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Biochar

REVIEW

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Remediation of emerging inorganic contaminants in soils and water using pristine and engineered biochar: a review

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Abstract

Emerging contaminants (ECs) pose a growing threat to the agricultural ecosystems and human health. Biochar (BC) may be applied for the remediation of ECs in soils and water. There are some research papers that have been published about the potentiality of BC for the remediation of ECs in soils and water; however, there have been no critical and comprehensive review articles published on this topic up to now. Therefore, this review explores the application of pristine and modified BC for the remediation of various emerging inorganic contaminants (EICs), including vanadium (V), antimony (Sb), thallium (Tl), mercury (Hg), fluoride (F^-), and rare earth elements (REEs) in soils and water. The review explores the specific mechanisms by which BC removes these EICs from water and soil. The roles of ion exchange, complexation, electrostatic interactions, and precipitation in the removal of these EICs from water by pristine and functionalized BC have been reviewed and discussed. Particular attention is also paid to the interaction and potential immobilization of those EICs in soils with pristine and functionalized BC, highlighting some applicable strategies for treating EIC-contaminated soils, particularly paddy soils, aiming to mitigate the associated ecological and human health risks. Finally, the potential environmental implications and further research on the applications of pristine and functionalized BC for remediation of EICs in water and soils have been summarized. This article provides a comprehensive overview on the potential applications of different pristine and engineered BCs for the sustainable remediation of EICs contaminated soils and water.

Highlights

- Remediation of emerging inorganic contaminates (EICs) in soil and water using pristine and modified biochar (BC) is reviewed
- Functionalized BC immobilize EICs via ion exchange, complexation, electrostatic interactions, and precipitation
- EICs immobilization using the pristine and modified BC is complex and highly element- and redox-specific

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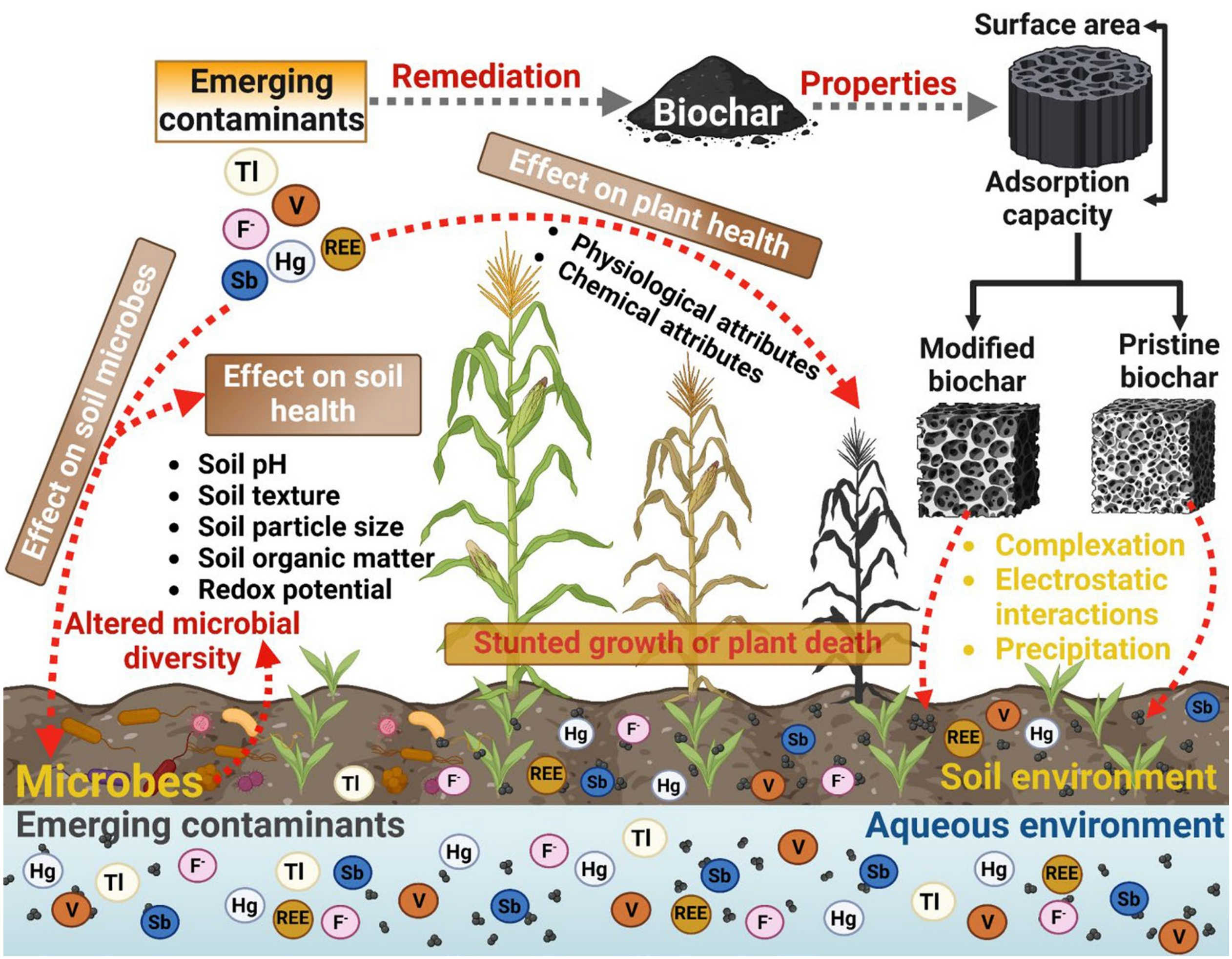
Keyword Emerging contaminants, Functionalized biochar, Soil and water remediation, Immobilization mechanisms

Graphical Abstract



1 Introduction

Emerging contaminants (ECs) are a new category of compounds, whose effects are yet to be fully understood, although known to pose a potential risk to the environment (Kumar et al. 2022). Industrial, agricultural, and domestic activities, all contribute significantly in generating vast amounts of wastewater. Wastewater often contains a complex mixture of chemicals and biological contaminants and these recently identified pollutants, some of which may be highly toxic (Nidheesh et al. 2022; Surana et al. 2022; Mosaffa et al. 2024a, b). Especially ECs may adversely affect soil and water resources (Yadav et al., 2021). These contaminants encompass a diverse range of organic and inorganic compounds (Kumar et al. 2022; Surana et al. 2022; Mosaffa et al. 2024a, b). Unlike routinely monitored pollutants, inorganic ECs can potentially enter the environment and cause ecological and human health problems, some of which are known while some are suspected (Rajput et al. 2024).

Contaminants of emerging concern include compounds that are not regulated under current environmental laws and have not yet been sufficiently studied although they may cause ecological and human health risks. Among the ECs in soils and water, vanadium (V), antimony (Sb), thallium (TI), mercury (Hg), fluoride (F^-), and rare earth elements (REEs) could be considered as emerging inorganic contaminants (EICs) because these elements have not yet been sufficiently studied, cause ecological and human health risks, and some of them are not regulated currently by environmental laws (Nidheesh et al. 2022). These EICs enter the environment through various natural and human-induced pathways. The presence of V, Sb, TI, and Hg primarily stems from rock weathering and soil runoff, but anthropogenic sources like mining, metal processing, and fossil fuel combustion significantly contribute to their enrichment in water and soil (Bolan et al. 2022a; Protano and Nannoni 2018; Shaheen et al. 2024). Ion F^-, while naturally occurring in rocks, can also be released into the environment by fossil fuel burning and runoff from various industries such as fertilizers, pesticides, and cosmetics (Fuge 2019). Similarly, the release of REEs originates from natural processes like rock weathering and soil runoff, but anthropogenic sources such as waste from medical facilities, mining, and various industries significantly impact their environmental presence (Sager and Wiche 2024; Fuge 2019). The impact of these ECs on the environment and human health constitutes a growing concern. Releasing such ECs into the environment and their bioaccumulation by plants, animals, microorganisms, and human could cause a series of biotoxicity problems and thus pose severe health hazards to humans. For example, ECs toxicity could affect or damage the functions of kidney, liver, lungs, and brain, as well as the blood composition and other important organs (Jaishankar et al. 2014; Antoniadis et al., 2023; Shaheen et al. 2024). Therefore, many recent studies are highlighting the need for a sustainable management of ECs contaminated soils and water aiming to mitigate their potential human health risks.

A range of physical, biological, chemical, and hybrid treatment technologies are being explored by scientists to effectively remove ECs from water and soil (Ahmed et al. 2021; Akhgari et al. 2023; Nabavi et al. 2023). Adsorption is a cost-effective and technically efficient method for removing ECs. As compared to other methods for the removal of ECs from water/soil, adsorption has some advantages and superiority, such as restricted byproduct formation, regeneration capability, low energy consumption, and ecological sustainability (Mahmood et al. 2022). It involves attracting and retaining ECs onto the surface of various sorbent materials including pristine and modified biochars (Bolan et al. 2022b; Mosaffa et al. 2023a; Deng et al. 2024; Mosaffa et al. 2024a, b). While traditional methods like physical remediation, excavation, incineration, and chemical treatment can quickly isolate hazardous contamination, they are often less efficient with complex EICs like V, Sb, TI, Hg, F, and REEs (Deng et al. 2024). Further, these approaches are expensive, unsustainable, and generate secondary environmental issues (Dhiman et al. 2023; Mahmood et al. 2022).

Biochar offers a more environmentally friendly alternative approach for improving soil health and the remediation of contaminants in soils (Zama et al. 2018; Shaheen et al. 2022a; 2023; Bolan et al. 2022b; Liu et al. 2023a, b, c, d, e). Its high surface area and porous structure effectively remove contaminants from soil and water. Moreover, the feedstock source and its content of cellulose, hemicellulose, lignin, metallic elements, and salts can also have an impact. Other important factors may be the ratios of carbon, nitrogen, hydrogen, and oxygen, and the presence of oxygen-rich functional groups. All these graphitic structure characteristics contribute to the BC ability to interact with these contaminants (Liang et al. 2021a, b; Mosaffa et al. 2023b; Shaheen et al. 2019a; Zhang et al. 2024). However, the applications of pristine BC for the effective removal of ECs from water/soil have some limitations related to (1) its limited range of functional groups, (2) the low adsorption capacity for many contaminants when present in high concentration, and (3) the presence of predominantly oxygen-containing functional groups, which lead to a negative surface charge resulting in low retention efficiency for anionic compounds (Zhang et al. 2022a). These limitations restrict the ability of pristine BC to interact with a diverse range of pollutants, particularly with metal anions (Shaheen et al. 2022b,c; Majumder et al. 2023; Deng et al. 2024). Therefore, to address these limitations, modification can be made in pristine BC to improve its low sorption and immobilization for pollutants in soils and water (Fang et al. 2024; Shaheen et al., 2022b, 2022c; Zhang et al. 2024). Tailoring engineered BC to target specific contaminants allows for a more effective solution for complex inorganic pollutants (Ullah et al. 2023). This BC-based approach aligns with the UN Sustainable Development Goals, being a promising solution for tackling the challenges posed by inorganic ECs (Lee and Park 2020; Liang et al. 2021a, b; Shaheen et al. 2022a).

There are some research efforts concerning the potential applications of pristine and engineered BC for the remediation of EICs in soils and water (e.g., Dong et al. 2023; Majumder et al. 2023; Deng et al. 2024; Rajput et al. 2024; Yang et al. 2025); however, there has been no any comprehensive review article published on this topic up to now. Therefore, the aims of this article are to review, discuss, summarize, and provide insights based on the current state of knowledge on the potential use of different pristine and modified BCs for the remediation of various EICs, including V, Sb, TI, Hg, F, and REEs in soils and water. The factors (e.g., redox and pH) and mechanisms (e.g., ion exchange, complexation, electrostatic interactions, and precipitation) that govern the adsorption/immobilization of each studied EICs by pristine and modified BCs have also been reviewed and discussed. Furthermore, the environmental implications and the future needs for the application of pristine and functionalized BCs for the remediation of EIC-contaminated soils and water have been discussed and summarized in this article. Overall, this article aims to provide a comprehensive overview about, and valuable insights into, the potential use of pristine and functionalized BCs as a sustainable and effective solution for the remediation of EIC-contaminated soils and water and the mitigation of their threats and the human health risks.

