption, while achieving similar remediation effectiveness when properly engineered

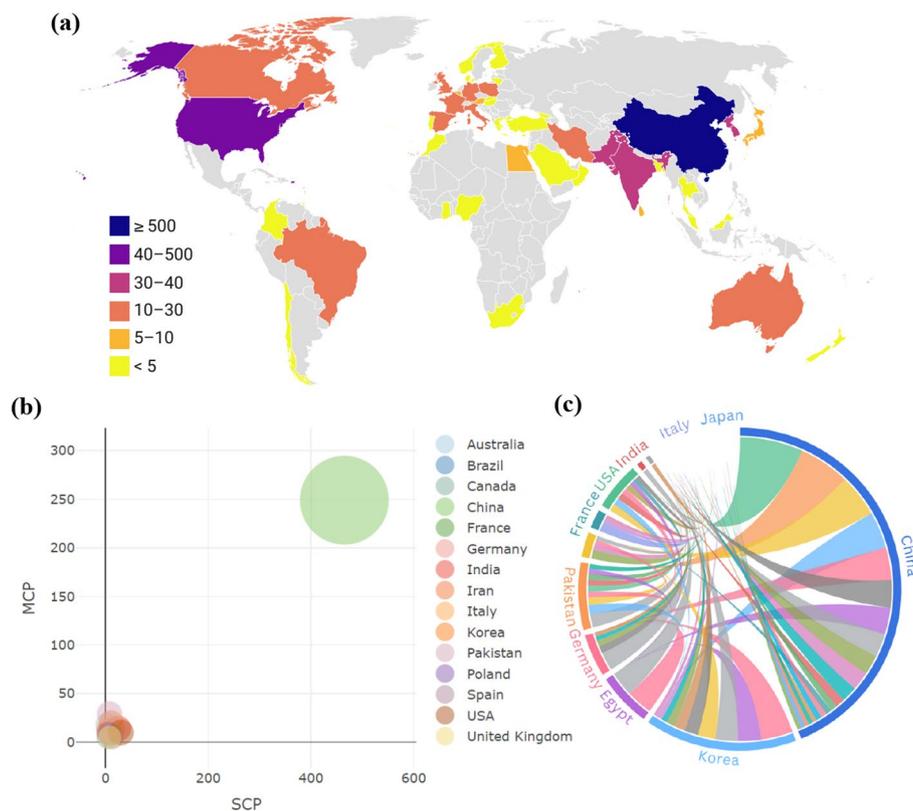


Fig. 3 **a** The analysis of research publications on PTEs remediation using biochar identifies the contributing countries. The map shown above is solely for academic interest only and the author does not intend to offend the sovereignty or territorial boundaries of the country. **b** Single-country publications (SCP) (X-axis) and multiple-country publications (MCP) (Y-axis) illustrate collaboration patterns between countries. A bubble chart visualizes the top 15 countries with SCP and MCP, where bubble size represents the number of articles produced. **c** The collaboration map shows moderate global partnerships

3.1.2 Geographical distribution of research publications

The continent-wise distribution of research articles shows that Asia leads consistently, with major contributions from China (714 articles), followed by India (39), Pakistan (37), Korea (31), Iran (27), and several other Asian countries (Fig. 3a). This dominant position

can be attributed to the rapid industrial growth, high rates of soil contamination, and a strong policy push toward sustainable land management in these regions. Moreover, institutional infrastructure, such as China's Chinese Academy of Sciences and India's ICAR institutes, along with generous government funding, has played a crucial role in accelerating research on biochar based soil remediation. Europe is the second most active region, with notable outputs from France (19), Germany (17), Italy (17), Spain (17), Poland (15), and the United Kingdom (13), among others. The European Union's Horizon 2020 and other coordinated funding mechanisms have supported transnational research collaborations and innovation in sustainable agriculture and environmental restoration, enabling wider adoption of biochar technologies. In North America, the United States contributes 40 articles and Canada 10. Oceania is represented by Australia (22) and New Zealand (1). Australia's contribution is notable, partly due to its arid and nutrient-depleted soils, which necessitate alternative soil enhancement technologies like biochar. National programs such as the Australian Biochar Industry Group (ABIG) have also supported biochar research and development. From South America, Brazil leads with 18 articles, followed by Chile (1) and Colombia (2). Africa shows modest contributions, with South Africa (1), Egypt (5), Nigeria (2), Morocco (1), and Ghana (1). The analysis of publication types based on country collaboration revealed that China leads with the highest number of Single Country Publications (SCP: 465) and Multiple Country Publications (MCP: 249), indicating both strong domestic and international research activities (Fig. 3b). The USA follows with 30 SCPs and 10 MCPs, while India shows a balanced contribution with 25 SCPs and 14 MCPs. Interestingly, countries like Pakistan (MCP: 29) and Korea (MCP: 20) demonstrate higher international collaboration relative to their domestic outputs. Other notable contributors with a strong mix of collaborative research include Australia (MCP: 18), Germany (MCP: 12), Italy (MCP: 12), and France (MCP: 11), highlighting the global and cooperative nature of research in the field of biochar and soil remediation. The collaboration analysis reveals that China is the most active hub of international research partnerships in the field, with its strongest collaboration observed with the USA (76 joint publications), followed by Pakistan (61), Australia (51), Korea (44), and Germany (39) (Fig. 3c). These partnerships reflect both scientific alignment and policy-driven research cooperation, such as China's Belt and Road Science, Technology and Innovation Cooperation Action Plan. Other significant partnerships include Korea-Germany (38), China-Hong Kong (33), China-Egypt (32), and Egypt-Germany (31). Several trilateral and bilateral collaborations also emerge, particularly among Asian and Middle Eastern countries, such as Korea-Saudi Arabia (27), Egypt-Saudi Arabia (30), and Pakistan-Saudi Arabia (16). Cross-continental collaborations like USA-Australia, USA-Germany, France-Italy, and China-United Kingdom further emphasize the global interconnectedness in biochar-related soil research. The pronounced dominance of research outputs from China introduces an inherent geographical bias that may influence the generalizability of findings drawn in biochar-mediated soil remediation studies. While extensive body of work from China provides valuable mechanistic insights and technological advancements, its findings are often derived from region-specific soil characteristics, climatic conditions, biomass feedstocks, and contamination profiles that may not be directly transferable to other agro-ecological zones [189, 213]. Consequently, the efficacy, stability, and environmental trade-offs of biochar applications reported in these studies may differ when applied in regions such as Africa, South America, or

parts of Southeast Asia, where soils, land-use practices, and socio-economic constraints vary notably [164]. This imbalance also affects the development of globally representative remediation frameworks, as underrepresented regions may face distinct challenges, including limited access to tailored biochar feed stocks, differing pollutant spectra, and weaker institutional or regulatory support [125, 140]. To address these gaps, future research should prioritize region-specific field trials, comparative cross-continental studies, and greater inclusion of locally relevant soil-pollutant systems. Strengthening international collaborations, capacity-building initiatives, and equitable funding mechanisms will be critical to ensuring that biochar based remediation strategies are scientifically robust, context-appropriate, and globally applicable.

3.1.3 Research trajectories of biochar for soil remediation

The thematic map was generated to systematically uncover, organize, and interpret the conceptual structure of biochar mediated soil remediation research by clustering high-frequency author keywords, enabling the identification of dominant, emerging, and underdeveloped themes, while simultaneously assessing their relative importance and maturity through centrality (x axis) and density (y axis) measures. A total of 150 high-frequency keywords were selected based on their occurrence, with a minimum cluster frequency threshold set at 5 to ensure the inclusion of significant thematic clusters using Walktrap clustering algorithm. Two levels of labels were applied to visualise thematic areas based on relevance degree/centrality (x axis) and development degree/density (y axis). The thematic map analysis reveals a nuanced structure of the research landscape in biochar-mediated soil remediation (Fig. 4a). Niche themes, such as *biochar aging and cadmium immobilization*, *meta-analysis and bioaccumulation*, and *modified biochar in paddy soils*, reflect specialized and narrowly focused investigations, often representing innovative but less-explored areas. In contrast, basic themes (including *cadmium*, *magnetic biochar*, *soil remediation*, and *biochar and PTEs*) constitute the foundational core of the field, highlighting well-established and widely researched topics essential for theoretical and applied development. Emerging or declining themes like *phytostabilisation and co-contamination*, *soil amendments with cadmium*, and *black carbon and charcoal* suggest areas undergoing dynamic shifts, either gaining traction due to current relevance. Motor themes, such as *pyrolysis temperature and PTE immobilization*, represent the driving forces of the domain, indicating cutting-edge topics with strong research momentum and centrality. Interestingly, the intersection between niche and motor themes, including *biomass and hydrochar* and *phytotoxicity and toxic metals*, points to evolving areas with the potential to become central in future research. Likewise, topics like *soil fertility and potentially toxic elements* and *rice and chromium*, which lie at the intersection of basic and motor themes, illustrate research areas that are both conceptually robust and practically influential, signifying their critical role in advancing sustainable soil management practices. The thematic analysis highlights a balanced progression in biochar research, where foundational areas like PTE remediation and soil health remain central, while emerging niches such as biochar aging and modified biochar in specific soils suggest growing innovation. The presence of dynamic themes like pyrolysis temperature and toxic metal immobilization as motor clusters indicates a strong research drive, with overlaps between core and niche themes pointing toward integrated, future-ready directions in sustainable soil remediation.

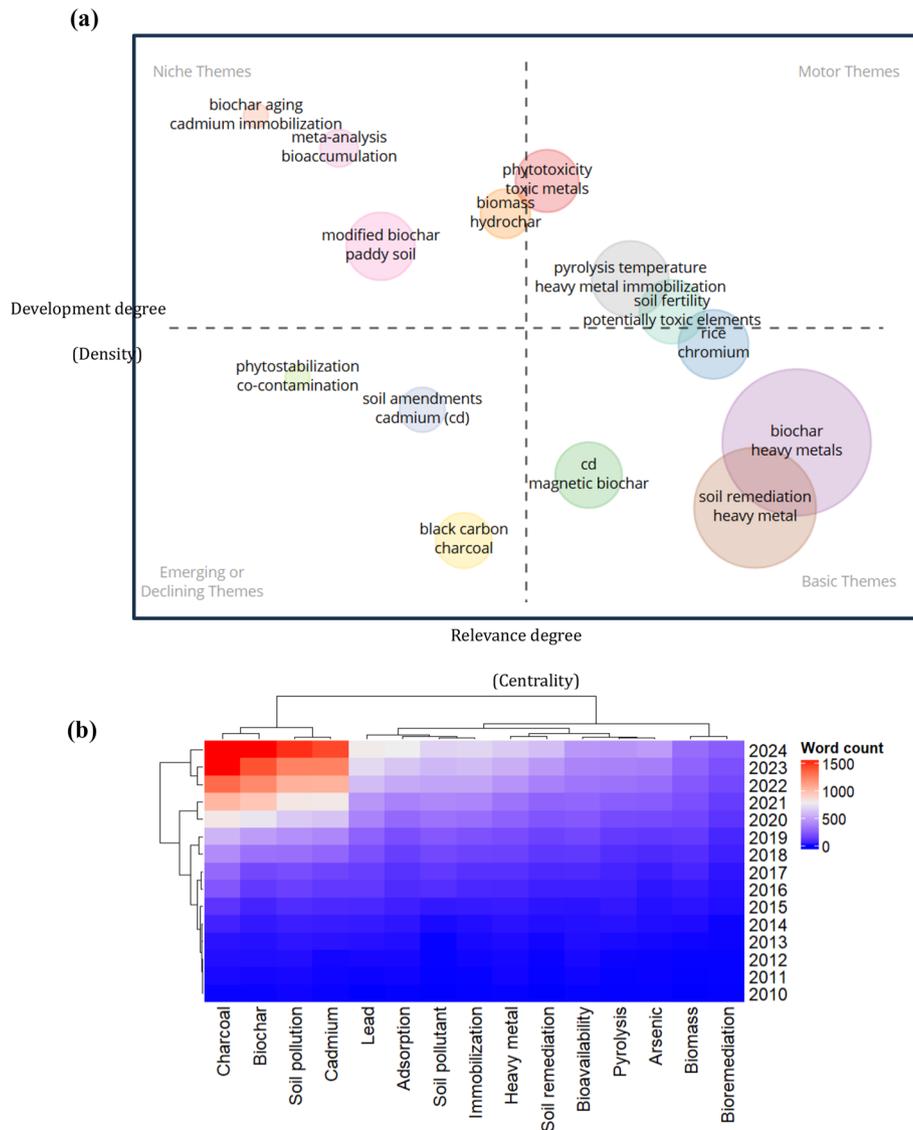


Fig. 4 **a** The thematic map illustrates the shifting research focus on PTEs remediation using biochar over two decades. **b** Clustering of keywords and publication years using k-mean reveals thematic shifts and temporal progression

The k-means clustering was employed to objectively group publication years and author keywords into clusters based on similarity in frequency and distribution, enabling the detection of dominant temporal patterns and coherent thematic structures. The k-means algorithm was executed 100 times to ensure stability and robustness in the clustering outcome. A consensus k-means clustering approach was then employed to derive the most consistent and representative clustering solution. The keyword clustering revealed three distinct thematic groups: the first cluster focused on soil remediation and bioremediation processes, highlighting terms such as *bioavailability*, *pyrolysis*, *arsenic*, and *biomass*, suggesting a foundational interest in environmental restoration mechanisms (Fig. 4b). The second cluster centered around *lead*, *adsorption*, and *immobilization*, indicating a concentration on PTE dynamics and stabilization in soil. The third cluster emphasized *biochar*, *charcoal*, *cadmium*, and *soil pollution*, reflecting an increasing focus on biochar based solutions for metal-contaminated soils. Year-wise

Frequent mentions of rice (*Oryza sativa*), maize (*Zea mays*), and wheat (*Triticum aestivum*) suggest that crop safety and food security are major concerns in areas affected by soil contamination. The inclusion of terms such as sequential extraction, paddy soil, fractionation, and soil stabilization points to interest in metal speciation and the evaluation of risk associated with PTEs. This cluster bridges environmental chemistry with agronomy and plant physiology, reflecting interdisciplinary research for sustainable land use.

- *Cluster 3: Organic waste recycling and nutrient management (blue)*: This cluster highlights organic waste management and its implications for soil health and pollution mitigation. Keywords such as compost, manure, biomass, sewage sludge, and nutrients indicate an emphasis on using organic amendments to enhance soil fertility while managing PTE contamination. The presence of nickel, copper, zinc, and lead suggests a continued concern about the metal content in organic fertilizers. Studies in this cluster likely assess the trade-offs between soil fertility improvement and environmental risks, incorporating aspects of mining and fertilizer residue management.
- *Cluster 4: Microbial ecology and bioremediation processes (yellow)*: The fourth cluster centers around microbial-driven remediation and the biogeochemical dynamics of polluted soils. Terms like bacteria, biodegradation, enzyme activity, urease, and catalase reflect a focus on microbial metabolism and its role in breaking down or transforming PTEs. The recurring mentions of bioremediation, phytoremediation, soil microbiology, and microbial community underscore the importance of biological processes in restoring soil quality. This cluster represents the ecological and biochemical aspect of pollution control, particularly emphasizing soil organic matter, nitrogen cycling, and soil quality enhancement through natural attenuation or engineered microbial interventions.

Future research should focus on integrating material innovation with ecological and biological processes to enhance the efficiency of soil and water remediation. The development of engineered biochars and composite adsorbents with tailored physicochemical properties (surface area, porosity, functional groups) can consistently improve the immobilization of diverse pollutants, including PTEs and metalloids. Simultaneously, there is a pressing need to advance our understanding of bioavailability, phytotoxicity, and plant-metal interactions, particularly in staple crops, to ensure food safety in contaminated agricultural lands. Further exploration of microbial consortia, enzymatic activities, and soil microbiome dynamics can unveil sustainable bioremediation pathways, especially under varying environmental and soil conditions. Additionally, recycling of organic wastes such as manure and compost must be optimized to balance nutrient enrichment with PTE risk mitigation. An interdisciplinary approach that combines omics technologies, field-scale validation, and long-term monitoring will be crucial to designing adaptive and resilient remediation strategies.

Before delving into the core objectives, we have examined (1) the natural and anthropogenic sources of PTE contamination in soils, and (2) the detrimental effects of PTE toxicity on the environment and soil biological health. This background provides a comprehensive understanding of the multifaceted threats posed by PTEs in the soil system. It also underscores the urgent need for innovative, science-driven solutions, particularly

the development and application of modified biochar, as a promising strategy for effective soil remediation.

3.2 PTE sources and its impacts in soil

3.2.1 *Natural and anthropogenic causes of PTE pollution in soil*

The PTE pollution in soil arises from natural sources (weathering of parent rocks and volcanic eruptions) and man-made sources (vehicular exhaust, burning of coal, industrial activities, use of fertilizers, pesticides and mining and smelting of ores, and dumping of municipal wastes) [66, 74, 121]. Black shale, which has high concentrations of sulfides, organic matter and toxic PTEs, is susceptible to chemical weathering under oxidative conditions, resulting in the release of hazardous elements to soil–water systems [138]. The combined use of Pb isotopic tracing and APCS/MLR receptor model revealed that in the urban surface soils, weathering of black shale is the prevailing source of Co (89.16%), Cd (76.79%), Ni (86.19%), Mo (83.51%), Zn (82.90%), and Ti (96.76%). The Pb comes mainly from vehicle exhaust (60.9–61.21%), whereas the As originates mostly from agricultural discharge (67.55%). In contrast, PTEs in rural surface soils are mostly derived from the geogenic impact of black shale weathering [196]. The suspended atmospheric PTEs, primarily originate from sources like volcanic eruptions, fossil fuel burning, smelting, vehicular emissions, bind to particulate matter and settle down through both dry and wet deposition [103]. Feng et al. [54] showed the impact of atmospheric deposition on soil-rice system and reported that atmospheric deposition accounted for 18.5–41.0% of Pb and 10.8–47.7% of Cd in brown rice and 13.7–60.3% of Cd and Pb in rice leaves. Also, atmospheric deposition reduced the soil pH consistently (0.17–0.66 units) and elevated the exchangeable Pb (3.3–26.1%) and Cd (27.1–62.1%) in surface soil. Liu et al. [111] analyzed that industrial areas had annual deposited particle fluxes 1.83 and 1.90 times higher than agricultural areas and reference site mainly because of burning of coal and contributed to 82.63% of Pb deposition. Ma et al. [120] studied that the soils around the municipal solid waste incinerator site were consistently contaminated with As and Cd, while moderately affected by Cu, Pb, Zn and Hg.

The potential sources of these PTEs include municipal solid waste incineration, natural occurrences, industrial waste and coal burning, contributing 36.08%, 29.57%, 10.07% and 4.55% respectively. The effluents from industrial sectors i.e., tanning, textiles, smelting, cement, petrochemicals, electroplating, fertilizers, pesticides and pharmaceuticals contain a variety of PTEs [121]. Guney et al. [62] studied the emission and transport of Hg in the vicinity of a chlor-alkali plant (CAP) and revealed that there were higher atmospheric Hg concentrations near CAP site (16–22 ng m⁻³) and around Lake Balkyldak (13–37 ng m⁻³) than in the city Pavlodar (4–10 ng m⁻³). The heavy use of agricultural chemicals has been a significant factor in the widespread pollution of cultivated soil. Over time, using phosphate fertilizers can lead to an increase in Cd levels in the soil. Application of mixed fertilizers (30% livestock manure and 70% phosphate fertilizers) or pure livestock manure causes drastically increased Cd pollution risk in the short term, the highest risk level being 55.21% [228]. The pesticides contain PTEs either as active ingredient or as impurities [149]. The annual inputs to agricultural soils near the former mining site were estimated to be 17.1, 59.2, 0.311 and 93.8 kg ha⁻¹ for Cu, Zn, Cd and Pb respectively, via surface runoff, atmospheric deposition and irrigation with affected mine water [173].

3.2.2 The effects of PTE toxicity on the environment and soil biology

The PTE pollution is a significant risk to soil microorganisms and higher life forms, including humans, because it can accumulate via food chains (Table 2). They lower food quality in agricultural soils by their toxic impact on plants and reduce land usability, ultimately leading to food insecurity [77]. They can disrupt essential biochemical processes such as photosynthesis and mineral absorption and also can damage various parts of plants, including roots, leaves and cellular components [158]. In animals, these substances can negatively affect vital organs like kidneys, liver, bones, brains and different body systems potentially leading to severe health issues including cancer [83, 152] (Fig. 6).

The Cd is the most toxic soil PTE because it is highly phytotoxic and mobile, particularly in acidic soils with low CEC. The Cd interferes with photosynthesis by substituting Mg^{2+} in chlorophyll as well as suppressing nitrate reductase activity, decreasing nitrate uptake and transport from roots to shoots. In microorganisms, the Cu toxicity can lead to the denaturation of proteins and the destruction of cell membranes [121]. Xiao et al. [203] reported that fungal abundance in soil contaminated with Cd dropped by over 75%, while actinomycetes declined by more than 88%. In soils tainted with Pb, fungal communities and actinomycetes were decreased by more than 31% and 88% respectively, with bacterial communities also decreasing by more than 27%. The urease and acid phosphatase activities were consistently affected by Cd and Pb with 94.3% and 85.2% inhibition at 28.0 mg kg⁻¹ of Cd and 41.4 mg kg⁻¹ of Pb respectively. Excessive levels of Cd, Cu and Zn disrupt soil homeostasis, damaging metabolic pathways and also triggering cell death, impairing processes like nitrification, ammonification and enzyme activity [201].

The PTEs lead to increase in intracellular reactive oxygen species, resulting oxidative stress, which can harm proteins, nucleic acids, lipids and cellular functions and damage DNA [199]. Loi et al. [115] showed that Cd toxicity profoundly inhibited the growth of lettuce, causing decrease in plant height by 29.7–77.5%, number of leaves by 16.4–61.3% and leaf area by 34.5–99%. Overall productivity of plants decreased sharply with declines ranging from 49.6 to 99.6%. Xie et al. [204] reported 25.50% reduction in yield when cherry tomato plants were exposed to 50 μM Cd concentration. Aponte et al. [15] reported that Pb, Zn, Cd, Cu and As contamination of soil consistently reduced the activity of seven enzymes and inhibition order of these enzymes was arylsulfatase > dehydrogenase > β-glucosidase > urease > acid phosphatase > alkaline phosphatase > catalase. Arylsulfatase and dehydrogenase recorded their activities reduction by 72% and 64% respectively. PTEs interfere with plant development and metabolism through the binding to functional groups such as –COOH, –NH₂, –SH and –C=O, thereby inactivating important enzymes and proteins [149].

3.3 Production and functionalization strategies for modified biochar in PTE remediation

3.3.1 Chemical modification

The chemical modification using oxidizing agents and acids is a widely adopted strategy to enhance the surface chemistry and functional properties of biochar. Xue et al. [210] modified peanut hull hydrochar with 10% H₂O₂, which consistently increased the –COOH group content, as confirmed by FTIR (stronger absorbance at ~ 1700 cm⁻¹) and XPS analysis (–COOH content increased from 2.1 to 8.2%). This modification enhanced

Table 2 Adverse effects of potentially toxic elements on plant growth, soil microorganisms and human health