2 Biochar for the remediation of vanadium contaminated soils and water

Vanadium is a toxic heavy metal with increasing prevalence in the environment due to pedogenic and anthropogenic processes (Shaheen et al. 2019b; Zhang et al. 2019a, b). Elevated concentrations of V are frequently observed in soil and aquatic systems (Shaheen et al. 2019b), imposing severe consequences to ecosystems and human health. Details about the potential human health risk of V are reported in Antoniadis et al. (2023) and Shaheen et al. (2024). V is a redox-sensitive metal and occurs in three valency states, + III, + IV, and + V (Shaheen et al. 2019b). Among these species, the most labile is the pentavalent, whereas the tetravalent is less mobile, forming precipitates with (hydr)oxide phases or organic complexes (He et al. 2023; Fei et al. 2023). Details about V speciation, mobilization, and potential precipitation as affected by redox and pH changes are reported in Shaheen et al. (2019b). Many research efforts have demonstrated the effective V remediation in soil and water using natural or engineered materials (Gao et al. 2017; Wisawapipat and Kretzschmar 2017; Vessey and Lindsay 2020; Abernathy et al. 2022; Wołowicz and Hubicki 2022), among which BC receives growing interest for alleviating the adverse environmental V impact.

The performance of BC in soil V immobilization has been examined in recent studies (e.g., Teng et al. 2024). Also the effectiveness of using BC for V adsorption in polluted water has been systematically evaluated. Various agricultural byproducts, including peanut shell, wheat straw, shrub, corncob, and corn straw, have been selected as BC feedstock (Table 1). Figure 1 showcases the advancements made in BC research for treating V contamination. In a work by Yu et al. (2020), BC derived from agricultural byproducts was added in a soil spiked with up to 1000 mg kg^{-1} V (Table 1). As a result, BC obtained from rice straw (pyrolyzed at 650 ℃) demonstrated superior performance, with up to 225.6 mg kg^{-1} bioavailable V immobilized in the treatment of 3% application. Meanwhile, the wood feedstock pre-pyrolyzed at 250 ℃ (LWB) and pyrolyzed at 500 ℃ (HWB) was mixed with a soil spiked with 3750 mg kg^{-1} V; it was found that LWB reduced the water soluble V by 46% and bioavailable V by 32%, while the HWB increased the solubility and bioavailability of V, as compared to the untreated soil (El-Naggar et al. 2021). Physical characterization suggested that even though lower surface area was obtained, the lower pyrolysis temperature led to greater abundance of oxygen-containing functional groups and higher hydrophilicity. Their conclusion was agreed by Aihemaiti et al. (2022), who found that a BC modified with ferrous sulfate to increase the oxygen-containing functional groups achieved increased removal of both water-soluble V (a 39.9-fold increase) and bioavailable V (a 3.7-fold increase) in soil. Surface modification also optimized soil pH, thereby promoting V adsorption via electrostatic attraction (Zhong et al. 2019).

Such achievements are not always attained. In some other works, the removal efficiency of V by BC was found to be less than promising, attaining 8–30% (Meng et al. 2018; Fan et al. 2020). Ghanim et al. (2020) added red mud with saw dust BC to boost V sorption and found that V removal had a 11-fold increase to 16.5 mg g^{-1}, while the performance was further enhanced in acidic pH values (pH 4). Similarly, engineered nanoscale zero valent iron was combined with corncob BC (Fan et al. 2020), and this led to a retention capacity of 48.5 mg g^{-1}, attaining 99% V removal. In addition to surface adsorption, modification also facilitated the co-precipitation of Fe with V to form Fe-V complexes, a process that further reduced pentavalent V with the concurrent oxidation of Fe(0). Another study implemented a Zn-modified BC in a permeable passive wall installed for a pilot-scale study and was found to achieve 100% V removal from a contaminated groundwater aquifer (Meng et al. 2018).

Rainfall events can induce leaching of V from soil, a major risk for groundwater. To decrease such risk, BC derived from rice straw was used and found to have decreased the bioavailable V from 129.6 mg kg^{-1} to 76.1 mg kg^{-1}, and V in leachate under an acid rain event (Yu et al. 2022). Other works have reported the opposite effect: El-Naggar et al. (2021) reported an increased leachable V content by up to 221%. The labile and leachable fraction of V which can be immobilized by biotic processes was reported to be its pentavalent species (Wang et al. 2017).

Studies showed that plants can take up soil V through their root systems and translocate it into aboveground shoots (Chen et al. 2021). El-Naggar et al. (2021) tested corn and sorghum in a BC-added soil and found that the labile soil V decreased, while V uptake was 1933 mg kg^{-1} (corn) and 2050 mg kg^{-1} (sorghum) in shoots.

Table 1 Summary of studies on the application of pristine and engineered biochars for the treatment of vanadium contamination in water and soil

Sorbent	Feedstock	Pyrolysis temp. (℃)	Average size (mm)	Surface area ($m^2 g^{-1}$)	Dosage	Initial V concentration	Removal efficiency, %	Maximum capacity ($mg g^{-1}$)	Optimized pH	Key influencing factor	Source
BC	corncob	600	0.149	90.2	0.5 mg L^{-1}	25 mg L^{-1}	8	5	5.7	Dosage	Fan et al. 2020
nZVI + BC				50–90.2			99	49			
BC	saw dust	600	< 0.75	9.6	2 g L^{-1}	100 mg L^{-1}	NA	2	5.7	pH	Ghanim et al. 2020
Red mud + BC				23.7				16.45			
BC	peanut shell	700	0.45	NA	4 g L^{-1}	50 mg L^{-1}	25–30	< 2.5	independent of pH 4 ~ 8	NA	Meng et al. 2018
	wheat straw						30–40				
	corncob						25–30				
	shrub						25–30				
	aquatic plant						25–30				
	corn straw			27.45	8 g L^{-1}	5–10 mg L^{-1}	65	4.71		Initial V concentration, pH for Zn(II) modified BC	
CsCl modified BC	corn straw			108.31	1 g L^{-1}		66	41.07			
Zn(II) modified BC				150.36			100	28.46			
Zr(IV) modified BC				85.58			28	23.84			
BC	corn cob	350 and 650	0.25–0.125	15.6–25.5 (350℃) 9.8–10.1 (650℃)	1, 2, 3%	1000 mg kg^{-1}	22.5 ~ 30.5	NA	9.4–9.6 @ 350℃; 9.7–10.1 @ 650℃	Pyrolysis temperature, source of material, application rate affected the performance	Yu et al. 2020
	rice straw		0.125–0.075	8.7–9.0 (350℃) 10.2–10.4 (650℃)					8.7–9.0 @ 350℃; 10.2–10.4 @ 650℃		
	wheat		< 0.075	8.9–9.1 (350℃); 9.8–10.0 (650℃)					8.9–9.1 @ 350℃; 9.8–10 @ 650℃		
O modified	pinewood sawdust	700	NA	NA	0.25 g L^{-1}	50 mg L^{-1}	35	70	4	Initial pH	Wu et al. 2021
N\O modified											
N\O\S modified									3		

Table 1 (continued)

Sorbent	Feedstock	Pyrolysis temp. (℃)	Average size (mm)	Surface area ($m^2 g^{-1}$)	Dosage	Initial V concentration	Removal efficiency, %	Maximum capacity ($mg\ g^{-1}$)	Optimized pH	Key influencing factor	Source
H_3PO_4 activation	dewatered activated sludge	400	NA	31.9	0.8 g L^{-1}	50 mg L^{-1}	25	15.63	4	No significant influence factor	Shahib et al. 2022
H_2O_2 activation				40.4			23	14.4			
K_2CO_3 activation				37.6			20	13.75			
NaOH activation				54.5			24	15.0			
BC	Birch sawdust	140	< 0.3	7.92	0.25 ~ 1 g L^{-1}	50 mg L^{-1}	6	11	3	Initial pH	He et al. 2023
Chitosan modified BC			< 0.45	3.31			50	110			
BC	rice hull	500	4	236	2.5, 5%	3750 mg kg^{-1}	101% increased leaching	NA	10.33	Pyrolysis temperature and source of material (resulting in higher O-containing functional group)	El-Naggar et al. 2021
	wood chip + forestry waste	250		1.8			46%		6.87		
		500		375			221% increased leaching		10.3		
BC	Dewatered sewage sludge cake	500; 700	7.5–10 for 500 ℃; 10–11 for 700 ℃	59.8 (500 ℃); 34.5 (700 ℃)	3, 5%	480 mg kg^{-1}	> 90	NA	7.7	Combined effects of pyrolysis temperature, dosage, addition of ferrous sulfate	Aihemaiti et al. 2022
Ferrous sulfate modified BC				64.2–71.1 (500 ℃); 42.4- (700 ℃)							
Biochar	Rice straw	650	0.075	62.77	3%	1174 mg kg^{-1}	41	4.03		Dosage	Yu et al. (2022)
H_3PO_4 activation	*Lantana camara*	500 ℃	0.425	NA	0.5–4%	600 mg kg^{-1}	64.6 decrease in leaching V	7.53	4.4	pH, dosage, initial loading	Teng et al. 2024

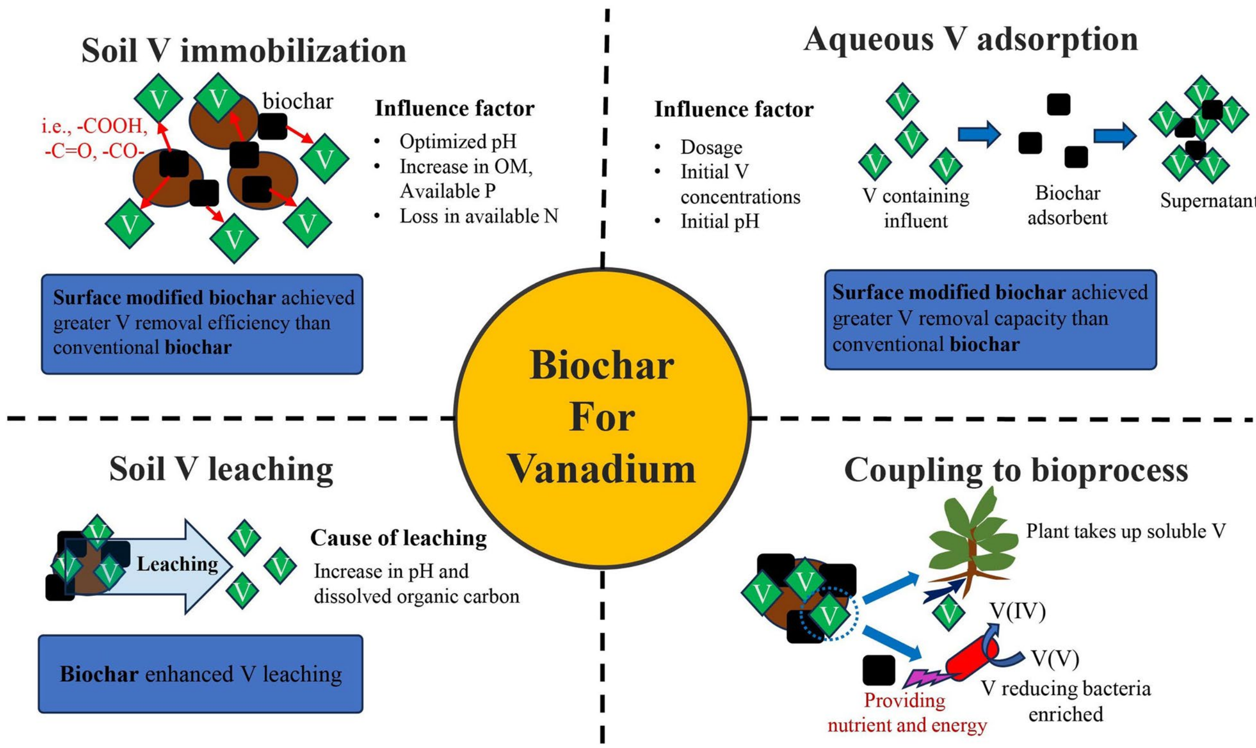


Fig. 1 Illustration of biochar applications for treatment of vanadium contamination in water and soil

Microbially mediated V reduction was also extensively studied (Zhang et al. 2019a, b; Shi et al. 2020; He et al. 2021; Zhang et al. 2021). Biochar addition induced redistribution of soil nutrient components (i.e., organic matter, iron species, available phosphorous), which acted as key factors to support the microbial reduction processes (Chen et al. 2021). According to gene sequencing results, the V reducing phylum *Proteobacteria* was promoted when BC was added to a soil (Aihemaiti et al. 2022)—the abundance of microorganisms was strongly and negatively correlated with bioavailable V ($p < 0.05$).

The interaction between V and biochar in soils/water could be governed by different mechanisms which highly depend on the biochar properties and the surface functional groups (El-Naggar et al. 2021). The oxygen-containing functional groups of biochar, such as carboxyl and hydroxyl, provide abundant adsorption sites to promote electrostatic attraction or complexation with V ions, reducing their mobility and bioavailability in soil (Wu et al. 2021; Teng et al. 2024). The adsorption/immobilization of V using BCs is limited by the abundance of various O-containing functional groups (i.e., C=O, and C–O/C–OH), hydrophilicity, reactive-surface, and acidity. In a study about the effects of wood and rice biochars on the immobilization of V in a highly contaminated soil, El-Naggar et al (2021) found that wood biochar with highly reactive surface sites, high hydrophilicity, and extensive surface O-containing functional groups was more effective in V immobilization than rice biochar. The results of El-Naggar et al (2021) indicated that chemisorption involving valency forces, and/or binding of V via electrostatic outer- and inner-sphere complexes could also govern V sorption onto biochar. The addition of modified biochar may alter the soil properties, including pH, contents of organic matter and available phosphorus, which promote the V immobilization (Yu et al. 2020; Aihemaiti et al. 2022; Teng et al. 2024). Furthermore, biochar facilitates microbial activities, contributing to the biotic treatment of V (Aihemaiti et al. 2022).

The findings above summarize that the biochars have contradictory effects on V mobilization and phytoavailability based on their pH and surface characterization. Also the results indicate the supplementary role of plants and indigenous microorganisms to decrease the mobility of V in conjunction with added BC. However, the elucidation of the details of these processes requires further study.

3 Biochar for the remediation of antimony contaminated soils and water

Antimony, a potentially toxic metalloid, is ubiquitously found in the ecosphere in large quantities, and can reach into soil/water bodies via many sources (Bolan et al. 2022a). Data acquired from recent published reports (42 investigation comprising 352 individual measurements) illustrate that the mean value of the world Sb concentration in soil is 87.96 mg kg^{-1} (Fig S1 A). Antimony exists in four oxidation states (−III, 0, + III, and + V) in the ecological bodies, among which the ecotoxicological hazard of Sb(III) is tenfold higher than that of Sb(V) (Dong et al. 2022). Sb(V) species (antimonic acid or $Sb(OH)_6^-$) are predominant at a wide range of natural pH conditions (3–10), while Sb(III) exists as antimonous acid ($Sb(OH)_3$) under anaerobic conditions (Rinklebe et al. 2020; He et al. 2024). In view of this, Long et al. (2019) reported that 33% of the overall dietary intake of Sb is due to the consumption of Sb-contaminated rice.

The spill of Sb in the natural hydrosphere has mostly occurred in the last few decades following the increased anthropogenic activities. For example, in January 2021, River Xiangxi in south China, a tributary of River Pingxi, was accidentally exposed to a Sb spill and caused alerts concerning downstream drinking water intake (Chen et al. 2022b). Data extracted from literature demonstrate that the average value of Sb in natural water bodies worldwide was 63.48 μg L^{-1} (Fig. S1 B). The average Sb in bottom sediments is as high as 18.18 (a value derived from 27 published works with 265 observations) (Fig. S1 C).

Antimony has been listed as a priority pollutant by the USEPA (Tao et al. 2021) with a maximum permissible limit of 36 mg kg^{-1} in soil and 20 μg L^{-1} in drinking water according to the WHO (Bolan et al. 2022a; World Health 2004). Occupational exposure to Sb, either directly through inhalation and ingestion or indirectly through the food chain, leads to reaction with sulfhydryls in human tissues that causes a high risk for human health (Gad 2024; Yang et al. 2015; Hua et al. 2021). Therefore, the removal of aqueous Sb is urgently needed in order to avoid any potential hazards to aquatic ecosystems. Consequently, non-highly sophisticated and efficient technologies must be used for Sb decontamination in soil and water ecosystems.

The effect of soil application of BC for the decontamination of Sb(III) ions is still debatable. Some reports have suggested the soil application of pristine BC for Sb(III) passivation due to its beneficial effect to alter soil bacterial community composition and subsequent Sb oxidation (Hua et al. 2021; Li et al. 2015; Safeer et al. 2024; Abhishek et a. 2023). However, there is a consensus that pristine BC application might in fact cause an enhancement in Sb phytoavailability. An early study reported that oyster shells BC maximized Sb(III) leachability, while its calcined form effectively immobilized Sb(III) due to the precipitation of calcium antimonate (Ahmad et al. 2013). In a study by Hua et al. (2019), original BC showed also a potential to mobilize Sb(III) following its application to an Sb-contaminated soil; this was due to the electrostatic repulsion of the anionic species with negative-charge sorption sites, the competition with other anions, and the biological reduction mechanisms in soil (Zhang et al. 2022a). The utilization of BC for amending rice basins in Sb-contaminated soils is also still questionable. In view of that, a 5% application of two BCs (pyrolyzed at 500 °C) was found to have caused an increment of soluble Sb (233.3% in the straw BC-amended soil and 74.8% in the husk BC-amended soil). The two biochars also increased the exchangeable Sb (straw 20% and husk 16%), while it reduced the residual fraction (straw 18.5% and husk 15.1%). Therefore, both biochars increased Sb content in rice shoots (Zhang et al. 2022b). These results indicate that application of pristine straw and husk biochar may increase the potential risk of Sb contamination. Consequently, BC functionalization for the immobilization of Sb(III) in soil matrix is urgently needed.

Recent literature also shows an average mobilization of Sb by about 21% following pristine BC applications. Conversely, functionalized BC application to Sb-contaminated soils shows an immobilization efficiency of 539% on average (Fig S2 A). Also in the literature there are numerous studies assessing the immobilization efficiency of Sb in water and soils by both pristine and functionalized BCs (Table 2). For instance, pristine BC application (20% w/w) to a shooting range soil was found to reduce Sb leachability by only 12%; however, an Fe-enriched BC minimized Sb leachability by about 40%, an effect that was also assisted by the BC-induced increase of soil pH and soil organic matter content (Silvani et al. 2019). Moreover, Yang et al. (2024) demonstrated that the application of an Fe/H_2O_2-BC decreased Sb(III) in a smelting site in Southern China by 93.2% compared to the untreated control due to the minimization of the release of Sb from Sb-bearing minerals. The application of a BC–$CaCO_3$ composite could maximize the passivation of Sb(III) ions and their migration in soil due to three potential mechanisms: (i) the precipitation of Sb(III) into their insoluble carbonate species, (ii) the enhancement of Sb(III) sorption due to the high degree of aromatization and surface π-electron density of the functionalized BC, and (iii) the formation of strong pyridine N and pyrrole N complexes with Sb(III), as also reported by Zhang et al. (2021).

Table 2 Summary of studies on the application of pristine and engineered biochars for the treatment of Sb contamination in water and soil

Feedstock	Modification	Pyrolysis Temp. (°C)	S_{BET} ($m^2 g^{-1}$)		Dosage ($g L^{-1}$)	pH	Initial Conc., $mg L^{-1}$	Removal efficiency (%)		Adsorption capacity ($mg g^{-1}$)		Removal/immobilization mechanisms	References
			BM	AM				BM	AM	BM	AM		
Water													
Pine–cone waste	$FeCl_3$ soaking $AlCl_3$ soaking	600	––	––	1.0	Pristine BC (7.67) Fe-BC (2.33) Al-BC (4.35)	10	52.11	Fe-BC (85.34) Al-BC (23.81)	2.49	8.68 Fe-BC 3.40 Al-BC	The high affinity of Sb(V) to Fe-associated functional groups The unoccupied orbitals on Fe might encourage formation of Fe–O–Sb complexes	Khanet al. (2023)
Sugarcane bagasse biomass	$FeCl_3$ soaking	500	4.69	6.62	1.0	Pristine BC (6.48) Fe-BC (1.92)	40	52.75	88.25	5.28	8.83	The higher capacity for electron donation toward Sb(III) oxidation The contribution of oxygen-containing functional groups and Fe reactive substances in the oxidation process	Gao et al. (2023)
Pomelo peels	Magnesium ferrite loading	300 500 700	––	100.08 78.04 113.27	0.05–2.0	––	30	––	95.33	11.03	139.5 43.5 106.1	Inner-sphere complexation H–bonding Electrostatic interactions	Yao et al. (2023)
Ficus microcarpa branches	Chitosan loading at different rates (0.2, 0.5, and 1.0)	500	4.96	CH0.2BC (4.14) CH0.5BC (3.18) CH1.0BC (2.23)	0.2–2.5	Pristine BC (9.3) CH0.2BC (5.9) CH0.5BC (5.5) CH1.0BC (4.8)	40	9.0	CH0.2BC (53.0) CH0.5BC (70.0) CH1.0BC (89.0)	10.01	86.22 115.03 167.80	Electrostatic interaction Chelation Surface complexation π-π interaction Hydrogen bonding	Chen et al. (2022a, b, c)
Rice straw	Nano zero-valent iron (NVI) loading	500 700	500BC (62.1) 700BC (56.6)	ZVI500 BC (122.2) ZVI700 BC (119.9)	1.25	––	10	500BC (28.7) 700BC (25.6)	ZVI500 BC (79.75–92.88) ZVI700 BC (89.6–97.4)	500BC (17.81) 700BC (35.51)	ZVI500 BC (49.2–98.2) ZVI700 BC (56.8–91.3)	The synergistic effects of monolayer and multilayer adsorption as well as chemisorption mechanisms	Ji et al. (2022)

Table 2 (continued)