PTE pollution	Toxicological effects on plant and soil	References
Cd and Hg	Soil catalase activity was reduced by 25.52–34.89% by Cd and Hg both, soil urease activity decreased by 76.50–89.88% at 30 mg kg ⁻¹ Hg and 30 mg kg ⁻¹ Cd, soil dehydrogenase activity reduced by 85.60–92.92% at 30 mg kg ⁻¹ Hg and 30 mg kg ⁻¹ Cd, soil acid phosphatase activity decreased by 15.18–32.64% at all Cd levels and 17.09–30.32% at Cd-Hg combination (≥ 3 mg kg ⁻¹)	Xin et al. [206]
Cr	Total C mineralization was reduced by up to 65%, while enzymatic activities decreased in the order: dehydrogenase (70%) > alkaline phosphatase (63%) > fluorescein diacetate (41%)	Dotaniya et al. [49]
Cr	Root fresh and dry weight, root length, spike length, number of tillers per plant and grain weight in wheat crop were reduced by 51.6%, 50.4%, 54.4%, 27.3%, 24.9% and 58.6% respectively at 200 mg kg ⁻¹ Cr	Ahmad et al. [8]
Cd	Induced growth inhibition, oxidative stress, and genotoxicity in wheat seedlings, increased antioxidant enzyme activities and proline accumulation, decreased the uptake of K and Ca	Çatav et al. [231]
Hg	Yield of ginger was reduced by 25.96% at 9 mg kg ⁻¹ Hg; plant height, leaf weight, stem weight and root weight were decreased by 24%, 36.48%, 30.45% and 25.92% respectively as compared to control after 120 days of exposure	Xu et al. [208]
Cr	Decreased the yield of aerial parts by 90% and of roots by 92% and plant height was decreased by 49% in maize crop; had an adverse effect on bacteria <i>Cellulosemicrobium</i> , <i>Rhodanobacter</i> , <i>Kaistobacter</i> , <i>Nocardioides</i> , <i>Rhodoplanes</i> and fungi <i>Humicola</i> and <i>Chaetomium</i>	Wysz-kowska et al. [200]
Cr	Seed germination of black gram was reduced 50.70% at 300 µM Cr concentration in nutrient solution, also root length, shoot length, carbohydrate content and reducing sugar were gradually decreased with increase in Cr concentrations	Rath and Das [150]
Cr	The lowest germination percentages in green gram were observed at a concentration of 100 mg l ⁻¹ of Cr, showing 54.83 ± 0.95 for Pusa Ratna and 53.53 ± 0.71 for Pusa Vishal. For Chickpea, the rates were 47.97 ± 0.49 for Pusa 2085 and 42.60 ± 0.62 for Pusa Green 112, respectively. Root length, shoot length, fresh and dry weight of both cultivars were reduced with increase in Cr concentrations	Singh and Sharma [167]
As	A drop in the CO ₂ assimilation rate, lower stomatal conductance, reduced transpiration rates, and decreased intercellular CO ₂ concentration in Soybean	Veza et al. [186]
As	Soybean seedlings showed a significant drop in root biomass, around 35%, for both As(V) and As(III) at 25 mM. The reduction in shoot biomass was 39% for As(V) and 55% for As(III) at the same concentration. Also root length and shoot length were reduced and cell death of root tips was observed. Total root area was reduced by 12.3 and 23.2% at 25 mM As(V) and As(III), respectively, with reduction in the cortex area of about 18.5% for As(V) and 29.5% for As(III)	Armen-dariz et al. [18]
Al	Net photosynthetic rate and transpiration rate in rice seedlings of RD35 variety were reduced by 74.76% and 47.71%, respectively over control, resulted in a decrease in root length by 26.57% and a drop in shoot fresh weight by 46.15% at 50 mM Al concentration. This treatment also showed significant increase in leaf temperature, chlorophyll degradation, limited CO ₂ assimilation	Phukun-kam-kaew et al. [139]
Cu	Leaf area, shoot dry matter and root dry matter of lettuce were decreased by 63%, 13% and 79% respectively at 400 µM Cu concentration over control	Shams et al. [163]
Pb	The Pb toxicity reduced photosynthetic pigments, such as chlorophyll and carotenoids and triggered oxidative stress, leading to an increase in the production of hydrogen peroxide, malondialdehyde and leachates from the leaves in three rice cultivars. The Pb stress reduced 15.70, 27.03, and 15.63% total tillers pot ⁻¹ , 24.10, 33.33, and 20.27% productive tillers pot ⁻¹ , 19.66, 21.02, and 12.03% grains panicle ⁻¹ , 58.05, 69.12, and 46.27% grain yield pot ⁻¹ were recorded highest in Meixiangzhan 2, Xiangyaxianzhan and Basmati-385, respectively	Ashraf et al. [19]
<i>Toxicological effects on human health</i>		
Cr	Formation of ulcers, allergic reaction, skin rashes, bronchitis, asthma, hepatic and kidney damage, lung cancer, premature abortion, fertility disorder, gastrointestinal haemorrhage	Hossini et al. [70], Ertani et al. [51]

Table 2 (continued)

PTE pollution	Toxicological effects on plant and soil	Refer-ences
Hg	Change in vision and hearing, memory problem, skin rashes, kidney damage, dyspnea, tremors, hallucinations, hypersalivation, neurodegenerative disorder, paraesthesia, affect cardiovascular, immune, endocrine system	Zulaikhah et al. [230], Madhav et al. [121]
As	Cancer of bladder, liver, lung, skin, nausea, vomiting, less production of erythrocytes and leukocytes, pulmonary and cardiovascular disease, hypertension, skin lesions, black foot disease, hyperkerotosis, kidney failure	Rehman et al. [152]
Al	Alzheimer's disease, mouth ulcers, skin ulcers, osteomalacia, Parkinson's diseases, inhibit haemoglobin synthesis, memory loss, tremors, chronic bronchitis	Rehman et al. [152]
Cu	Wilson disease, anemia, cardiovascular disease, disturb memory and learning ability, hepatic and neurodegenerative disorder, renal failure	Rehman et al. [152]
Pb	Neurodegenerative disease, inattentiveness, irritability, hyperactivity, headache among children, decrease bone density, anaemia, weight loss, sperm dysfunction, preterm birth, encephalopathy	Evens et al. [52]
Cd	Mitochondrial dysfunction, renal damage, osteoporosis, cardiovascular disease, lung, kidney and prostate, pediatric cancer, decrease in height and weight of infant at birth, rheumatoid arthritis, osteoarthritis, Alzheimer's and Parkinson's diseases	Chunhabundit [38], Gardner et al. [57], Reyes-Hinojosa et al. [155]

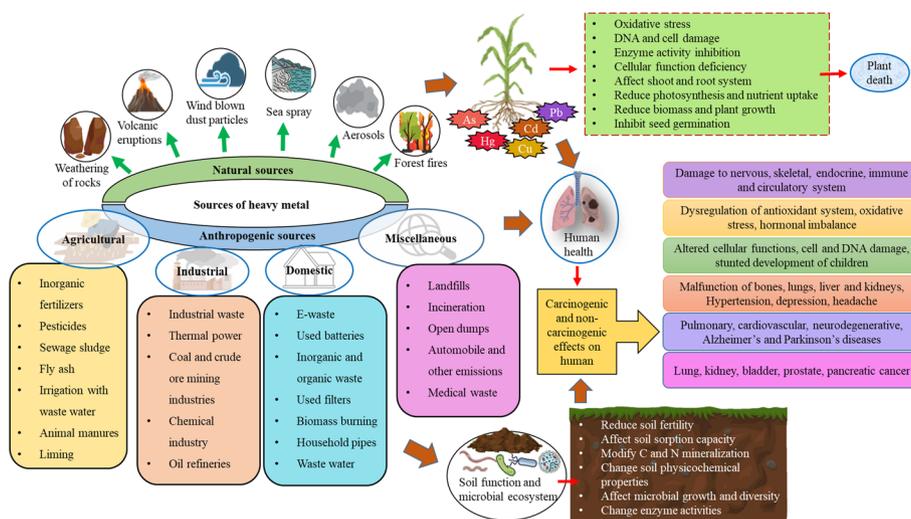


Fig. 6 Sources, pathways, and impacts of environmental contamination by potentially toxic elements (PTEs). This diagram illustrates the origins and consequences of PTE contamination from both natural sources (volcanic activity, weathering, and forest fires) and anthropogenic sources, which are categorized into agricultural (fertilizers and pesticides), industrial (mining and chemical industries), domestic (e-waste and household waste), and miscellaneous (landfills and incineration). These contaminants accumulate in the soil, affecting its fertility, microbial diversity, and biochemical processes. In plants, PTEs lead to oxidative stress, cellular damage, and impaired growth, potentially resulting in death. In humans, exposure causes a wide range of toxic effects, including neurological, respiratory, and cardiovascular disorders, developmental issues in children, and increased risks of various cancers

the Langmuir maximum Pb(II) adsorption capacity by nearly 25 times (from 1.04 to 22.82 mg g⁻¹). Similarly, Liu et al. [106] treated coconut shell biochar with 1 M HCl under ultrasonication, resulting in cleaner surfaces, more defined pore structures, and increased surface area. This improved the immobilization of PTEs in soil, with reductions in acid-soluble Cd, Ni, and Zn by 30.1%, 57.2%, and 12.7%, respectively, at 5% amendment rate. He et al. [69] modified rice straw biochar using 15% H₂O₂ and a 1:1

HNO₃/H₂SO₄ mixture, which led to a marked increase in Cd(II) adsorption. Acid modification was more effective, raising Cd(II) sorption capacity up to 535 mmol kg⁻¹ (2.03 times higher than control), compared to H₂O₂-modified biochar (1.32 times increase). These enhancements were attributed to the amplification of surface -COOH groups, which play a dominant role in metal binding.

3.3.2 Metal or mineral impregnation

Iron-modified biochar enhances heavy-metal immobilization and alleviates metal-induced oxidative stress in plants by improving surface reactivity and antioxidant defense mechanisms [3]. Behrooz et al. [25] synthesized MgCl₂-modified biochar by impregnating 500 g rice husk with 2.5 L of 1 M MgCl₂ for 24 h, drying, and pyrolyzing at 450 °C and 600 °C under argon. The modification consistently enhanced biochar surface area (from 28 to 66 m² g⁻¹ at 450 °C and 195 to 231 m² g⁻¹ at 600 °C) due to increased porosity from volatile gas release. The FTIR spectra confirmed stronger -O-H and -Si-OH signals in modified biochars, reflecting higher hydrophilicity. Cd adsorption capacity increased markedly from 7.6 to 97.6 mg g⁻¹ after modification. Wei et al. [197] prepared Fe-biochar (Fe-BC) by mixing corn straw with FeCl₃ solution, followed by pyrolysis under N₂. Despite a reduced surface area (11.12 m² g⁻¹), Fe-BC showed higher adsorption of [Fe(CN)₆]³⁻ and [Ni(CN)₄]²⁻ due to surface charge reversal at pH 4.5 (IEP: 6.8–7.2), enabling electrostatic attraction. Sha et al. [161] produced phosphorus-modified biochar (PBC) by impregnating cornstalk with K₂HPO₄ and pyrolyzing at 550 °C. The XRD confirmed formation of phosphate minerals ((Ca/Mg)₃(PO₄)₂). The PBC shifted Cd, Pb, and Zn from exchangeable/carbonate-bound forms to more stable organic/residual fractions in Pb-Zn mining soil, reducing their mobility. The increase in residual Cu was linked to complexation with surface -OH and -COOH groups. However, slight mobilization of As occurred due to anionic repulsion with phosphate. These findings suggest mineral impregnation enhances the contaminant immobilization efficiency of biochar in polluted soils.

3.3.3 Physical activation

Sakhiya et al. [160] produced rice straw-derived activated biochar via physical activation using CO₂ and H₂O as activating agents. The carbonization was carried out at 600 °C under N₂, followed by activation at 700–900 °C. The endothermic Boudouard reaction (CO₂ + C ↔ 2CO) facilitated carbon removal and pore development, with CO₂-activated biochar showing yields between 9.85–30.03% and BET surface areas ranging from 168.64 to 640.73 m² g⁻¹. The CO₂-activated biochar exhibited higher porosity than steam-activated biochar due to stronger Si-O-Si and Si-O-C bonding. The adsorption of As and Mn increased with dosage, with CO₂-activated biochar achieving 99% and 94% removal, respectively. Higher As adsorption was attributed to its smaller ionic radius (0.46 Å) compared to Mn (0.66 Å). Qi et al. [142] applied microwave-assisted pyrolysis using wheat straw and activated carbon (1:3 ratio), with N₂ purging. The resulting biochars showed enhanced surface roughness and debris, providing more adsorption sites. The BET surface areas ranged from 2.6 to 156.1 m² g⁻¹, consistently higher than conventional microwave biochar. Functional groups (e.g., -COOH, -OH) and carbonate precipitation (CdCO₃ and PbCO₃) were the main mechanisms for metal adsorption. Kong et al. [90] used palm kernel shell biochar, carbonized at 500 °C and activated via microwave-steam

at 700 °C. The palm kernel shell activated carbon exhibited a high BET surface area ($539.75 \text{ m}^2 \text{ g}^{-1}$) with evident mesoporosity and showed superior adsorption of Pb^{2+} and Cd^{2+} on heterogeneous surfaces. These studies underscore that physical activation significantly enhances the surface characteristics and adsorption efficiency of biochars.