Feedstock	Modification	Pyrolysis Temp. (°C)	S_{BET} (m^2 g^{-1})		Dosage (g L^{-1})	pH	Initial Conc., mg L^{-1}	Removal efficiency (%)		Adsorption capacity (mg g^{-1})		Removal/immobilization mechanisms	References
			BM	AM				BM	AM	BM	AM		
Mugwort seedlings	Bacterial modification by *Acidithiobacillus ferrooxidans*	500 700	BC500 (1.30) BC700 (38.04)	Mod. BC500 (42.9) Mod. BC700 (198.7)	1.6	––	30	BC500 (15.64) BC700 (21.15)	Mod. BC500 (99.68) Mod. BC700 (88.74)	BC500 (2.95) BC700 (3.92)	Mod. BC500 (18.81) Mod. BC700 (16.64)	Electrostatic interaction and pore filling	Liu et al. (2023a, b, c, d, e)
Biosolids	Zr–O, Zr–Fe, Zr–$FeCl_3$, Fe–O and $FeCl_3$ coated BC	300	––	––	4.0	––	10	57.2	24–99	17.54	31.54–98.04	Electrostatic attraction, surface complexation and nodule formation via hydrogen bonding	Rahman et al. (2021)
Tea branches	Co-precipitation with $MnFe_2O_4$	500	2.35	30.38	1.0	––	50	44.0	100	199.60	237.53	-Chemisorption -Deprotonation of hydroxyl groups associated with Fe on the $MnFe_2O_4$–BC surface -Co-adsorption onto $MnFe_2O_4$–BC	Wang et al. (2018b, c, a)
Anaerobic digested distillers' grain	Phosphogypsum modification	300–600	0.92	13.67	2.0	––	––	6.67	31.12	3.487	8.123	-Electrostatic adsorption -Formation of Ca–O–Sb complexes -amorphous surface precipitation	Li et al. (2022a, b)
Soil													
Feedstock	Modification	Pyrolysis Temp (°C)	S_{BET} (m^2 g^{-1})		Dosage, % (w/w)	pH	Total Sb Conc., mg kg^{-1}	Removal efficiency (%)		Immobilization efficiency (%)		Immobilization mechanisms	References
			BM	AM				BM	AM	BM	AM		
Pine–cone waste	$FeCl_3$ soaking	600	––	––	1, 2.5, and 5	Pristine BC (7.67) Fe-B (2.33)	28	NA	NA	33.33	37.5	Formation of stable Sb minerals with Fe, O and Si elements in the modified-biochar amended soil	Khan et al. (2023)
Straw	Fe/H_2O_2 modification	400	––	128.75	0.5, 1.0 and 1.5	4.57	320	NA	NA	––	90.7—95.7	-Formation of Fe-bearing minerals -Stabilization by surface complexation and co-precipitation	Yang et al. (2024)

Table 2 (continued)

Feedstock	Modification	Pyrolysis Temp. (°C)	S_{BET} ($m^2 g^{-1}$)		Dosage ($g L^{-1}$)	pH	Initial Conc., $mg L^{-1}$	Removal efficiency (%)		Adsorption capacity ($mg g^{-1}$)		Removal/immobilization mechanisms	References
			BM	AM				BM	AM	BM	AM		
Tea branches	$MnFe_2O_4$ modification	––	2.35	30.38	0.5, 1.0 and 2.0	-Pristine BC (9.01) -Modified BC (10.01)	79.2	NA	NA	12.7–33.9	33.8–43.5	-Adsorption onto the biochar surfaces via oxygen-containing functional groups -Formation of Sb–Fe oxides/hydroxides and Sb–O complexes	Wang et al. (2019a, b, c)
Shredded timber waste for pristine BC *Eupatorium adenophorum* for modified BC	Enrichment with powdered iron oxide-hydroxide	500–650	133.6	978.4	20	––	100 and 10 for low and high TOC soil	NA	NA	12	40	Sorption by surface functional groups, electrostatic attractions and less by precipitation	Silvani et al. (2019)
Corn straw	Fe–Mg modification	600	0.62	162.7	0.1 BC 0.05–1.0 FeMgBC	––	Total Sb is 1530	NA	NA	––	23.0	Inner sphere Fe/Mg complexes formation with Fe–Mg on modified biochar surface	Jiao et al. (2022)
Commercial	––	400–550	––	––	1.0 and 4.0	9.31	Total Sb is 200	NA	NA	12	––	Transformation of available Sb into stable Fe and Al oxides bound fractions	Zhu et al. (2020)

BM Before modification, *AM* After modification, *NA* not applicable

Apart from its functionality in decreasing Sb mobility, BC can be used as an electron donor/receptor in redox reactions in the antimonate/antimonite dipole. In the study of Cui et al. (2017), BCs derived from *Canna indica* at 300–600 °C showed limited sorption capacity of aqueous Sb (ranging from 7.8 to 16.1 mg g^{-1}), with the BC pyrolyzed at 300 °C being superior. Besides, a *Canna indica* BC induced the immobilization of Sb with a process that included first the oxidization of Sb(III) to Sb(V) and then the sorption of the latter species; the BC pyrolyzed at 400 °C was superior since it had a higher content in electroactive polyphenolic and was lower in electroinactive cellulose macromolecules. This finding highlights the urgent need to functionalize hybrid BCs (e.g., via grafting nanoscale zero-valent iron and iron oxides in particular) to maximize the oxidation and sorption capacities of pristine BCs.

Data acquired from recent literature show the limited sorption capacity of pristine BC for Sb ions (22.5 mg g^{-1} as an average value) (Fig S2 B). Functionalized BC shows a higher sorption capacity with an average value of 83.4 mg g^{-1}; such increase is the result of the enhancement of surface area, porosity, oxidization potential and maximization of the abundance of active functional groups.

In this regard, magnetite in Fe-modified BC offered a sorption energy of −0.22 eV (fivefold higher than the raw BC) and imparted to the engineered BC a higher capacity for electron reception towards Sb(III) oxidation (Gao et al. 2023). In another study, BC supported by magnesium ferrite was synthesized for the remediation of Sb(III)-contaminated groundwater (Yao et al. 2023): it exhibited a high immobilization Sb(III) capacity (77.44 mg g^{-1}) due to the Sb(III) oxidation via the iron redox reaction, reactive oxygen species origination and oxidization of functional groups. Similarly, pristine BC (from tea branches) functionalization using natural ores (jacobsite, $MnFe_2O_4$) proved highly efficient for Sb(III) retention (maximum of 237.53 mg g^{-1}). Ji et al. (2022) further reported that nano zero-valent Fe embedded in BC maximized the decontamination of aqueous Sb(III) through its oxidation into the less hazardous Sb(V), the complexation of Sb(III) onto active functional groups of nZVI-BC surfaces, and the formation of precipitates (e.g., $FeSbO_4$ and $FeSb_2O_4$) via the formation of complexes of Fe(II)/Fe(III) with the negatively-charged Sb(III)/Sb(V).

Biologically modified BC showed also a contribution in alleviating the Sb(III)/Sb(V) bioavailability in the ecosphere. In Liu et al. (2023d), *Acidithiobacillus ferrooxidans* was isolated from mining wastewater leachates in order to functionalize mugwort seedlings BC. The sorption capacities of this BC concerning Sb(III) and Sb(V) reached 18.81 and 14.64 mg g^{-1}, respectively, due to pore filling and with the mechanism of electrostatic interaction. The incorporation of positively charged compounds such as chitosan onto the carbonaceous lattice of BC can have a synergistic effect through (a) the enhancement of sorption of negatively charged metal(loids) like Sb(III) and (b) providing a high surface area with a plethora of active functional groups (Zhang et al. 2020). In view of this, chitosan-loaded BC showed higher sorption capacity than a raw BC derived from *Ficus microcarpa* at 500 °C for the removal of aqueous Sb(III) (168 vs. 10 mg g^{-1}) (Chen et al. 2022a).

In a number of works (e.g., Wang et al. 2018b, c, a; Rahman et al. 2021; Lai et al. 2023), the efficient removal of aqueous Sb(III) using pristine and modified BC has been attributed to the mechanisms of electrostatic attraction, inner-sphere complexation, -π interaction, hydrogen bonding, and chelation (Fig. 2). The outstanding performance of Zr-based metal BC composites (Zr–, Zr–Fe and Fe–O) was reported to passivate antimonite in a study by Rahman et al. (2021), where Zr-based metal BC composites showed high removal efficiency of Sb(V) (31.54–98.04 mg g^{-1}) due to electrostatic attraction, surface complexation and nodule formation, and hydrogen bonding.

4 Biochar for the remediation of thallium contaminated soils and water

Thallium is a trace metal with high toxicity with two oxidation states, Tl(I) and Tl(III), but the usual species is the monovalent. Recent investigations show an increasing number of Tl pollution incidents occurring worldwide (Liu et al. 2019c; Wang et al. 2019a, b, c). Such incidences include those in Lujiang River, China (Xu et al. 2019), Miocene colored waters, Poland (Wojtkowiak et al. 2016), Baccatoio stream basin, Italy (Perotti et al. 2018), River Carnon, UK (Tatsi and Turner 2014), and Carnoule's Pb–Zn mine, France (Casiot et al. 2011). All of these cases have threatened the safety of drinking water and the health of agricultural soils, and have ultimately posed an enormous threat to human health (Liu et al. 2019a, 2023c; Zhong et al. 2022). Therefore, due to the high toxicity and widespread presence of TI in ecosystems, many countries have taken the initiative to set industrial emission standards for TI, prompting governments to implement official response strategies (Liu et al. 2019b). Although TI emissions are beginning to be limited, already contaminated aquatic environments and agricultural soils are in urgent need of remediation.

Biochar, particularly engineered BC, has a high capacity for Tl remediation (Rinklebe et al. 2020). For example, engineered BC derived from pomelo peel and waste pomelo was found to have a maximum sorption capacity of 4283.9 μg g^{-1} (pomelo peel) and 5286.0 $\mu g g^{-1}$

(waste pomelo) (Gao et al. 2020). The two grapefruit-derived BCs increased soil pH, had distinct microporous structures and oxygen-rich functional groups, and the sorption process was in both cases accompanied by chemisorption. In a similar study with bamboo-derived BC, it was found that Tl in a soil from a pomelo orchard was retained at 96.9% of the initial added concentration (Kayiranga et al. 2021) via chemisorption due to O–H groups and phosphate.

To maximize pollutant sorption efficiency, BC modification is a research highlight (Zhao et al. 2018; Shaheen et al. 2022b,c). Numerous studies have shown that engineered BC is a low-cost and environmentally friendly sorbent that efficiently removes Tl(I) from wastewater with bright application prospects (Wang et al. 2020). A common modification is the addition of metal-precipitating substances to BC (Gong et al. 2022). Jacobsite ($MnFe_2O_4$)–BC composite (MFBC) was used in Tl sorption in highly acidic soils and it proved efficient (Liu et al. 2023b). Labile Tl decreased from 1.51 mg kg^{-1} to 0.88 mg kg^{-1} in a soil amended with MFBC, while pH increased from 3.05 to 3.97. In another work by Zhang (2020), straw BC, Fe-modified BC and Mn- modified BC were added to a Tl-polluted farmland soil, and it was found that bioavailable Tl decreased very efficiently, with the most efficient among the three BCs being the Fe-based (Fig. 3). The retention of Tl was agreed also by Liu et al. (2022a). Moreover, BC extracted from watermelon showed a capacity of retaining 174 mg $g^{-1}$for Tl(I) (Li et al. 2019). Likewise, KOH- and HCl-modified BCs retained Tl(I), were able to reversibly adsorb and desorb Tl(I), and also able to have a regenerated capacity. The analogous unmodified BC in that study showed its maximum capacity at a pH range of 4–12. In another work, goethite-supported BC achieved high distribution coefficient values of $K_d > 5000$ mL g^{-1} for a wide pH range of 5.0–11.0 (Liu et al. 2023a). It was also reported by that work that after adsorption the Fe content in the BC decreased, indicating possibly the mechanism of ion exchange. This was rather agreed by Shi et al. (2021), who found that FeOOH is able to readily form complexes with different anions and cations. However, studies on the mechanism of Tl immobilization are limited. Nevertheless, the development of efficient engineered BC for Tl soil pollution is a promising and growing field.