3.3.4 Nano-modification

The nanoparticle modification consistently enhances the surface reactivity, porosity, and adsorption efficiency of biochar. Ghandali et al. [58] synthesized ZnO nanoparticle-modified biochar (BC@ZnO) via precipitation using 0.1 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.15 M KOH. After mixing with 1 g biochar, the solution was stirred and filtered, and the composite was oven-dried at 100 °C for 30 h. The SEM–EDX revealed a porous honeycomb-like biochar surface covered with ZnO clusters. Compared to plain BC, BC@ZnO consistently reduced Pb, Ni, and Cd uptake in ryegrass shoots, though Zn uptake increased with BC@ZnO due to nanoparticle contribution. Efficacy improved with increasing application rate (0.5–1%). Zhou et al. [227] developed nano MnO_x -modified biochar (BCHMn) by treating biochar with HCl followed by potassium permanganate and manganese sulfate addition at 90 °C. The nano- MnO_x aggregated on the surface, reducing pore diameter (6.99 to 0.06 nm) while increasing surface area (17.88 – $22.13 \text{ m}^2 \text{ g}^{-1}$) and pore volume (0.03 – $12.59 \text{ cm}^3 \text{ g}^{-1}$). The BCHMn showed a marked increase in maximum adsorption capacity for Cd^{2+} (108.21 mg g^{-1}) and Pb^{2+} (312.16 mg g^{-1}), representing 2.6- and 6.6-fold improvements over unmodified biochar, respectively. Ahmed et al. (2022) produced nano-hydroxyapatite modified biochar by blending rice straw with nHAP, followed by calcination at 700 °C. The SEM and TEM revealed a uniform, compact nano-layered structure, enhancing adsorption potential. The Langmuir isotherm analysis showed Pb(II) adsorption capacities ranging from 335.88 mg g^{-1} at 288 K to 216.45 mg g^{-1} at 318 K, significantly higher than unmodified biochar (63.04 – 32.39 mg g^{-1}), indicating an exothermic, temperature-sensitive process. The nZVI-modified eggshell biochar reduced soil bioavailable Pb and Cd by 62–75%, lowered metal leaching by up to 75%, and decreased human carcinogenic and non-carcinogenic health risks by 25–47% [2]. It also more effectively immobilized Pb and Cd than pristine biochar, reduced metal accumulation in *Brassica chinensis* leaves, alleviated oxidative stress, and enhanced beneficial soil bacterial groups [2]. The nZVI-supported coconut-husk biochar immobilized Pb (57.5–62.1%) and Cd (64.1–75.9%), reduced their accumulation in *Brassica rapa* below safety limits, alleviated oxidative stress via enhanced antioxidant activity, and lowered human health risks ($\text{HQ} < 1$; CR within 10^{-6} – 10^{-4}) [5]. These nano-modifications impart multifunctionality to biochar, making it highly effective for remediating PTE-contaminated soils and wastewater.

3.4 Mechanisms for PTE immobilization using modified biochar

The use of biochar, particularly modified and engineered forms, as a remediation material for PTE-contaminated soils is gaining increasing attention due to its tunable surface chemistry, mineral functionality, and cost-effectiveness. Modified biochar immobilizes PTEs through multiple physicochemical mechanisms, including adsorption, ion exchange, electrostatic interaction, surface complexation, precipitation, and co-precipitation (Fig. 7). The dominance of these mechanisms depends strongly on PTE

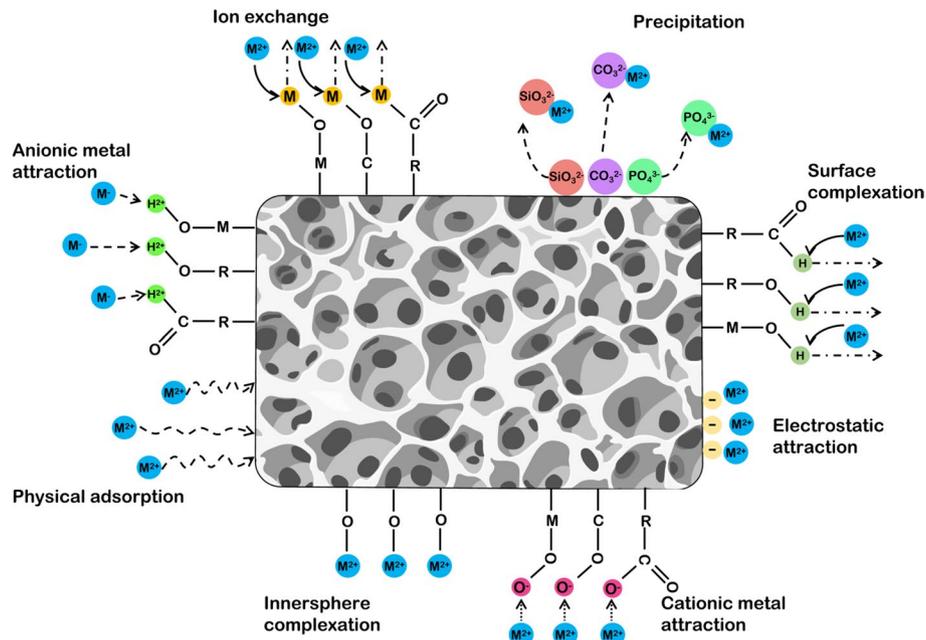


Fig. 7 Schematic illustration of major mechanisms governing immobilization of potentially toxic elements (PTEs) by modified biochar, including physical adsorption and ion exchange (Eqs. 1, 2, 4), electrostatic attraction (Eqs. 7, 9), inner-sphere complexation (Eqs. 10, 11, 12, 13, 14), precipitation (Eqs. 15, 16, 17), and co-precipitation (Eqs. 18, 19, 20, 21, 22, 23) [Authors' own creation using BioRender tool]

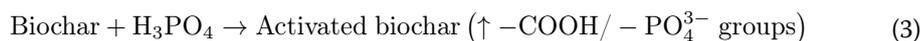
speciation, soil pH, redox potential (Eh), ionic strength, and the type of biochar modification [112, 226].

3.4.1 Adsorption

The biochar possesses a porous structure and high surface area that facilitates adsorption of PTEs. The adsorption process can be broadly classified into two types: physical adsorption and chemical adsorption. The physical adsorption is primarily driven by the Van Der Waals forces and is more reversible, whereas the chemical adsorption includes covalent or ionic bonding, resulting in stronger and more lasting binding of metal ions. Ion exchange is a key adsorption-related mechanism for cationic metals such as Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} (Fig. 7: ion exchange and physical adsorption; Eqs. 1, 2), whereby these ions replace exchangeable base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) on negatively charged biochar surfaces [22]. These reactions are enhanced by surface oxidation or acid/base activation that increases the density of oxygen-containing functional groups.

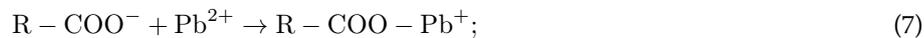
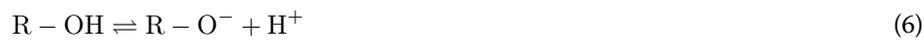


Phosphoric acid activation increases CEC and introduces $-PO_4^{3-}$ and $-COOH$ rich binding sites, enhancing the retention of metals such as Ni^{2+} and Zn^{2+} (Eqs. 3, 4).



3.4.2 Electrostatic interaction

Electrostatic interactions play a major role under acidic to neutral pH conditions and are governed by the surface charge of biochar (Fig. 7: electrostatic attraction). These interactions are represented by surface deprotonation reactions (Eqs. 5, 6) and subsequent cation association (Eq. 7).



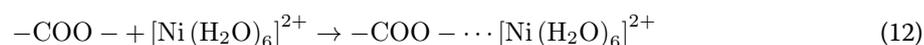
For redox-sensitive oxyanions, electrostatic attraction is often coupled with reduction or ligand exchange, particularly on Fe- or Mn-modified biochars (Eqs. 8, 9). For example, Cr(VI), present predominantly as CrO_4^{2-} under oxic conditions, can be reduced to Cr(III), followed by surface complexation or precipitation:



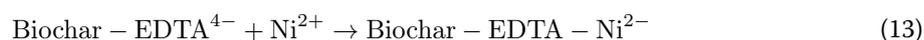
Such coupled electrostatic–redox mechanisms are frequently observed in magnetized or metal-oxide-loaded biochars and are strongly influenced by pH and Eh [114, 180].

3.4.3 Surface complexation

Surface complexation involves the formation of inner-sphere complexes between metal ions and functional groups on biochar surfaces (Fig. 7: inner-sphere and surface complexation; Eqs. 10, 11, 12, 13, 14). The inner-sphere complexes involve direct ligand–metal bonding and are typically stronger and more stable than outer-sphere complexes. This mechanism is particularly relevant for transition metals (Cu^{2+} , Zn^{2+} , and Ni^{2+}) and becomes more dominant at neutral to alkaline pH [192, 194, 221].



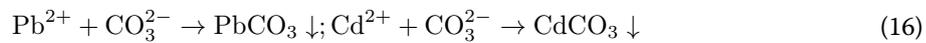
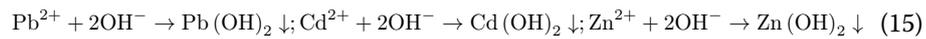
Functionalization with chelating ligands further enhances complexation strength:



3.4.4 Precipitation

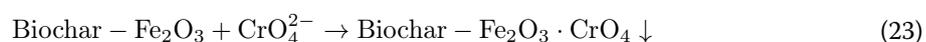
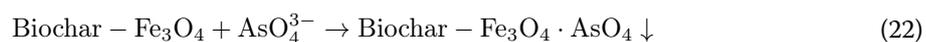
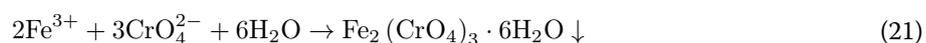
The precipitation is the development of insoluble metal compounds (hydroxides, carbonates, and phosphates) on or near the biochar surface (Fig. 7: precipitation; Eqs. 15, 16, 17), which frequently results in permanent sequestration [159]. At higher pH levels, metal ions such as Pb^{2+} , Cd^{2+} , and Zn^{2+} become less soluble due to the production of insoluble hydroxide or carbonate phases, making this process more favorable [170]

(Eq. 15). Ca-rich biochar can precipitate Pb^{2+} as PbCO_3 or $\text{Pb}(\text{OH})_2$ in polluted soils, ensuring long-term stability. Phosphate-modified biochars have two benefits: (1) they act as adsorbents and suppliers of phosphate ions, (2) these ions combine with PTEs to generate low-solubility phosphate minerals ($\text{Pb}_3(\text{PO}_4)_2$ and CdCO_3), which are chemically stable and resistant to leaching even under shifting environmental circumstances [212] (Eqs. 16, 17).



3.4.5 Co-precipitation

The co-precipitation is the simultaneous precipitation of PTEs and other chemicals, which is commonly done in the presence of biochar-mineral composites. Metals are trapped inside developing mineral matrices, such as iron or manganese oxides, which are either naturally occurring or injected during the biochar modification process (Fig. 7: precipitation/co-precipitation; Eqs. 18, 19, 20, 21, 22, 23). Co-precipitation processes are crucial in redox-active systems where iron transitions between Fe^{2+} and Fe^{3+} states, trapping metals such as As or Cr inside iron oxide frameworks (Eqs. 18, 19, 20, 21). Magnetic biochars with iron oxide nanoparticles (Fe_3O_4 or Fe_2O_3) effectively immobilize arsenate and chromate via surface complexation and co-precipitation [46, 171] (Eqs. 22, 23). These structures are designed for simple separation from solution and regeneration for further usage.



The oxygen containing functional groups and mineral coatings enhance binding through complexation and precipitation, while redox-active phases stabilize oxyanions via transformation and co-precipitation. Understanding these interacting pathways is essential for optimizing modified biochar performance under realistic soil conditions.

3.5 Integrated mechanisms and long-term stability of modified biochar for PTE immobilization

Understanding the effectiveness of modified biochar for PTE remediation requires not only identifying individual immobilization mechanisms but also integrating how biochar modification strategies alter physicochemical properties, influence target PTE

interactions, and determine long-term stability under field conditions. The performance of modified biochar is governed by interconnected processes involving surface functionalization, mineral associations, and redox activity, which collectively control metal speciation, binding strength, and persistence over time. Moreover, these mechanisms evolve following soil incorporation due to aging, environmental variability, and soil–plant–microbe interactions.

3.5.1 Linking biochar modification, physicochemical properties, target PTEs, and remediation mechanisms

Establishing clear linkages between biochar modification strategies, resultant physicochemical properties, target pollutants, and dominant remediation mechanisms is essential for translating mechanistic understanding into practical design principles. Modification methods such as chemical activation, mineral impregnation, redox-active loading, and biological functionalization systematically alter key properties including surface area, functional group density, mineral phases, surface charge, and redox activity [222]. These physicochemical changes, in turn, determine the preferential immobilization pathways for specific classes of PTEs (cationic vs. oxyanionic), governing whether adsorption, surface complexation, precipitation, or redox transformation dominates [22]. To synthesize these interrelationships, Table 3 presents a knowledge map linking major biochar modification approaches with their characteristic property enhancements, target pollutants, and dominant remediation mechanisms.

Although individual biochar modification strategies are widely reported, their relative advantages and limitations are rarely evaluated in a comparative manner. To facilitate informed selection of modification approaches, Table 4 presents a decision matrix comparing major biochar modification methods across key criteria, including cost, environmental impact, target PTE specificity, and long-term stability under field conditions. This synthesis highlights trade-offs among performance, sustainability, and practical feasibility, and supports context-specific decision-making for soil remediation applications.

Table 3 Correlation between biochar modification strategies, physicochemical properties, target potentially toxic elements (PTEs), and dominant immobilization mechanisms

Biochar modification method	Key physico-chemical property enhanced	Dominant target PTEs	Primary immobilization mechanisms	References
Acid/alkali activation	↑ Surface area, ↑ –COOH/–OH, ↑ CEC	Pb ²⁺ , Cd ²⁺ , Zn ²⁺	Ion exchange, inner-sphere complexation	Uchimiya et al. [180], Bandara et al. [22]
Phosphate modification	↑ PO ₄ ³⁻ availability, ↑ alkalinity	Pb ²⁺ , Cd ²⁺	Precipitation (metal phosphates)	Yang et al. [212]
Fe/Mn oxide impregnation	↑ Metal oxide sites, ↑ surface charge	AsO ₄ ³⁻ , CrO ₄ ²⁻	Inner-sphere complexation, co-precipitation	Deng et al. [46], Su et al. [171]
Sulfur functionalization	↑ –SH groups, ↑ affinity for soft metals	Hg ²⁺ , Cu ²⁺	Strong surface complexation, precipitation	Wang et al. [192, 194]
Redox-active modification	↑ Electron transfer capacity	Cr(VI), As(V)	Reductive transformation + immobilization	Liu et al. [112]
Biochar-clay composites	↑ Surface heterogeneity, ↑ stability	Mixed-metal systems	Adsorption + co-precipitation	Feng et al. [55]
Pristine biochar (high ash)	↑ pH, ↑ carbonate content	Pb ²⁺ , Zn ²⁺	Carbonate/hydroxide precipitation	Saeed et al. [159]

Table 4 Decision matrix comparing biochar modification strategies for potentially toxic elements (PTEs) remediation

Modification strategy	Relative cost	Environmental impact	Target PTE specificity	Long-term stability	Key advantages	Major limitations
Pristine biochar (high ash)	Low	Low	Cationic metals (Pb, Cd, Zn)	Moderate–high	Low cost; improves soil fertility	Limited effectiveness for oxyanions
Acid/alkali activation	Moderate–high	Moderate	Broad (mainly cationic metals)	Moderate	Increased surface area and CEC	Chemical inputs; cost increase
Phosphate modification	Moderate	Low–moderate	Pb, Cd	High	Stable metal phosphate precipitation	Risk of excess P release
Fe/Mn oxide impregnation	Moderate	Moderate	As, Cr (oxyanions)	Moderate	Strong inner-sphere binding; redox control	Aging-induced remobilization risk
Sulfur functionalization	High	Moderate–high	Hg, Cu	High	Strong affinity for soft metals	Costly; potential toxicity
Biochar–clay composites	Low–moderate	Low	Mixed PTE systems	High	Good stability; low chemical input	Lower sorption capacity
Redox-active modification	High	Moderate	Cr(VI), As(V)	Variable	Enables reduction-driven immobilization	Sensitive to redox fluctuations

■ Low
 ■ Low-moderate
 ■ Moderate
 ■ Moderate-high
 ■ High

3.5.2 Evolution of surface chemistry and long-term stability of immobilization mechanisms under field conditions

Although the primary mechanisms governing PTE immobilization by modified biochar are well established, their long-term effectiveness under field conditions is strongly influenced by progressive changes in biochar surface chemistry [213]. Following soil incorporation, biochar undergoes aging driven by abiotic (oxidation, mineral deposition, and pH buffering) and biotic (microbial colonization and enzymatic oxidation) processes, which collectively alter surface functional groups, pore accessibility, and redox activity [130].

The oxidative aging generally increases the abundance of oxygen-containing functional groups (–COOH and –OH), enhancing CEC and strengthening inner-sphere complexation of divalent metals such as Pb^{2+} and Cd^{2+} (Wang et al., 2022). Concurrently, mineral encrustation by Fe, Al, or Ca phases may either stabilize metals through co-precipitation or partially occlude reactive surfaces, reducing sorption capacity [218]. These opposing effects explain why aging can result in sustained or even enhanced immobilization for some cationic PTEs, while diminishing performance for others. In contrast, immobilization of oxyanion-forming and redox-sensitive elements (As and Cr) exhibits greater vulnerability to environmental fluctuations. Under reducing field conditions such as in flooded paddy soils, microbially mediated redox transformations can convert As(V) to more mobile As(III) or destabilize Fe-oxide-bound chromate, leading to partial remobilization despite initial immobilization [30]. Aging-induced depletion of redox-active functional groups or surface-bound metal oxides further weakens long-term retention of these species.

Importantly, long-term field exposure introduces soil–plant–microbe feedbacks that are rarely captured in short-term laboratory studies. Root exudates, organic acids, and rhizosphere pH shifts can locally disrupt surface complexes or promote ligand exchange, influencing PTE bioavailability over cropping cycles [177]. Climatic drivers such as

wet–dry cycles and freeze–thaw events also accelerate biochar weathering, altering pore structure and surface reactivity [192, 194]. These observations underscore that PTE immobilization by modified biochar is not a static process, but rather a dynamic outcome of evolving surface chemistry and soil conditions. Consequently, remediation strategies must account for aging trajectories, particularly for redox-sensitive contaminants, through appropriate biochar modification, periodic reassessment, and adaptive management to ensure long-term stability and regulatory compliance.

3.6 Factors affecting modified and engineered biochar remediation efficiency

3.6.1 Soil parameters

Soil pH directly influences modified biochar's surface charge, ion exchange capacity, and PTE bioavailability. The creation of carbonate and hydroxide during pyrolysis causes most biochars to be alkaline. Applying 20 t ha⁻¹ of hardwood biochar improved soil pH from 6.06 to 6.47 in acidic soils [82]. This alkalinity neutralizes acidic soils, lowering Cd and As solubility by adsorption or precipitation. The phosphorus (P) enriched modified biochar improves soil pH while converting exchangeable Cd into stable carbonate-bound and residual forms. The P modified biochar decreased soil Cd concentrations by 73% in acidic soils by elevating pH from ~4.45 to 5.33. This promoted Cd precipitation as CdCO₃ and Cd(OH)₂ [107]. Temperature consistently influences the efficiency of biochar in environmental remediation operations. Biochar's electron shuttle capability increases PTE breakdown at 20–35 °C. When temperatures are > 40 °C, oxygen solubility diminishes, boosting anaerobic reactions that may mobilize redox-sensitive metals like As while concurrently enhancing the hydrolysis of organic molecules [107]. In contrast, temperatures < 10 °C reduce microbial activity unless the biochar is pre-inoculated with cold-adapted microbial strains. At low temperatures, phytoremediation efficacy is diminished unless biochar can buffer thermal fluctuations, thereby creating a more stable milieu for plant and microbial interactions [207].

3.6.2 Physicochemical properties of biochar

Biochar's performance in heavy-metal remediation derives from its multifunctional surface properties, which facilitate adsorption, ion exchange, and precipitation. Its typically alkaline pH, especially in manure-derived or high-temperature biochars, helps neutralize acidic soils and drives metal precipitation as hydroxides or carbonates. The CEC reflects biochar's ability to retain and swap cations; low-temperature biochars often exhibit higher CEC due to abundant polar functional groups. Conversely, high-temperature biochars tend to develop larger specific surface areas via volatile loss and micropore formation, providing more active sites for metal binding. Oxygen-containing moieties (–OH, –COOH, –C=O) common in low-to-medium-temperature biochars form complexes with metal ions, a feature that can be enhanced through oxidative post-treatments [43]. Porosity not only boosts water retention but also mechanically entraps ions, with micropores particularly effective for small cations like Pb²⁺ and Cd²⁺. Ash residues contribute by generating mineral phases, such as carbonates and phosphates that precipitate metals. Elevated electrical conductivity may signal soluble salts that could compete with metal sorption, yet also indicate nutrient-rich biochar useful in agronomic contexts [45]. Aromaticity, heightened at higher pyrolysis temperatures, suggests structural resilience critical for long-term stability. Zeta potential, which varies with pH, governs electrostatic

attraction of metal cations and underpins colloidal stability and sorptive capacity [86, 172]. Metal affinity varies by species, for example, poultry-manure biochar adsorbs Pb^{2+} more readily than Cd^{2+} or Zn^{2+} , with capacities spanning $0.10\text{--}9.99\text{ mg g}^{-1}$ [169].

3.6.3 Feedstock type and pyrolysis temperature

Biochar qualities required for PTE cleanup are strongly dependent on feedstock type and pyrolysis circumstances (Table 5). Wood-derived biochar pyrolyzed at $500\text{--}600\text{ }^\circ\text{C}$ had larger surface area ($153\text{--}268\text{ m}^2\text{ g}^{-1}$) and microporosity than manure-derived biochars, resulting in up to 92.3% Cd^{2+} adsorption. The pyrolysis temperature had a major impact: biochar made from coconut husk at $700\text{ }^\circ\text{C}$ had a pH of 10.3 and 4.5 times better metal sorption capacity than at $400\text{ }^\circ\text{C}$ due to ash content and alkaline surface development [133, 168]. High pH biochars ($\text{pH} > 9.0$), as those from chicken litter, effectively remove Pb^{2+} and Ni^{2+} by electrostatic repulsion and hydroxide precipitation. Surface functional groups were discovered to be critical for surface complexation. The FTIR measurements confirmed their increase after modification with HNO_3 and FeCl_3 treatments. One study found that Mn-modified biochar improved Cr(VI) removal effectiveness from 64 to 98% via redox and complexation mechanisms [14].

3.6.4 Nature of modification

The efficiency of biochar in immobilizing PTEs largely depends on the nature and extent of its surface modifications. Both physical and chemical modifications enhance the biochar's reactivity, surface functionality, and binding affinity toward toxic metal ions (Table 6). These modifications tailor biochar to perform specific sorption mechanisms, including surface adsorption, complexation, and precipitation, thereby improving its remediation potential in contaminated soils. Surface adsorption is prominent, especially in untreated and weakly modified biochars. Electrostatic interactions were particularly efficient in alkaline settings, where surface charge was largely negative, increasing metal absorption by up to 80% above acidic counterparts [61]. Surface complexation and precipitation are the most common chemical binding processes for modified biochars. ZnCl_2 activated rice husk biochar removed 97.6% of Pb^{2+} , predominantly

Table 5 Effect of different feedstocks on different soil properties and their adsorption capacity for remediation of PTE

Feedstock type	Pyrolysis temperature ($^\circ\text{C}$)	pH	CEC (Cmol_c (+) kg^{-1})	Surface area (m^2g^{-1})	Functional groups	Ash content (%)	Metal adsorption capacity (mg g^{-1})	References
Rice husk	500	9.1	18.3	84.6	$-\text{COOH}$, $-\text{OH}$	34.5	21.5 (Pb^{2+})	Li et al. [99]
Sewage sludge	450	8.3	27.5	52.4	$-\text{OH}$, $-\text{NH}_2$	46.2	14.9 (Cd^{2+})	Van Wesenbeeck et al. [185]
Wood chips	700	11.4	8.2	312.8	$-\text{OH}$	9.3	25.0 (Zn^{2+})	Kim et al. [88]
Coconut shell	550	9.8	12.5	250.6	$-\text{COOH}$, $-\text{OH}$	7.8	30.2 (Ni^{2+})	Liu et al. [108]
Peanut hull	500	8.9	20.1	102.5	$-\text{COOH}$	22.6	18.6 (Pb^{2+})	Bacirhonde et al. [21]
Wheat straw	400	7.2	24	90.4	$-\text{OH}$	16.5	20.3 (Cr^{3+})	Amin et al. [12]
Bamboo	600	10	14.3	280.1	$-\text{COOH}$, $-\text{OH}$	11.2	28.4 (Cu^{2+})	Ramola et al. [148]
Palm kernel	650	10.7	13	200	$-\text{COOH}$	19.7	26.5 (Zn^{2+})	Imran-Shaukat et al. [76]
Pine bark	500	8.5	17.8	140.2	$-\text{OH}$, $-\text{COOH}$	20	22.1 (Cd^{2+})	Koetlisi and Muchaonyerwa [89]