To adequately remove Tl(I) from wastewater with high Tl content, precipitation/adsorption after its oxidation has also been tested (Huangfu et al. 2015; Liu et al. 2019b). Therefore, a technique would be to convert Tl through BC from its active state (monovalent) to the stable trivalent species. Thus, BC-induced retention combined with Tl oxidation is a highly important research topic. $MnFe_2O_4^-$ composite BC prepared by co-precipitation demonstrated an outstanding Tl(I) removal capacity with a maximum adsorption capacity of 170.6 mg g^{-1}(Liu et al. 2021). This research reported that Tl(I) was oxidized to Tl(III) during adsorption and that the OH^- signal was slightly weakened after adsorption, suggesting that ion exchange between the Tl^+ and OH^- groups may have also contributed to Tl(I) removal. Moreover, hypochlorite oxidation in a magnetite-based BC achieved a TI retention of as high as 1123 mg g^{-1} (Li et al. 2020a, b). This BC served as an efficient sorbent and catalyst, while hypochlorite oxidation assisted in the removal of Tl(I), with the predominant retention mechanisms being the re-dissolution of Tl compounds and ion exchange between Tl and protons from the BC. In another work, nanowire γ-MnOOH@BC combined with persulfate (PS) achieved a high Tl removal of 164.4 mg g^{-1} (Wang et al. 2023a). Mn^{3+} in that BC reacted with persulfate and was reduced to Mn^{2+}, while persulfate $S^{VIII}O_5{}^{2-}$ was reduced to $S^{VI}O_4{}^{2-}$, thus causing the oxidation of Tl(I) to the inactive Tl(III). In turn, Mn^{2+} reacted with H_2O to produce $Mn^{II}OH^+$, which effectively catalyzed PS to further produce $SO_4{}^{2-}$ and $Mn^{III}O^+$, completing the cycle from Mn^{3+} to Mn^{2+} and back to Mn^{3+}. Also, $MnFe_2O_4$–BC composite (MFBC) has been used as PS activator to remove Tl from wastewater (Liu et al. 2022b; Wang et al. 2023a). The redox reactions of Tl species and their ion exchange and precipitation are the predominant mechanisms of the removal of Tl from wastewater.

In summary, the dominant Tl removal mechanisms seem to be sorption by electrostatic attraction, assisted by ion exchange and surface complexation; chemical precipitation is also important due to the elevation of soil pH after BC amendment, caused by the addition of the alkaline ash and the presence of carbonates and phosphates (Guo et al. 2020). The sorption mechanisms of Tl using pristine and modified BC are illustrated in Fig. 3.

5 Biochar for the remediation of mercury contaminated soils and water

Mercury is an extremely toxic pollutant that is widely distributed in the environment. The global treaty-Minamata Convention on Hg was adopted in 2013 to protect the environment from the adverse effects of Hg. According to the environment standards set by the Chinese government, the maximum permissible limit of total Hg in paddy soil is 1.0 mg kg^{-1} (pH > 7.5) and 100 ng L^{-1} in drinking water sources. Mercury still remains a contaminant of emerging concern, because of major problems of rice Hg contamination in Hg-polluted regions in Asia where paddy fields and surface water are contaminated with Hg (Amin et al. 2021).

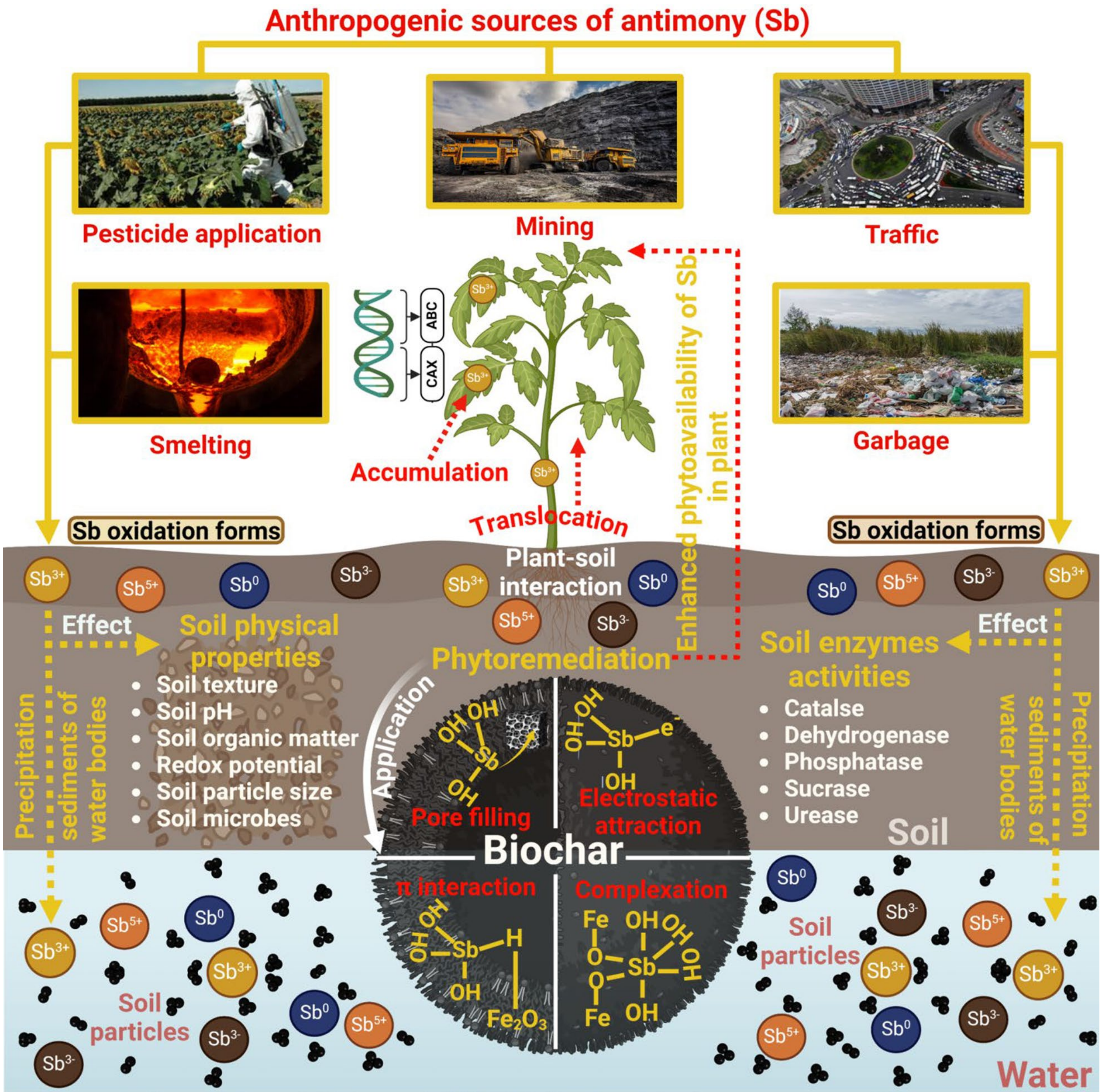


Fig. 2 Sources, fate, and adsorption mechanisms of Sb in water/soils using pristine and modified biochar

Agricultural and animal-derived BCs have been used for the Hg remediation in soils and water (Liu et al. 2017; Liu et al. 2018a, b; Betts et al. 2021; Xing et al. 2019; Zhang et al. 2019a, b). Plant biomass-based BCs are more popular, likely due to plant biomass being more available than other feedstocks. In a work by Park et al. (2019), Hg sorption was studied with the use of a pristine wood BC (WB) and a sulfurized wood BC (SWB) and the maximum sorption equaled 57.8 for WB and 107.5 mg g^{-1} for SWB, with the Hg sorption by SWB being more stable than WB under a wide range of pH values and temperatures (Park et al. 2019).

Hg retention is achieved to a great extent by the BC surface functional groups. For example, Xu et al. (2016) reported that Hg sorption by bagasse-derived BC was attributed to phenolic and carboxylic groups that formed $(–O)_2Hg^{2+}$ and $(–COO)_2Hg^{2+}$ complexes, while a hickory chips- and a wood-derived BC retained Hg by forming C=C and C=O Hg–π bonds (Xu et al. 2016). Brazilian pepper pyrolyzed at 300–450 ℃ was also found to have

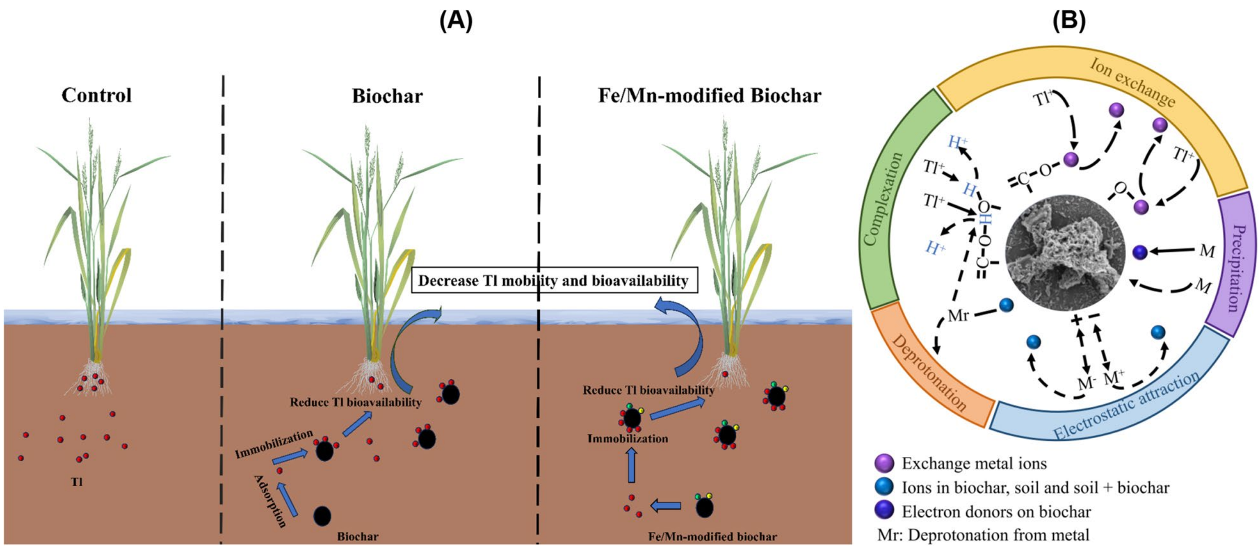


Fig. 3 Schematic illustration of the effects of pristine and modified biochar on Tl phytoavalaiblity in paddy soils (**A**), and the potential mechanisms governing Tl interactions with biochar in soil/water (**B**)

removed 23–77% Hg(II) via complexation with the carboxylic and phenolic hydroxyl groups, while that at 600 ℃ removed 91% of Hg(II) by the graphite-like domains on its aromatic structure (Dong et al. 2013). Hg adsorption by wood BC was due to Hg–C π bond formation and interaction with –OH and –COOH, whereas in sulfurized wood BC thiophenic groups and C-SO_x-C forms and interaction with C=C and -COO were the responsible groups (Park et al. 2019). A composite of graphene/BC was found to retain Hg by forming complexes of Hg with the groups C–O, C=C, –OH, and O=C–O (Tang et al. 2015). Also, the hydroxyl groups of rice hull- and straw-BC were those involved in Hg sorption in a work by Man et al. (2021). The role of BC functional groups on Hg immobilization is illustrated in Fig. 4.

These works show that BC modification improves Hg immobilization. Indeed, in comparison to corn straw BC, its Na_2S modified analogues increased Hg retention by 77% in a work by Tan et al. (2016). This was achieved due to the formation of an insoluble HgS precipitate. Also, the reactive surface functional groups greatly contributed (Tan et al. 2016). This concurs with Liu et al. (2018a, b), who reported that > 99.5% of added Hg was retained by sulfurized BCs. X-ray fine structure analyses indicated that Hg in the pristine BC was mainly bound to chlorine, while in the modified BC to sulfur. These two works agree that Hg retention becomes more efficient through the formation of strong Hg−S bonds in S-containing functional groups of the sulfurized BCs. In a thorough work by Liu et al. (2016), different feedstocks pyrolyzed under a variety of temperatures produced 36 BCs, which were evaluated concerning Hg. BCs at 600 and 700 °C decreased THg by > 90%, while a lower efficiency (40–90%) was measured for those BCs pyrolyzed at 300 °C. Among these BCs, sulfurized BCs retained Hg due to added S, while in BCs with low S content −O and −CI groups were those that retained Hg (Liu et al. 2016). Another way to increase Hg retention by BC is the impregnation with Fe on BC (Feng et al. 2020).