Table 6 Adsorption capacity of biochar before and after modification (*Adapted from [146]*)

PTE	Plant materials	Modification method/modifier	Adsorption capacity (mg g ⁻¹)	
			Before modification	After modification
Pb (II)	Rice husk	KMnO ₄	1.11	10.41
	Peanut shells	H ₂ O ₂	0.88	22.82
	Pine	MnO ₂	2.35	47.00
Cd (II)	Rice husk	Fe(NO ₃) ₃	0.87	6.57
	Peanut shells	H ₂ O ₂	1.50	4.00
Cr (VI)	Rice husk	Polyethyleneimine	23.09	435.70
	Rice bran	Fe ³⁺	–	0.68
	Corn straw	radiation	1.11	20.04
As (V)	Municipal solid waste	KOH	24.49	30.98
	Pine	γ-Fe ₂ O ₃	0.27	0.43
	Cactus	Al ³⁺	–	50.00
Cu (II)	Cactus	MnO ₂	38.40	80.60
	Sawdust	Amino	3.02	15.10
	Switch grass	KOH	31.00	34.00

Table 7 Combined effects of biochar and compost applications on PTE immobilization and soil property enhancement

Biochar feedstock	Compost feedstock	Rate of application	Effects on PTE	Effects on soil properties	References
Rice straw	Agricultural waste	10% (w w ⁻¹)	Cd and Zn contents decreased by 87.1% and 86.4%, respectively	Enhanced soil EC, OM, TOC, pH	Tang et al. [175]
Rice husk	Pig slurry	1% (w w ⁻¹)	Cd and Zn availability decreased	Improved value of soil pH, DOC and TOC	Liang et al. [100]
Holmoak wood	Horse and rabbit manure	20% (w w ⁻¹)	Reduced the phytoavailability of Co, Cu, Fe, and Ni	Enhanced soil pH, total carbon, N, and K	Rodríguez-Vila et al. [157]
Garden peat	Farm manure	2% (w w ⁻¹)	–	Enhanced soil EC, OM, total N and K	Qayyum et al. [141]

by Pb-phosphate mineral production and inner-sphere complexation, as shown by XRD and XPS investigations. Co-precipitation of metals with biochar-derived carbonates was shown to lower Cr, Cu, and As mobility by more than 90% in multimetal polluted soils [171, 190]. Using oxidizing agents such as potassium dichromate and potassium permanganate on biochar's surface increases its ability to adsorb PTEs [78]. Eggshell biochar modified with nZVI/activated carbon efficiently immobilized Pb and Cd by transforming them into insoluble carbonate, hydroxide, and iron-oxide forms via adsorption, co-precipitation, reduction, and surface complexation, while also improving soil nutrient status [4].

3.6.5 Co-application with soil amendments

Organic supplements, such as biochar and compost, are often recommended for repairing damaged soils due to their environmental friendliness, cost-effectiveness, and demonstrated efficacy in improving soil quality [85, 145]. The judicious addition of biochar and compost to problem soils has a high potential to enhance their quality [131] (Table 7). There are three primary techniques of manufacturing and applying biochar combined with compost to soil: (1) biochar and compost mixture (BCM); (2) co-composted mixture; (3) composted biochar (Fig. 8) [143]. In greenhouse experiments with *Brassica juncea* L. Forján et al. [56] found that BCM treatment consistently reduced Cu, Ni, Pb,

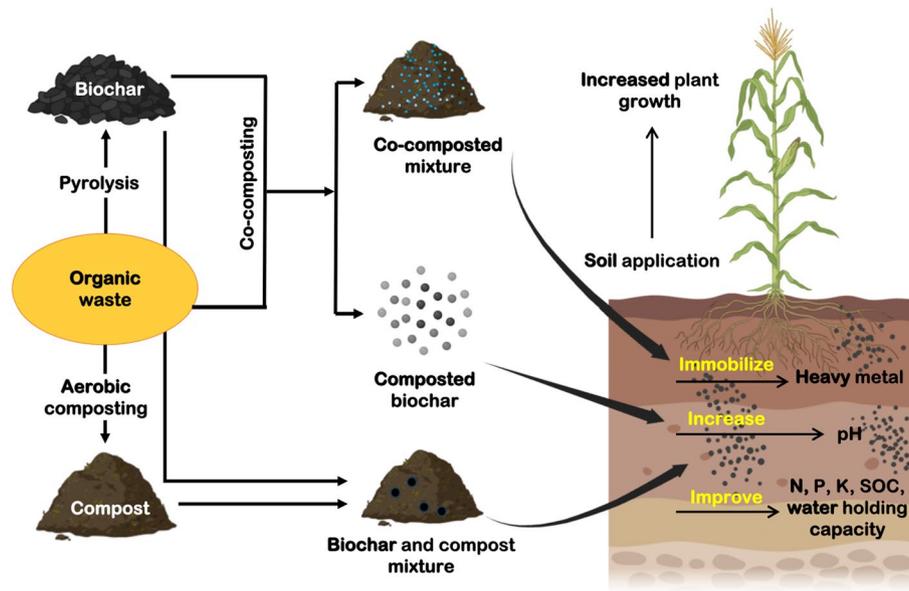


Fig. 8 Integrated pathways of organic waste conversion and soil amendment effects. This diagram illustrates the transformation of organic waste into soil amendments through pyrolysis and aerobic composting, resulting in biochar and compost, respectively. These products can be applied individually or combined via co-composting to form co-composted mixtures, composted biochar, or biochar-compost blends. Upon soil application, these amendments contribute to PTE immobilization, pH enhancement, and improved nutrient content (N, P, and K), soil organic carbon, and water holding capacity, ultimately promoting increased plant growth [Authors' own creation using BioRender tool]

and Zn concentrations in soil pore water while also improving soil fertility traits such as pH, nutrient availability, and CEC, resulting in increased biomass. Tang et al. [175] found that in Cd and Zn-contaminated soils, the BCM resulted in the greatest reduction in extractable Cd and Zn (87.1% and 86.4%, respectively). The improved immobilization effect of BCM is mostly owing to biochar and compost's different affinity for specific metal ions. Karami et al. [84] found that the combination of BCM resulted in even higher decreases in Pb (96%) and Cu (63%) compared to application of biochar or compost alone, demonstrating the synergistic impact. Borchard et al. [29] and He et al. [68] found that humic acid rich compost increases the adsorption capacity of biochar surfaces for Cu^{2+} . Liang et al. [100] and Yang et al. [214] found that BCM combinations with greater compost content improved Cd and Zn adsorption. Biochar-rich mixes (20–40%) considerably increased soil pH while decreasing PTE availability, with pH emerging as an important component in developing efficient BCM ratios.

3.7 Agricultural and environmental advantages of modified biochar

Because of its many uses in atmospheric, marine, and terrestrial systems, modified biochar is critical to fostering environmental sustainability [188]. Its numerous uses include carbon sequestration, enhancing soil fertility, remediating contaminated water and soil, storing energy, and recycling agricultural waste and byproducts [7, 174] (Fig. 9).

3.7.1 Soil remediation

The application of synthetic fertilizers containing nitrogen (N) causes soil acidity. Adding biochar has been proven to increase soil pH [65]. Biochar containing mineral oxides (Ca, K, Mg, Na, and Si) reacts with H^+ and monomeric Al species in acidic soils to elevate pH

impregnated with hydroxides of magnesium, aluminium and iron oxide, enhancing their GHG adsorption capability [39]. The TEPA-modified biochar was used to construct a solid amine adsorbent that effectively collects CO₂ from flue gas [178]. Further enhancement of CO₂ adsorption has been achieved by incorporating salts of Na, Al, Ca, Ni, Fe, and Al into biochar [229]. Beyond targeting GHGs, biochar derived from various feedstocks has also been physically and chemically modified to serve as a promising adsorbent for the removal of HgO from flue gases [165].

3.7.3 Waste water treatment

Excessive PTEs in water, including Pb, Cd, Cr, Cu, and As, constitute a severe environmental danger due to their negative impacts on aquatic life and human health [102, 176]. This problem emphasizes the critical necessity for a cost-effective and technically possible technique of PTE cleanup. Many studies have shown that biochar based materials may successfully remove PTEs from water via a variety of adsorption methods [104]. Biochar has several advantages, including a distinct porous structure, a large specific surface area, a variety of surface-active functional groups, and chemical stability. These features lead to its high capacity for PTE adsorption, immobilization, and passivation, which aids in environmental cleanup operations.

3.7.4 Reduction of nutrient loss

Incorporating biochar into soil can impact N dynamics, such as transport and transformation [188]. Using 1% iron-modified biochar enhanced nitrate retention in Luvisols and boosted N levels in cotton seedlings. These findings show that biochar's improved surface structure and functional groups play an important role in adsorbing inorganic N and minimizing N loss from soil [191]. The chemical activation is a key step in biochar alteration. It includes treating biochar with substances such as KOH, H₃PO₄, or ZnCl₂. This procedure consistently enhances the surface area and porosity of the biochar, hence improving its potential to adsorb PTEs, organic pollutants, and important nutrients such as P [109]. The hardwood biochar impregnated with Mg showed a 34% increase in adsorption capacity, making it ideal for phosphate recovery and application as a slow-release fertilizer [16]. Furthermore, polyacrylamide-modified biochar was found to dramatically increase accessible P levels in soils by 12.7–85.4 mg kg⁻¹ when compared to control treatments, while decreasing colloidal P concentrations by 26.7–51.4% [97]. According to redundancy analysis, differences in P inputs and crop types had the greatest impact on P runoff losses.

3.7.5 Improvement in soil properties

When employed as a soil amendment, biochar has the potential to increase soil fertility by changing its physical and chemical characteristics [64]. Duan et al. [50] discovered that several types of biochar including virgin, composite-modified, particle-sized, and acid-treated biochars contributed to an increase in the concentration of water-stable soil aggregates. Liu et al. [103, 106, 108] found that adding 5% coconut shell biochar by weight increased soil pH, increased CEC, and encouraged microbial communities such as bacteria, fungi, and actinomycetes. This treatment consistently increased enzyme activities for acid phosphatase, dehydrogenase, and urease, whereas invertase activity was unchanged. Similarly, Moradi and Karimi [129] found that applying 2% Fe-modified

biochar increased soil organic matter and organic carbon content. Gholami and Rahimi [59] discovered that an 8% application of thiourea-modified biochar improved soil pH, CEC, organic carbon, and electrical conductivity. Furthermore, Zhen et al. [225] found that applying 2% rhamnolipid-modified biochar increased soil dehydrogenase activity as well as bacterial and fungal diversity indices.

3.8 Constraints and long term challenges in biochar based soil remediation

In practical applications, biochar based materials can deteriorate over time due to environmental factors and the activity of microbes, its effectiveness depends on crop species, biochar properties, fertilization as well as local field conditions like soil characteristics and climate. Biochar has been widely used to remediate soils contaminated by PTEs, but as it ages, its physicochemical characteristics may change. Hence results in a specific region should not be applied to other regions with varying climate regimes since farming practices vary considerably. Biochar alkalinity can decrease after some years owing to leaching of alkaline minerals and gradual surface oxidation, which can lower its ability to bind PTEs and metalloids [134, 216]. Biochar is unable to completely immobilize all metal species in soils that are contaminated with both oxyanionic and cationic PTEs. Alaboudi et al. [9] revealed that applying biochar raised the soil pH contaminated with Cd, Cr and Pb, which increased the solubility and uptake of Cr (VI) by maize plant. Although biochar consistently decreased extractable Cd and Pb by 85.14% and 28.68% but higher pH also encouraged the mobilization of Cr oxyanions ($[\text{CrO}_4^{2-}]$ and $[\text{Cr}_2\text{O}_7^{2-}]$), resulting in more leaching. Wen et al. [198] showed that Fe-modified biochar effectively lowered As levels in contaminated soil but resulted in higher accumulation of Cd and Pb in straw and brown rice. This result was due to acidic nature of the biochar ($\text{pH } 4.41 \pm 0.03$), which made it easier for Pb(II) and Cd(II) to be released into the soil solution. When using biochar for in-situ remediation of soils tainted by PTEs like Cd (II), it's crucial to pay close attention to the pyrolysis temperature. This is especially important for the complex and varied nature of contaminated soils, which can change under different organic matter and ionic strength conditions. Chen et al. [34] investigated the effects of biochar nanoparticles (BNPs) made from wheat straw that were pyrolyzed at temperatures of 350 °C and 500 °C (referred to as BNP350 and BNP500) on the movement of Cd(II) in saturated soil columns. They found that at low ionic strength of 1.0 mM KCl, both BNP500 and BNP350 consistently boosted Cd (II) mobility by 69 and 54 times, respectively, when compared to the limited movement of Cd (II) on its own. This suggests that BNPs can serve as carriers that help facilitate the movement of Cd (II) through the soil. Moreover, humic acid further enhanced the movement of BNPs with Cd (II) at low ionic strength. Pyrolysis process during production of biochar can create some hazardous by products, which need cautious handling to ensure sustainable production methods [215, 224]. Technological obstacles to scaling biochar manufacturing include availability and quality of feedstocks, high cost of production, limited infrastructure, and absence of standardized quality certification. Market development, demand, environmental, and social issues also present challenges [151].

3.9 Aging-induced transformation of biochar and divergent PTE responses under pot and field conditions

Aging of biochar in field experiment actually enhanced the bioavailability of PTEs but interestingly, pot experiments revealed the opposite trend. This difference mainly stems from various external factors present in field conditions, like soil acidification from acid rain, fertilization, root exudates, organic acids coming from organic matter decomposition [216]. In soils with pH lower than 6.0, aged biochar tends to become more acidic as its ash content dissolves more readily [31]. Additionally, biochar produced at lower temperatures often develop more oxygen-containing functional groups over time, because of their naturally rich surface functionality and lower resistance to oxidation, and biochar pH is decreased [67, 137, 216]. It was predicted that the ability of biochar-amended soils to adsorb PTEs will return to untreated levels after about 2.5 years of aging [154]. Additionally, it seems that immobilized PTEs could eventually leach back into the environment over a longer aging period [144]. Cui et al. [40] showed that biochar aging increases the bioavailability of PTEs, and changes the physicochemical properties of biochar (reduces maximum carbon content by 47.70% and increases oxygen content up to 49.17%) and decreases the pH value of the biochar (from 9.91 to 4.99 and 4.92 for CFTs and CDWs respectively). The long-term physical breakdown of biochar-derived materials can lead to the formation of micro- and nanoscale particles, enhancing their movement, solubility, and clumping together over time. Fragmentation is probably responsible for the degradation in PTE remediation efficacy and release of already adsorbed PTEs [104, 106].

Given the growing evidence that biochar aging alters surface functionality, redox activity, and metal binding strength over time, translating mechanistic insights into practical field guidance remains challenging. Aging-induced performance decline is metal- and soil-specific, with cationic metals often showing sustained immobilization, while oxy-anion-forming elements may exhibit remobilization under changing redox or pH conditions. A context-specific decision framework is proposed to guide biochar selection and application strategies based on soil properties, target PTE speciation, crop sensitivity, and regulatory limits (Fig. 10). Together, these tools aim to bridge laboratory-scale understanding with field-level risk management and support informed implementation of modified biochar for safe and effective soil remediation.

3.10 Conceptual and predictive frameworks for aging-driven decline in biochar remediation efficiency

Although aging effects on modified biochar performance are increasingly reported, most studies describe these changes qualitatively rather than within predictive frameworks. To support long-term assessment, aging-induced changes in biochar functionality and remediation efficiency can be conceptualized using time-dependent decay or transition models, which link physicochemical transformations to immobilization performance under contrasting environmental conditions [130]. At a conceptual level, the decline in remediation efficiency (E) with time (t) can be expressed as a function of biochar surface reactivity and environmental stressors (Eq. 24):

$$E_t = E_0 \cdot f(\text{pH}, \text{Eh}, M, T) \cdot e^{-k_a t} \quad (24)$$

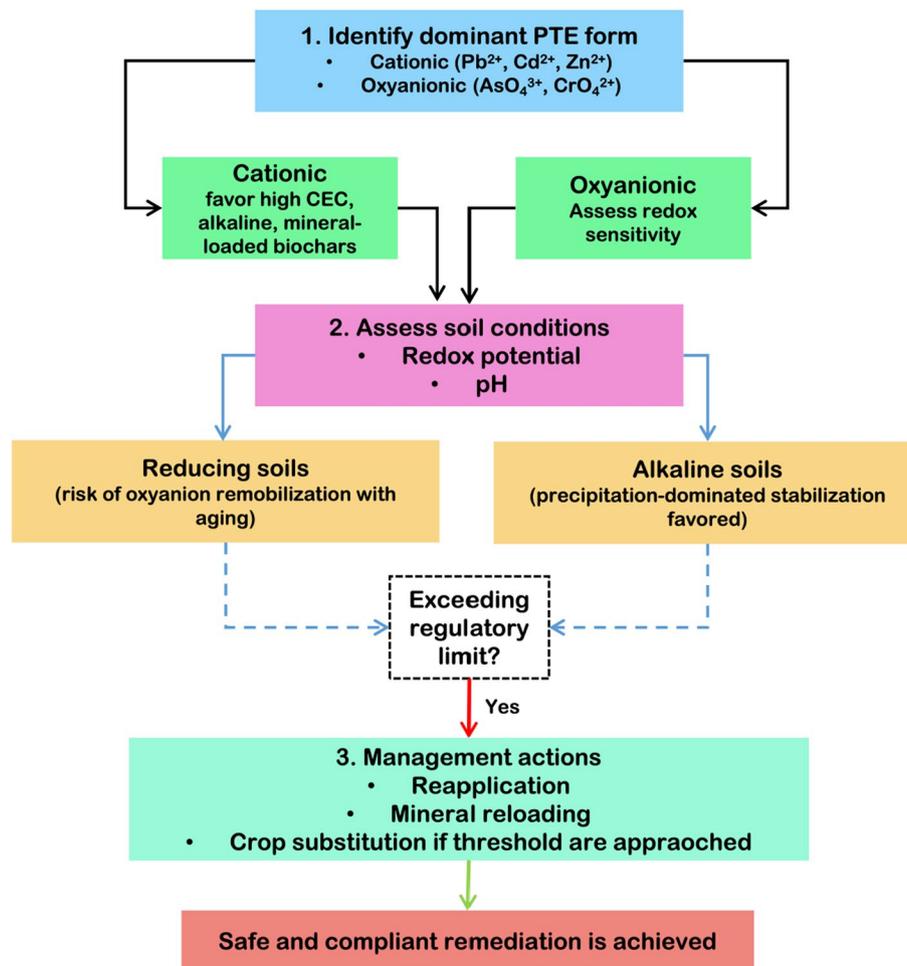


Fig. 10 Schematic decision framework for selecting and managing modified biochar in PTE-contaminated soils based on PTE speciation, soil pH–redox conditions, and regulatory compliance under aging scenarios

where E_0 represents initial immobilization efficiency, k_a is an aging rate constant, and $f(\text{pH}, E_h, M, T)$ captures modifying effects of soil pH, redox potential, microbial activity (M), and temperature (T). Under stable oxic and alkaline conditions, k_a is typically small, resulting in sustained immobilization, whereas redox-dynamic or biologically active environments accelerate functional group transformation and increase k_a .

For cationic metals, aging often leads to a mechanistic shift rather than simple decline, which can be described by a two-stage model (Eq. 25) [118]:

$$E_t = E_{\text{ads}} \cdot e^{-k_1 t} + E_{\text{min}} (1 - e^{-k_2 t}) \tag{25}$$

where early-stage adsorption and electrostatic interactions (E_{ads}) diminish over time, while mineral-controlled mechanisms (E_{min}), such as precipitation and co-precipitation, become increasingly dominant and stable. k_1 represents the aging-related decay constant of fast, surface-controlled immobilization processes, whereas k_2 describes the rate at which slower, mineral-controlled stabilization mechanisms develop over time.

In contrast, oxyanion-forming and redox-sensitive elements (As and Cr) exhibit non-monotonic behavior, particularly under fluctuating redox regimes. In such systems, aging may reduce redox-active surface sites or destabilize Fe/Mn oxide phases, resulting

in partial remobilization despite initial stabilization [166]. Conceptually, this behavior can be represented by threshold based or oscillatory models linked to redox cycling rather than simple exponential decay. These predictive formulations are not intended as universal kinetic models but as conceptual tools that integrate time, environment, and mechanism dominance. Incorporating such frameworks helps bridge laboratory observations with long-term field performance and highlights the need for parameterization using harmonized, multi-year field datasets.

3.11 Field-scale applicability, scalability, and real-world challenges of modified biochar remediation

The effectiveness of modified biochar for PTE remediation under field conditions is strongly mediated by soil properties, climatic variability, and crop-specific interactions, which collectively govern contaminant mobility, biochar reactivity, and long-term stability. Soil pH and buffering capacity exert primary control over PTE speciation and immobilization pathways [213], with alkaline and Ca-rich soils favoring precipitation and surface complexation of cationic metals [119], whereas acidic or redox-dynamic soils may promote remobilization of oxyanion-forming elements [124]. The soil texture and mineralogy further influence biochar–soil interactions, as clay-rich soils with high Fe and Al oxide contents often enhance co-precipitation and inner-sphere binding [104, 105, 110, 112, 114], while sandy soils may exhibit reduced retention capacity due to limited sorption sites [193].

Climatic conditions introduce additional complexity at field scale. Seasonal wet–dry cycles, flooding regimes, and temperature fluctuations accelerate biochar aging, alter surface functional groups, and drive redox oscillations that are particularly critical for As and Cr behavior [192, 194]. In monsoon-driven or irrigated systems, repeated reduction–oxidation events can destabilize initially immobilized oxyanions [123], whereas arid and semi-arid environments may favor more persistent immobilization through carbonate precipitation and reduced microbial turnover [132].

The crop type and rooting behavior also play a decisive role in remediation performance. The deep-rooted or high-biomass crops can influence rhizosphere pH, redox potential, and organic ligand availability through root exudation, thereby modifying metal speciation and bioavailability over successive growing seasons [94]. The crops with edible tissues sensitive to PTE accumulation (leafy vegetables and cereals) require stricter stabilization thresholds than non-food or industrial crops, underscoring the need for crop-specific remediation strategies.

From a scalability perspective, successful field deployment of modified biochar must balance cost-effectiveness, environmental trade-offs, and potential risks. High application rates or complex modification strategies may be economically prohibitive, while poorly characterized feedstocks or metal-loaded biochars may pose secondary contamination risks [183]. Additionally, trade-offs between contaminant immobilization and soil nutrient dynamics, greenhouse gas emissions, or microbial activity must be carefully evaluated. These challenges highlight the importance of context-specific biochar selection, realistic application rates, and post-application monitoring to ensure sustainable and regulation-compliant remediation at field scale.

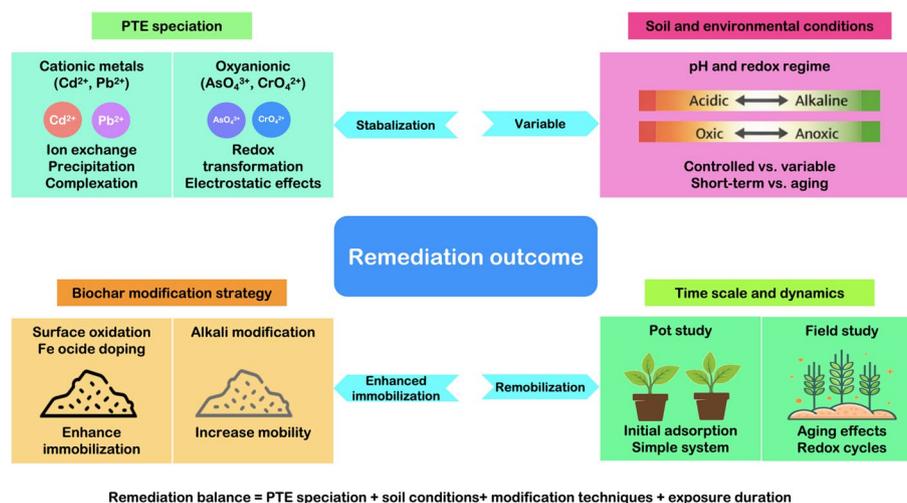


Fig. 11 Conceptual framework illustrating the context-dependent remediation outcomes of modified biochar for potentially toxic elements (PTEs) in soils. The framework integrates PTE speciation (cationic vs. oxyanionic), biochar modification strategies, soil pH and redox regime, and exposure duration (pot vs. field scale) to explain contrasting outcomes ranging from enhanced immobilization to partial remobilization

3.12 Reconciling apparent contradictions: a context-dependent framework for modified biochar–PTE interactions

Apparent contradictions in the reported effects of biochar on PTE behavior, such as enhanced mobility of chromium alongside reduced bioavailability of Cd or Pb [37, 48], or divergent aging effects observed in pot versus field studies reflect the context-dependent nature of biochar–soil–PTE interactions rather than inconsistencies in underlying mechanisms [44, 192, 194, 202]. These outcomes arise from differences in contaminant speciation, soil redox dynamics, biochar properties, and temporal scales of observation. For example, cationic metals such as Cd^{2+} and Pb^{2+} are predominantly immobilized through ion exchange, surface complexation, and precipitation processes that often strengthen with biochar aging due to increased surface oxidation and mineral association [35, 205]. In contrast, Cr frequently occurs as oxyanionic Cr(VI), whose mobility is governed by redox-sensitive transformations and electrostatic interactions [26]. Biochars that raise soil pH or lose redox-active functional groups over time may inadvertently enhance Cr(VI) mobility, even while stabilizing cationic metals [153]. Thus, divergent responses among PTEs reflect fundamentally different controlling mechanisms rather than contradictory behavior.