In studies related to soil, a cassava straw BC was tested as an amendment to a Hg-polluted soil at a mass ratio of 1% planted with spinach for 30 days. Results showed that the fractional amount of bioavailable Hg in the BC-treated soil decreased by 11.5%, and Hg concentration in spinach was reduced by 65% as compared to the control (Wei et al. 2022). Likewise, Bussan et al. (2016) added pinewood BC into a Hg-polluted sediment at a mass ratio of 5% and incubated it while periodically flushing it with N_2 under dark conditions for 14 days to induce methylation. It was found that the methylation rate of Hg decreased by 88% in sediments, while Hg demethylation rates remained unchanged. The reduction of Hg methylation rate was attributed to the decrease of Hg availability by BC via the mechanisms of complexation and electrostatic interactions. The modification of BC with sulfur (S) could further enhance Hg adsorption in soils. A sulfur-modified rice husk BC was added at 5% into a Hg-polluted soil under conditions of varying moisture: the soil had constant water content for 5 days and it was then dried for another 5 days. The results showed that Hg concentration in soil leachates decreased by 99.3% (O'Connor et al. 2018). The combination of BC and other amendments further improved the remediation efficiency, like in the case of co-added selenium (Se). A bamboo BC was added in a polluted soil also spiked with Se at 0.5% and planted with rice. It was found that CH_3Hg^+ decreased by 25–59% in the BC-treated soil compared to the control. Further, the concentration of CH_3Hg^+ in rice of the BC-treated soil was decreased by 82–87% in grain, 71–84% in straw, and 2–38% in root relative to the control. The decrease of availability of CH_3Hg^+ was due to the co-added Se, i.e., the formation of Hg–Se and CH_3Hg^+ complexes (Wang et al. 2019a, b, c). Furthermore, in a field study, Xing et al. (2020) used rice husk BC to remediate a Hg-polluted paddy soil. The BC was applied to the soil at rates from 24 to 72 t ha^{-1}. The concentration of Hg in soil pore water decreased by up to 44%, attributed to Hg immobilization due to reduced sulfur compounds in soil caused by the BC addition. Hg concentration in rice was reduced by up to 62% in bran, 43% in hull, and 70% in polished rice relative to the control. In another work related to redox reactions, Liu et al. (2018a, b) conducted a 524-day microcosm experiment with four types of BC; THg decreased by 8–80% compared to the control and water soluble methylated-Hg (MeHg) also decreased. It is notable that 12 species of Hg methylation organisms were identified. Microbiome was affected by changes in C sources, such as dissolved organic C and organic acids as electron receptors ($N^{V}O_3^{-}$, Fe^{III}, and $S^{VI}O_4^{2-}$).

Apart from microcosm studies, the BC impact on MeHg in soils has been studied under field conditions. Shu et al. (2016) found that rice straw-derived BC increased soil MeHg; they attributed this increase to the enhanced activities of sulfate reducing bacteria (SRB), and consequently enhanced SRB-mediated Hg methylation caused by the sulfate content of the BC, as also agreed by Hsu-Kim et al. (2013) and Saquing et al. (2016). Man et al. (2021) also concurred that an increase in the relative abundance of Hg-methylation microorganisms is indeed connected to the soil Hg methylation.

All these works exhibit the fact that the mechanisms of reduction of Hg^{II} and CH_3Hg^{II} due to added BC in water/soils are rather complicated (Fig. 4). Firstly, BC can stimulate activities of sulfate reducing bacteria, promoting the reduction of $S^{VI}O_4^{2-}$ to S^0 and of $S^{VI}O_3H^+$ to HS^{-I} (Liu et al. 2018a, b; Xing et al. 2019; Xing et al. 2020; Yang et al. 2021). This can result in the presence of polysulfides such as $Fe^{II}(S)_n$, thiols R-HS, and sulfides, which are able to immobilize both CH_3Hg^+ and Hg^{2+} through chemisorption onto S groups. Secondly, the functional groups of BC, i.e., S-containing groups, Cl- and O-containing groups can immobilize Hg^{2+} by forming Hg–S, Hg–Cl and Hg–O bonds (Ma et al. 2018; Kabiri et al. 2015). Thirdly, BC can impact the microbial methylation of Hg^{2+} in soils by providing sulfate to SRB, promoting MeHg production (Shu et al. 2016; Man et al. 2021; Liu et al. 2018a, b). The transformation of Hg and its immobilization mechanisms using biochar are illustrated in Fig. 4 and Fig. S3.

6 Biochar for the remediation of fluoride contaminated soils and water

Fluoride sources can be mining, coal combustion, smelting, F-containing fertilizers, and pesticides (Khan et al. 2022), all of which may pose a significant risk to both environmental integrity and human health (Fan et al. 2003; Ma et al. 2014). Biochar is an easy-to-handle, simple-to-design, and low-cost de-fluoridation sorbent aimed at limiting F exposure (Dong et al. 2021; Hota et al. 2024). However, BC produced through thermochemical conversion has limited polar oxidized surface groups, low porosity and surface area; thus it may not be efficient enough for F removal (Roy et al. 2018). It must be noted that electrostatic repulsion of anions like F by negative surface charges of BC further reduces its efficiency (Hettithanthri et al. 2023). However, several raw BCs have been tested for F^- removal; they have all been found to have relatively low sorption capacity: rice husk BC (3.42 mg g^{-1}) (Tang et al. 2022), wheat straw BC (1.93 mg g^{-1}) (Yadav et al. 2013), *S. pinnata* BC (7.66 mg g^{-1}) (Mohan et al. 2012), de-oiled *Pongamia pinnata* seed cake BC (0.985 mg g^{-1}) (De et al. 2018), and *S. ravannae* BC (2.44 mg g^{-1}) (Saikia et al. 2017).

To overcome this problem, researchers have engineered BC to increase F sorption by chemical treatment, physical activation, impregnation, and magnetic modification to increase surface area and create positive surface charge (Khan et al. 2022; Meilani et al. 2021; Foroutan et al. 2024). Among them, modification of BC with multivalent metal ions has gained attention (Fan et al. 2022). In a work by Wan et al. (2019), MgO peanut shell BC (MgO BC), rich in cellulose and thus with high surface area (S_{BET} = 182.3 m^2 g^{-1}), was prepared by one-step pyrolysis. It was found that the maximum F sorption was 83.05 mg g^{-1}, whereas the pristine analogues was unable to sorb F anion due to electrostatic repulsion (Wan et al. 2019). On the other hand, magnetic nanoparticles have been used as a magnetic source for BC, allowing BC to be quickly and easily separated from the solution when applying an external magnetic field (Bombuwala et al. 2018; Li et al. 2016; Mohan et al. 2014; Yadav and Jagadevan 2021). In addition, several REE oxides have been used due to their high stability and acid and alkali resistance to form REE-F complexes and thus increase F retention in recent years (Fan et al. 2022; Yu et al. 2015). Among them, literature reports BCs impregnated with Fe-La (Fan et al. 2022), Fe-La-Ce (Li et al. 2023), La-Fe-Al

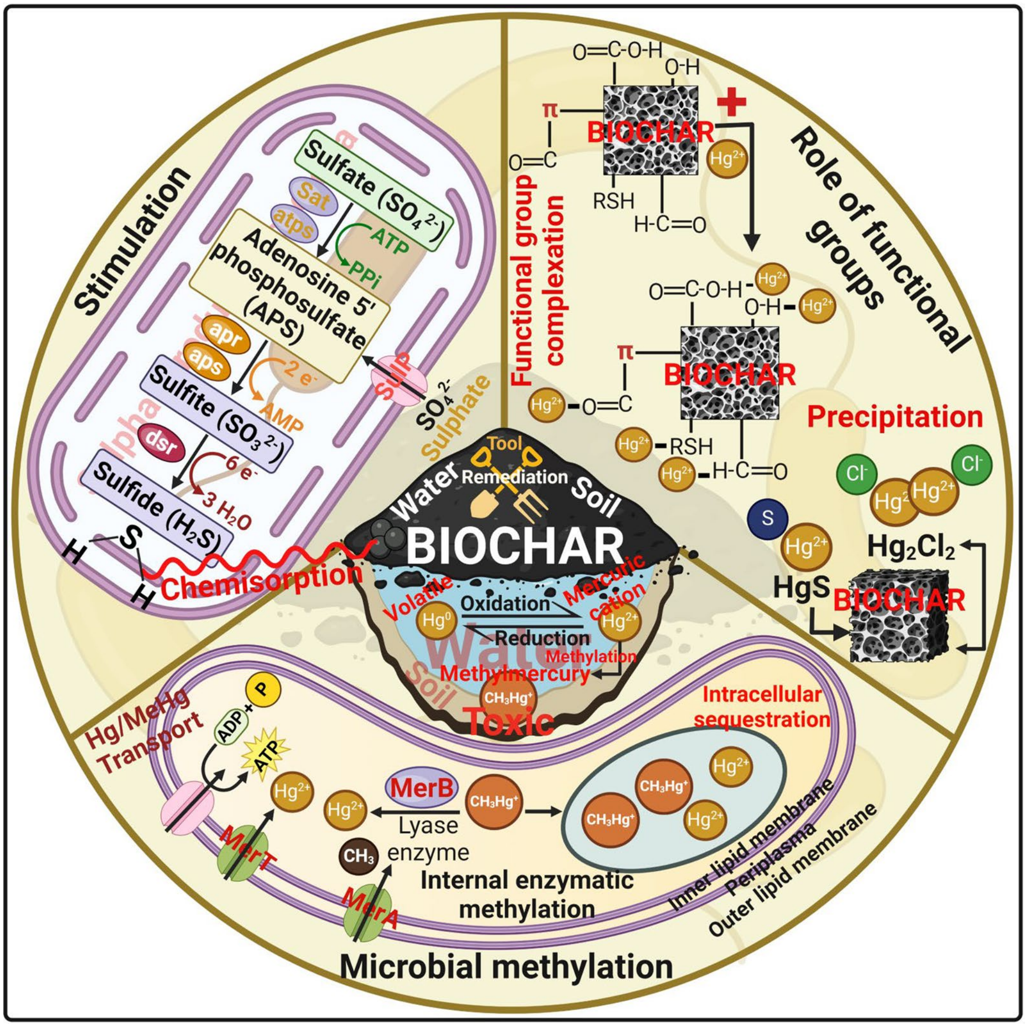


Fig. 4 Schematic illustration of Hg transformation and its interactions with biochar in soils and water

(Zhou et al. 2021), and zirconium compounds (Mei et al. 2020). Wang et al. (2018b, c, a) found that in a solution with 10 g L^{-1} of F further added with 1.0 g L^{-1}, a pristine teak peals BC achieved the retention of 0.96 mg g^{-1}, while the lanthanum analogous 7.62 mg g^{-1}. Meanwhile, BC can be used to formulate composites with low-cost metals such as Fe and Al (Yu et al. 2015).

Although there is a large number of studies on F^- reduction by BC in water, for soils the studies are rather few. Fan et al. (2022) first proposed an Al-La-modified BC amendment for the remediation of a F-contaminated soil. As the dose of Al-La-modified BC increased, water soluble F in soil decreased from 12 mg L^{-1} to 2.39 mg L^{-1}, with a reduction of 80%, indicating that Al-La-modification converted water soluble F to a form of lower mobility and bioavailability. Wang et al. (2023b) applied different rates of BC to soil to reduce the accumulation of F in tea; they found that water-soluble F content in tea decreased compared to the unamended control. In the same work, the application of BC to soil reduced the soil exchangeable Al content compared to the control (46.37 ~ 91.90%) and increased soil exchangeable calcium (Ca^{2+}) content (12.02 ~ 129.74%), indicating an increase in base saturation and thus a decrease of residual acidity in soil, an effect that led to the decrease of F in tea leaves.

Adsorption of F by BC in soil and aqueous phases involves complex interactions of physical, chemical and electrostatic interactions (Abeysinghe and Baek 2022; Kumar et al. 2023a, b; Li et al. 2023; Sadhu et al. 2021). These mechanisms include surface adsorption, ion exchange, complexation and precipitation, which are influenced by solution chemical reactions, BC properties and environmental conditions, mainly dependent on pH (Table 3). Specific sorption mechanisms are shown in Fig. 5. Electrostatic interactions for F removal by BC depend on the electrostatic repulsion and attraction between the sorbent (here, BC) and the sorbate (F), which is also related to protonation (which tends to occur at low solution pH) and deprotonation (at higher solution pH) of the surface functional groups. Therefore, pH greatly affects the F species and the surface charge of BC, and, in turn, F sorption (De et al. 2018). In general, in neutral to slightly acidic pH, BC exhibits higher F removal capacity due to favorable surface interactions. Indeed, several studies exhibit the effective removal of F^- at low pH (≤7) (Mukherjee et al. 2023). However, there is still a void in knowledge regarding F interactions with BC, hence BC-induced remediation strategies need to be further explored; to this end, analysis techniques should be further utilized, such as sophisticated spectroscopic techniques, so that F chemistry and interactions may be elucidated.

7 Biochar for the remediation of rare earth elements contaminated soils and water

The retention of REEs from water and soil using BC involves multiple mechanisms. These mechanisms vary under different environmental conditions, as depicted in Fig. 6. The sorption efficiency of BC for removing REEs from aqueous solutions or REE-contaminated soils is also presented in detail in Table 4. Rare earth elements can be sorbed or immobilized by BC with the mechanisms of ion exchange, complexation, electrostatic and cation-π interactions, and precipitation (Pei et al. 2024; Zou et al. 2024). Ion exchange involves the substitution of common cations like sodium (Na^+), calcium (Ca^{2+}) and hydrogen (H^+) found in BC with solution REE cations (Chen et al. 2022a, b, c). This process was examined by Serra-Ventura et al. (2022), who studied the release of Na^+ from BC in a solution with and without samarium (Sm). It was found that the cations (such as potassium (K), Ca, and Mg) in BC significantly influenced the efficiency of ion exchange in the removal process. An important aspect to consider in ion exchange is the role of pK_a and coexisting ions. Proper pH adjustment and the introduction of small amounts of anions like sulfate (SO_4^{2-}) or nitrate (NO_3^-) were found to enhance threefold the sorption onto BC of europium (Eu^{3+}) (Wilfong et al. 2020). The impact of these changes was further evidenced by exploring sorption at the point of zero charge (PZC; the solution pH value at which surface protonation exactly equals deprotonation of the BC external surfaces) and the interference effects of abundant mono- and divalent cations such as Na^+, K^+, ammonium (NH_4^+), Mg^{2+}, and Ca^{2+}. It was found that with decreasing pH levels and the addition of divalent cations, sorption competition of Sm with H^+, Ca^{2+}, and Mg^{2+} became more pronounced and this reduced Sm retention (Mahmoud et al. 2021). At solution pH exceeding the PZC, BC surface acquires a negative charge, thereby enhancing the capture of REE cations.

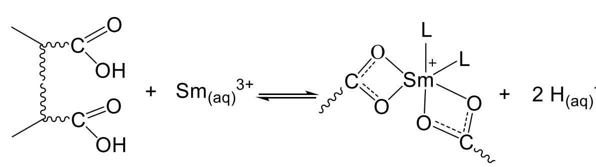
In an experiment involving Ca-aluminum (Al) layered double hydroxides (LDH)-modified BC used for the sorption of Eu, X-ray photoelectron spectroscopy analysis (XPS) revealed a decrease in Al intensity on the BC post-sorption. This suggests that ion exchange occurred between Al^{3+} and Eu^{3+}. The reaction can be represented as follows (Eq. 1):

$$\equiv Al^{3+}(S) + Eu^{3+}(L) \rightarrow \equiv Eu^{3+}(S) + Al^{3+}(L) \quad (1)$$

with S denoting the solid phase and L the liquid phase.

This finding highlights the enhanced sorption capabilities of BC for Eu through ion exchange, which seems to be the predominant retention mechanism of REEs, as also agreed by Li et al. (2020a, b).

The surface of BC is abundant in functional groups, notably carboxyl groups, which play a pivotal role in the adsorption process. In high solution pH, these carboxyl groups are deprotonated and more capable of reacting with Sm^{3+}, forming inner-sphere surface complexes (Eq. 2). This reaction was evidenced in a Sm removal experiment using loofah BC, stimulated with salicylic acid and sodium salicylate (Liatsou et al. 2017). The shift of the O1s signal in C = O to a lower binding energy in the spectroscopic analysis further corroborated the complexation between the carboxyl groups and Sm^{3+}, as follows (Eq. 2):



(2)

Moreover, in a study of Sm^{3+} sorption by cactus fiber-derived BC, similar interactions were revealed. The observed attenuation in the carboxyl groups and the bending vibrations post-sorption indicated a direct interaction and complex formation with Sm^{3+} (Hadjittofi et al. 2016). Beyond carboxyl groups, other oxygen-containing functional groups like hydroxyl, carbonyl and phenol also engage in surface complexation with lanthanide ions such as lanthanum (La^{3+}), cerium (Ce^{3+}), and neodymium (Nd^{3+}), significantly impacting their sorption and removal from solution (Kołodyńska et al. 2018; Pei et al. 2024; Zou et al. 2024).

In soil-based experiments, the sorption of Ce onto modified BC was found to alter the surface functional groups. This alteration is a testament to the role of surface complexation in the sorption of REEs by BC, underlining its significance in environmental applications (Li et al. 2022a, b). Surface of biochar is predominantly

Table 3 Summary of studies on the application of pristine and engineered biochars for the treatment of fluoride contamination in water

Biochar	Modified reagents	Pyrolysis temp (°C)	S_{BET} (m^2g^{-1})		Dosage (g L^{-1})	pH	Removal efficiency (AM)	Fluoride concentration range (mg L^{-1})	Maximum F adsorption capacity(mg g^{-1})		Interaction mechanism (AM)	References
			BM	AM					BM	AM		
Rice husk biochar	$FeCl_3.6H_2O$, $FeSO_4.7H_2O$	700	1.94	196.11	4	4	95.4% (5 mg L^{-1})	5–35	–	4.45	Electrostatic attraction, anionic fluoride interaction, surface complexation, surface diffusion, physical adsorption, inner-sphere complexation	(Yadav and Jagadevan 2021)
Tea-waste biochar	H_2SO_4, $NaNO_3$, $KMnO_4$	400	5.07	11.83	10	–	98.31% (50 mg L^{-1})	–	–	52.5	Electrostatic attraction	(Roy et al. 2018)
Peanut shell biochar	PPy, $FeCl_3.6H_2O$	600	83.50	37.24	10	–	–	4.6–87.8	–	17.15	Surface adsorption, mesoporous diffusion, the replacement of doped ionizable chloride ions (Cl^-) coupled with positively charged nitrogen (N^+)	(Li et al. 2016)
Douglas fir biochar	$FeCl_3.6H_2O$	900–1000	663	494	2	7	–	1–60	–	9.04	Electrostatic attraction	(Bombuwala et al. 2018)
Corn stover biochar	Fe^{2+}/Fe^{3+} solution	500	ND	3.61	5	2	30–75% (50 mg L^{-1})	1–100	6.42	4.11	No report	(Mohan et al. 2014)
Pomelo peel biochar	$La(NO_3)_3$	800	506.30	269.48	1	6.5	82% (10 mg L^{-1})	10–300	0.96	19.86	Anionic fluoride exchange	(Wang et al. 2018b, c, a)
Food waste biochar	$AlCl_3$	315	–	3.62	3.33	7.1	–	10–900	0.41	123.4	Inner-sphere complexation, precipitation	(Meilani et al. 2021)
Peanut shells biochar	$MgCl_2$	500	339.2	182.3	10	8.0	–	–	ND	83.05	Inner-sphere complexation, electrostatic attraction	(Wan et al. 2019)
Camellia seed biochar	Zirconium	400	–	–	1.6	6.8	–	5–70	ND	11.04	Ion exchange	(Mei et al. 2020)
Nutshell biochar	$AlCl_3.6H_2O$, $LaCl_3.7H_2O$	–	833.94	204.02	4	7	80.08–91.75% (12 mg L^{-1})	0–1000	27.92	74.91	No report	(Fan et al. 2022)

Table 3 (continued)

Biochar	Modified reagents	Pyrolysis temp (°C)	S_{BET} (m^2g^{-1})		Dosage ($g\ L^{-1}$)	pH	Removal efficiency (AM)	Fluoride concentration range ($mg\ L^{-1}$)	Maximum F adsorption capacity($mg\ g^{-1}$)		Interaction mechanism (AM)	References
			BM	AM					BM	AM		
Pinecone-derived biochar	$AlCl_3$	600	–	–	1	7	–	0.5–40	11.11	12.10	Ion exchange, complexation, chemical interaction	(Khan et al. 2022)
Rice husk biochar	$FeCl_3$, $AlCl_3{\cdot}6H_2O$, $MgCl_2{\cdot}6H_2O$	600	205	114	1	5	–	1–50	4.28	21.59	Coulomb attraction, ligand exchange, halogenation, inner-sphere complexation	(Shen et al. 2021)

BM Before modification, *AM* After modification, *NA* not applicable

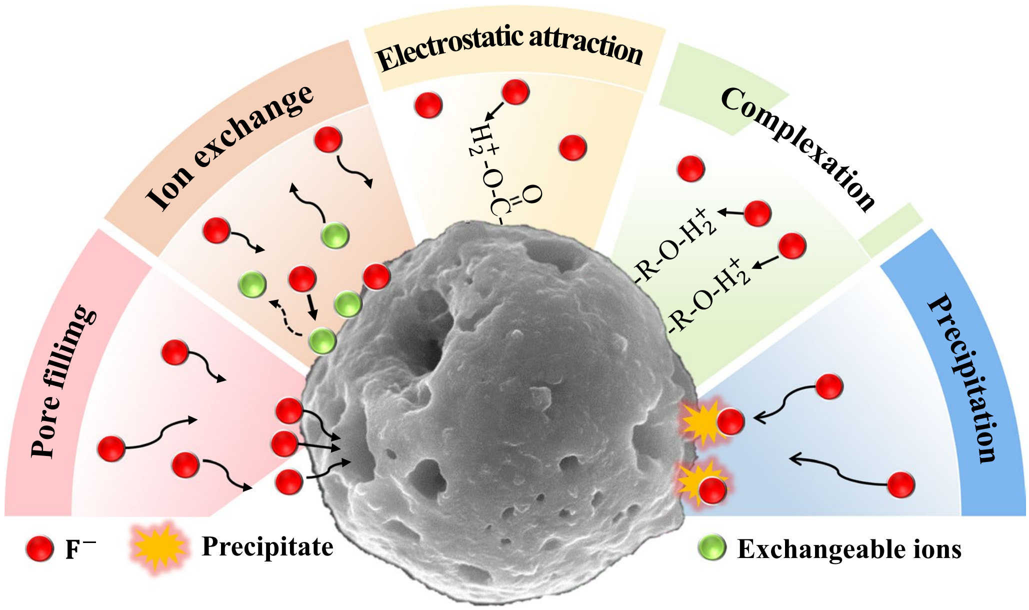


Fig. 5 Illustration of the potential mechanisms of fluoride adsorption on biochar

electronegative. This characteristic facilitates the preferential sorption of metal cations, such as those of REEs, through electrostatic interaction (Huang and Hu 2020). Furthermore, the ionic radius of REEs decreases as the atomic number increases, influencing both electrostatic and π-metal interactions with BC (Migaszewski and Galuszka 2015). In an experiment by Wan et al. (2023) focusing on three REEs (ytterbium (Yb), gadolinium (Gd), and La) using nano-BC, a notable increase in sorption was observed in the metals with smaller ionic radius. This increase was attributed to the increased charge density in metals with smaller ionic radius, which strengthened electrostatic interactions.