Similarly, discrepancies between pot and field studies can be attributed to differences in environmental complexity and time scale. Pot experiments typically operate under controlled moisture, limited redox fluctuation, and short durations, often capturing early-stage immobilization dominated by adsorption and surface complexation [28]. Field conditions, by contrast, introduce aging, wet–dry or redox cycles, plant–microbe interactions, and mineral transformations that may weaken some mechanism (electrostatic attraction) while reinforcing others (precipitation or co-precipitation) [72, 130]. Consequently, aging effects that appear beneficial in pot studies may attenuate or reverse under long-term field exposure. Integrating these observations, a context-dependent framework emerges in which remediation outcomes are determined by the interaction among PTE speciation (cationic vs. oxyanionic), soil pH and redox regime, biochar modification strategy, and exposure duration (Fig. 11). Recognizing this multidimensional

control space helps reconcile seemingly contradictory findings and underscores the need for site-specific biochar selection and adaptive management rather than universal remediation prescriptions.

3.13 Environmental and agronomic trade-offs of modified biochar based remediation

The application of modified biochar for PTE remediation in soils presents a complex balance between environmental risks and agronomic co-benefits, both of which must be considered to ensure sustainable implementation. While modified biochar can effectively immobilize PTEs, long-term field exposure may induce partial remobilization of certain elements, particularly redox-sensitive or oxyanion-forming contaminants such as As and Cr [22, 219]. Aging processes, including surface oxidation, mineral transformation, and microbial activity, can alter binding strength and contaminant speciation, emphasizing the need for long-term monitoring and adaptive management strategies. Biochar amendments also exert significant influences on soil microbial communities, which can have both beneficial and adverse implications [135]. Enhanced habitat availability, improved aeration, and increased organic carbon inputs often stimulate microbial biomass and functional diversity, potentially supporting nutrient cycling and soil resilience [41, 73]. Conversely, metal-loaded or highly modified biochars may exert selective pressure on microbial populations, altering community composition or enzyme activity, particularly in heavily contaminated soils. Such microbial shifts can indirectly affect PTE mobility through redox transformations, organic ligand production, or changes in soil pH. From an agronomic perspective, modified biochar frequently contributes to improvements in soil structure, nutrient retention, and water-holding capacity, which can enhance crop productivity and reduce fertilizer inputs. These benefits are particularly evident in degraded or low-organic-matter soils, where biochar acts as a long-term carbon reservoir and nutrient buffer. In addition, biochar application offers a carbon sequestration pathway, with its recalcitrant carbon fraction contributing to long-term soil organic carbon stocks and climate change mitigation. However, these agronomic and environmental benefits must be weighed against potential trade-offs, including nutrient immobilization, altered soil nutrient ratios, or unintended interactions with agrochemicals. The net outcome of biochar application therefore depends on biochar type, modification strategy, soil conditions, crop system, and time scale. Integrating remediation objectives with soil health and carbon management goals is essential for maximizing co-benefits while minimizing risks in long-term field applications.

3.14 Regulatory frameworks, permissible limits, and policy relevance of modified biochar based remediation

The practical deployment of modified biochar for remediation of PTEs must be evaluated within the context of existing soil quality standards, food safety regulations, and environmental policies, which define permissible contamination limits rather than prescribing specific remediation technologies. Internationally, regulatory thresholds for PTEs in soils and agricultural products are established by organizations such as the World Health Organization (WHO), the United States Environmental Protection Agency (USEPA), and the European Union (EU), with limits varying by land use, soil type, and exposure pathway. Under these frameworks, modified biochar is best positioned as a soil amendment for risk mitigation, rather than a stand-alone remediation

technology. Its role lies in reducing bioavailable metal fractions, limiting plant uptake, and lowering human and ecological exposure, thereby assisting contaminated sites in achieving compliance with regulatory thresholds for agricultural soils and food products. For example, WHO and EU guidelines primarily regulate maximum allowable concentrations of metals such as Pb, Cd, As, and Cr in edible crops, while USEPA soil screening levels focus on human health and ecological risk pathways. Importantly, regulatory acceptance of biochar use is contingent on feedstock origin, contaminant content of the biochar itself, and long-term stability of immobilization. Waste-derived biochars may face stricter regulatory scrutiny due to potential secondary contamination, whereas biochars derived from clean agricultural residues are more readily aligned with current soil amendment regulations. Aging-induced remobilization of PTEs further underscores the need for post-application monitoring to ensure sustained compliance over time. From a policy perspective, modified biochar aligns strongly with circular economy and sustainable land management strategies, particularly where it enables reuse of biomass residues, carbon sequestration, and rehabilitation of marginal or contaminated soils. However, its widespread adoption will require clearer regulatory guidance, standardized quality criteria, and integration into existing soil protection frameworks rather than technology-specific approvals.

4 Limitations of this study and future perspective

While this systematic review presents a rigorous and integrative framework for understanding the role of modified biochar in soil PTE remediation, several important limitations must be acknowledged. First, the exclusive reliance on the Scopus database may have excluded relevant studies from complementary sources such as Web of Science, PubMed, Google Scholar, and regional or national repositories, potentially limiting the thematic and geographic breadth of the synthesis. Second, the language restriction to English publications introduces a linguistic bias, underrepresenting important research conducted in non-English-speaking regions where biochar applications are particularly relevant, such as Latin America, Southeast Asia, and sub-Saharan Africa. Third, while bibliometric tools are effective for mapping research trends and co-authorship networks, they are less capable of capturing the mechanistic depth and contextual variability that influence the real-world effectiveness of modified biochar, especially under field-scale or ecologically complex conditions. This is particularly relevant for the rapidly evolving domain of biochar surface modification, where new methods such as heteroatom doping (N, S, Fe, Mn), surface oxidation, acid–base treatments, functional group grafting, and nanoparticle impregnation are altering biochar's sorption capacities and redox behaviors in novel ways. Many recent studies exploring synergistic mechanisms, such as phosphate-induced precipitation, complexation with engineered oxides, or electrostatic binding at engineered interfaces remain fragmented in the literature and may not be fully captured through standard keyword based searches or bibliometric clustering. Fourth, although some grey literature (e.g., technical reports, NGO case studies, and policy briefs) has been included through lateral review, a broader and more systematic inclusion of such materials would strengthen the synthesis, particularly by incorporating on-ground experiences, regulatory challenges, and farmer-led innovations. Fifth, despite covering a notable temporal range (2010–2024), disparities in scientific capacity, funding availability, and monitoring infrastructure across regions may result in geospatial skew,

with a concentration of data from high-income regions, while under-representing data-deficient or contamination prone zones in the Global South. Finally, many studies still rely on batch sorption experiments under controlled laboratory conditions, which may not adequately reflect biochar behavior in heterogeneous field soils, especially under variable pH, organic matter content, or competitive ion presence. The lack of long-term field trials and insufficient integration of soil–plant–microbe interactions limits our understanding of how modified biochars function as part of broader soil remediation systems. Despite these limitations, the review provides a robust interdisciplinary platform that synthesizes both material-level innovations and broader system-level implications, offering valuable guidance for future research aimed at designing biochar materials tailored to specific contaminants, soil types, and agro-ecological contexts.

Although significant advances have been made in modified biochar based PTE remediation, important knowledge gaps remain. Future research should prioritize the integration of modified biochars with complementary soil amendments (mineral additives, and microbial inoculants) to enhance immobilization efficiency and mitigate aging-related performance decline. Greater attention is also needed on biochar–plant–microbe interactions, as rhizosphere processes, root exudates, and microbial activity can notably influence PTE speciation and bioavailability over time. Long-term, multi-season field studies that couple contaminant dynamics with crop performance and soil health indicators are essential to assess real-world effectiveness. Finally, the development of hybrid remediation strategies, combining modified biochar with phytoremediation or microbial-assisted approaches, represents a promising pathway for improving sustainability and scalability.

5 Conclusions and prioritized research outlook

Modified biochar holds considerable promise for the remediation of PTE contaminated soils, while simultaneously delivering agronomic and environmental co-benefits. Bibliometric analysis indicates that biochar mediated soil remediation has rapidly evolved into a dynamic and globally collaborative research domain, transitioning from foundational studies on adsorption principles toward applied investigations emphasizing modified biochars, mechanistic immobilization pathways, and sustainable remediation strategies. Thematic clustering reveals three dominant research trajectories: bioremediation processes, PTE immobilization mechanisms, and biochar based soil pollution solutions, highlighting the maturation of the field and its growing relevance to ecosystem restoration.

Despite this progress, the effectiveness of modified and engineered biochars remains highly context-dependent. Their remediation performance is governed by modification-induced physicochemical properties (surface functionality, mineral incorporation, and redox activity) that enable multiple immobilization pathways (adsorption, ion exchange, surface complexation, co-precipitation, and redox transformation). These mechanisms, however, interact dynamically with soil pH, ionic strength, moisture regime, crop type, and climate, resulting in spatially and temporally variable outcomes.

A critical constraint is the aging-induced decline or transformation of remediation efficacy under field conditions. Processes such as leaching of alkaline components, surface oxidation, carbon loss, fragmentation into micro- and nanoparticles, and shifts in functional group chemistry can weaken metal binding strength over time. Importantly,

aging may induce divergent responses among co-existing PTEs, whereby stabilization of cationic metals (Cd and Pb via precipitation or complexation) coincides with enhanced mobility of oxyanion-forming elements (As and Cr), particularly in redox-dynamic agroecosystems such as rice-based systems. Field evidence further suggests that, in some cases, immobilization efficiency may decline to near pre-treatment levels within a few years, underscoring the need for long-term performance evaluation. Beyond mechanistic limitations, practical implementation challenges remain notable. These include production scalability, cost-effectiveness of modification strategies, quality standardization, potential release of pyrolysis by-products, and environmental risks associated with biochar degradation. Addressing these challenges requires moving beyond laboratory optimization toward region-specific, crop-specific, and regulation-aligned deployment frameworks supported by sustained monitoring.

To advance modified biochar from a promising remediation material to a reliable soil management tool, future research should be strategically aligned:

- Short-term research priorities should focus on mechanistic refinement and standardization. Key questions include identifying dominant immobilization mechanisms for specific PTE classes across defined pH and redox ranges, and quantifying early-stage aging effects on surface chemistry and metal speciation. These efforts require harmonized laboratory and mesocosm experiments, standardized reporting of biochar properties, and advanced spectroscopic and speciation analyses.
- Medium-term research priorities should emphasize field-scale validation and system integration. Multi-season field trials are needed to resolve how aging, rhizosphere processes, and climatic variability influence long-term PTE stability, crop uptake, and soil health. Integrating modified biochars with complementary amendments and evaluating trade-offs among remediation efficiency, agronomic performance, and ecological impacts will be critical at this stage.
- Long-term research priorities must address scalability, economic viability, and regulatory alignment. Long-term observatories, life-cycle assessments, and techno-economic analyses are essential to determine whether biochar based remediation remains effective and safe over decadal timescales. Concurrently, integrating machine learning and data-driven modeling offers a promising frontier for predicting biochar behavior and optimizing application strategies, provided that robust, high-quality field datasets underpin model development.

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Author contributions

J.R. Conceptualization, Methodology, Data curation, Software, Literature search and review, Formal analysis and Interpretation, Supervision, Resources, Project administration, Writing—original draft, Writing—review and editing; S.D. Conceptualization, Supervision, Methodology, Formal analysis, Software, Writing—section, Writing—review and editing; T.P. Literature search and review, Writing—section; S.G.S. Literature search and review, Writing—section; C.S. Literature search and review, Writing—section; T.R. Literature search and review, Writing—section. All authors have read and approved the final version of the manuscript for publication.

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Declarations

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