Another mechanism, i.e., π-electron interaction, can also contribute to REE retention by BC. Raman spectroscopy, specifically the analysis of peak changes of the G band of sp2 carbon post-sorption of La^{3+} and Nd^{3+}, indicated that π-electron interactions can contribute to adsorption (Tan et al. 2015; Zhao et al. 2021). X-ray diffraction (XRD) analysis of ammonium citrate-modified BC post La sorption revealed an amorphous sorption of La, suggesting that the sorption of it was not in the form of carbonate and was primarily driven by electrostatic interaction (Wang et al. 2016). Another study highlighted a shift in the wavenumber of C–H on BC aromatic ring from 854 to 877 cm^{-1} after scandium (Sc) sorption, confirming the presence of metal-π interactions (Dai et al. 2022). In this work, the initial stages of the sorption process were dominated by electrostatic interaction. Enhancing the electronegativity of the BC surface could improve the efficiency of this step, with the atomic number of REEs determining the sequence of sorption through electrostatic interaction.

Precipitation can also play a crucial role in ability of BC to remove REEs from water and soils, as the mineralogical composition within BC significantly influences this process (Liu et al. 2016). To ensure the application efficiency, selectivity, and attraction of BC to REEs, modification is of primary importance. This could be achieved by loading compounds containing elements like Fe, Mn, Al, silicon (Si), and P onto BC, thereby boosting its remediation capabilities (Royer-Lavallée et al. 2020; Liang et al. 2021a, b). The solution pH is another key factor in REE removal through precipitation. As pH increases, REEs tend to form precipitate phases with various elements (Zhang and Honaker 2018). For instance, at a pH range of 2.7–4.1, REEs mainly form precipitates with Fe. Between pH 4.6 and 4.8, and the process is dominated by Al. At higher pH levels of 6.1–10.8, Ca and Mg become the primary elements in co-precipitation. In addition, P-rich BCs, such as bone char, play a unique role. They contain P in forms like apatite and $Ca_3(PO_4)_2$, which gradually release phosphate ions. These ions are capable of interacting with REE ions to form phosphate precipitates (Jin et al. 2019; Li et al. 2022a, b). All these works show that precipitation is largely affected by the elemental composition of the BC and the ambient solution pH levels, as also agreed by Pourret and Houben (2018). Understanding the specific acting elements within BC under various conditions is crucial for optimizing its effectiveness of REE remediation.

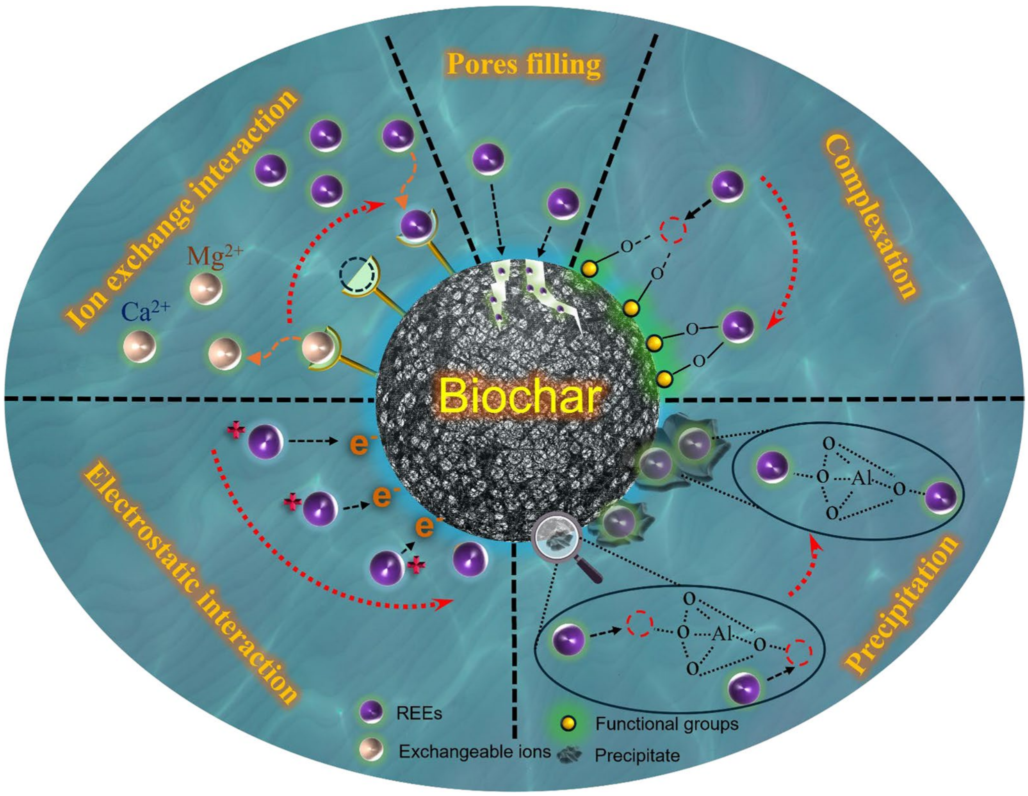


Fig. 6 Proposed removal mechanisms of REEs from water using biochar

8 Conclusions, environmental implications, and future directions

Biochar holds a significant potential for remediating EICs in soil and water. However, harnessing its full potential requires careful consideration of its limitations and potential environmental implications. One key limitation is the inherent low sorption efficiency of BC, potentially hindering its effectiveness in removing contaminants (Cheng et al. 2021). This challenge can be addressed through low cost and easy-to-apply modifications of the pristine biochar to enhance its ability for contaminant sorption (Majumder et al. 2023). This tailored approach paves the way for optimizing BC effectiveness in overcoming its initial limitations. Another crucial aspect to consider is the coexistence of different EICs in aquatic environments. While research shows the effectiveness of BC with heavy metals (Dong et al. 2023), a deeper understanding of the underlying mechanisms of removal/immobilization of EICs in multi-contaminated water/soil using pristine and modified biochar is essential. Therefore, in this article we reviewed, discussed, and summarized the potential application of pristine and modified BC derived from different feedstocks for the remediation of various EICs in soils and water, including V, Sb, Tl, Hg, F, and REEs. The potential mechanisms that govern the interactions between EICs and pristine and functionalized BC have been also reviewed and discussed.

This article provides a comprehensive overview on how well different pristine and engineered biochars can be utilized for the sustainable remediation of EICs in multi-contaminated soils and water. On a broader scale, the outcomes from this article could have profound implications for policy-making and local agricultural practices, enabling them to draft and implement more effective measures for managing EICs contaminated soil/water and the mitigation of the associated risks. Therefore, this article is of great environmental interest and concludes that selected pristine and engineered biochars are promising amendments for mitigating the contamination and risk of EICs in water and soil. Moreover, the information provided in this article can serve as a foundation for future research efforts, focusing on enhancing the removal/immobilization efficiency of BC for EICs in contaminated soils/water.

Further research is crucial to ensure the safe mitigation of EIC threats in various environmental settings, as recommended below:

- Production of BC: The selection of environmentally friendly feedstock for BC production is crucial, as

Table 4 Summary of studies on the application of pristine and engineered biochars for treatment of REEs contamination in water

Biochar Feedstock	Elements	Modification	Pyrolysis Temp (℃)	S_{BET} ($m^2 g^{-1}$) BM	S_{BET} ($m^2 g^{-1}$) AM	Dosage ($g L^{-1}$)	pH	Concentration ($mg L^{-1}$)	RE %	Adsorption capacity ($mg g^{-1}$) BM	Adsorption capacity ($mg g^{-1}$) AM	Removal mechanisms	References
Castor meal	Sm	NA	350	< 1	NA	0.01–1.5		10–220	84.3–99.9	25		IE, CMP	Serra-Ventura et al. 2022
Eucalyptus forest residues		NA	350	< 1	NA					13.4			
Sugarcane bagasse		NA	350	1.3	NA					3.5			
Green pericarp of coconut		NA	350	< 1	NA					19.1			
Pine wood sawdust	Sc, Nd		350	4.7		1–10	3.7	20	38-88	1.1–8.0		EI, CMP	Komnitsas et al. 2017
Sargassum fusiforme	La (III)	ammonium citrate	300	1.5	45.5	1	7.0	25–500	99	170	362	EI, IE	Wang et al. 2016
			500	2.7		1	7.0			185			
			700	76.1		1	7.0			275			
Cactus fibres	Sm (III)		600	< 5		0.3	3.0 6.5	53	40 98	90 350		IE, CMP	Hadjittofi et al. 2016
Cynara scolymus leaves	Sm (III)		350			0.67	7.0	200–1002	15–90	303	98	IE, PCP, CMP	Mahmoud et al. 2021
Solidago canadensis	Eu (III)	CaAl-LDH	700			0.07	7.0	40	5–13		120	IE, PCP, CMP	Li et al. 2020a, b
Luffa Cylindrica sponges	Sm (III)		650			0.33	3.0	75	95	360		CMP	Liatsou et al. 2017
Agriculture industry wastes	La (III) Ce (III) Nd (III)	$FeSO_4$				5	4.0	50–200	45–97	9.7–10.5 10.0–12.0 10.7–14.7	10.2–12.7 9.8–14.1 10.4–18.1	EI, IE, CMP, PCP	Kołodyńska et al. 2018
Wheat straws	La (III) Nd (III)		400			0.03–0.08	5.0	5–50	2–58	80.4 71.6		EI, IE, CMP	Zhao et al. 2021
Pitaya peel	Sc (III)	H_3PO_4	350	1.7	884	2	3.0	30	69–86	1.0	7.0	EI, CMP	Dai et al. 2022
			550	132	901	2	3.0	30		1.0	13.8		
			750	541	1052	2	3.0	30		4.9	18.6		
Sewage sludge	La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu		500			0.2	5–7	0.05	10–60		< 50	CMP	Pourret and Houben 2018

[*] *IE* Ion exchange, *EI* Electrostatic interaction, *CMP* Complexation, *PCP* Precipitation, *BM* Before modification, *AM* After modification, *NA* not applicable

certain organic waste materials may contain harmful contaminants that could be released during the pyrolysis process. Sustainable practices that prioritize clean or pre-treated feedstocks are essential to ensure the overall environmental responsibility of using BC for remediation purposes. Research should focus on readily available, sustainable, and preferably pre-treated organic waste materials to minimize environmental impact during pyrolysis

- Optimizing modifications: While pristine BC offers a cost-effective solution, future research should optimize modification methods to achieve high removal efficiency without significantly increasing cost. Minimizing the environmental impact of these modifications is also crucial.
- Developing robust BC regeneration techniques: For long-term use this is essential in practical terms. Future studies should evaluate regeneration under various conditions and extended durations.
- Integrating BC with other technologies like photocatalysis: This is highly promising for enhanced EC removal. Exploring such combinations can lead to more comprehensive remediation strategies.
- Leveraging AI for data analysis, predictive modeling, and process optimization: This can contribute to efficient and cost-effective BC application in EC removal. This interdisciplinary approach can accelerate innovation in BC-based remediation strategies.
- Developing comprehensive and well-defined guidelines: This essential process should outline the specific data needed to assess the safety and efficacy of modified BC. These data would encompass details about the BC itself, soil and water properties, and relevant environmental factors. The guidelines should also establish criteria for determining whether the desired soil–water improvements justify a large-scale use of BC.
- Producing BC at industrial level: The biochar produced in large, industrial, scale is of high importance. There are some limitations for the biochar industrialization and there are several factors that can hinder the large-scale implementation of BC, including: (1) availability of sufficient and sustainable feedstock, (2) the fact that the energy cost of operating at high temperatures and large-scale production remain as obstacles, (3) low sorption efficiency of pristine biochar, (4) the economic infeasibility of pristine biochar using expensive materials (nanomaterials) , (5) the fact that some biochars are metal selective adsorbents, and (6) the fact that organic pollutants in biochar cannot be avoided. Therefore, apparently, the economic, social, and environmental benefits of this technology must be discussed so as to enhance the commercial feasibility of BC production.

Supplementary Information

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Additional file 1.

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