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Agricultural waste-derived biochar in heavy metals remediation of soil-food crops for human health and sustainable agriculture

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ABSTRACT

Heavy metals (HMs) contaminations in 'soil and food crops' interface perturb food safety, soil quality, environmental sustainability, and public health. In global agricultural landscapes, challenges are further exacerbated by agricultural-waste biomass burning-driven emissions of hazardous particulate matter, black carbon, and greenhouse gases. Together, environmental repercussions are realized as pollution, land degradation, climate change, and expanding marginal lands. This discussion therefore explores biobased methods associated with 'agricultural waste-derived biochar (ARBC)' for HMs remediation, wise management of crop harvesting/processing residues or left-over remnants in farmlands by biomass valorization, and sustainable agriculture. Further, multiple mechanisms and physico-chemical attributes are explored with ARBC deployments to leverage HMs remediation from agroecosystems in an eco-sustainable way. In this respect, the designer ARBC, especially those manoeuvred with magnetic and nano-scale particles offer better potential to deal with HMs remediation from soil-food crops. However, critical analysis revealed that the success of ARBC-technology in decontaminating HMs contaminated soil-food crops is tightly regulated by multiple factors such as pyrolysis conditions, application doses, biochar-microbe interactions, soil physico-chemical characteristics, and nature of feedstocks. In conclusion, sustainable ARBC applications should ensure abridging of biobased technology driven HMs remediation and human health risks mitigation. Last, the limitations in techno-economic and life cycle assessment need to be urgently addressed for scale-up of biobased technology in the HMs remediation. Future researches to conquer the limitations in secondary pollution from aged ARBC and nanotoxic effects of designer biochar can benefit stakeholders, global regulatory institutions, and policymakers for designing eco-sustainable future. Such panoramic advancements in biomass-driven technology for soil pollution remediation and human well-being can leverage biorefinery, boost circular bioeconomy, facilitate decarbonization, and accelerate climate action to help achieve 'United Nations-Sustainable Development Goals'.

1. Introduction

In the Anthropocene, the heavy metals (HMs) concentrations escalated sharply, perturbing global agricultural landscapes, environmental sustainability, sustainable agriculture, food safety, and public health [1]. To this end, a global-scale study, covering 1493 agrarian regions, revealed that 14–17 % of food crops in farmlands exceeds agricultural thresholds, at least for one hazardous HM [2]. Moreover, Hou et al. [2] opined that such global agroecosystem regions contaminated with HMs impose serious ecological risks and human health implications to about 0.9 and 1.4 billion of exposed residential people. The anthropogenic sources of HMs such as those arising from modern intensive agriculture and industrial mining waste far exceeded the natural geological sources, such as volcanic eruptions, wild forest fire, and weathering of rocks [3–5].

In agriculture systems, the applications of inadequately treated sewage waste water, sludge, fertilizers, and pesticides can be potential sources of HMs pollution [1,6]. Since the agroecosystem-soil act as major sink for HMs, their eco-toxic effects can perturb soil health in terms of physico-chemical and biological or microbial attributes [7]. In the sense, 'United Nations Environment Protection (UNEP)' (2020) calculated that annually about 9 million people die prematurely due to exposure to environmental pollutants. In this sense, 'United States Environmental Protection Agency (USEPA)' and 'International Research Agency on Cancer (IARC)' and 'Agency for Toxic Substances and Disease Registry (ASTDR)' also affirmed the HMs contamination in soil as serious global concern [8]. Therefore, HMs contamination in soil-food crops interface can pose serious threats to agroecosystem and human

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health. Consequently, such global regulatory institutions on environmental pollution devised risk analysis methodologies to validate their eco-toxic effects and delineate their rank, especially in terms of human health risks [7,8].

Incidentally, HMs contamination in agroecosystem soil can be readily transferred to food crops, imposing serious threats to the organisms of cognate trophic levels, including a profound negative effect on environment and human health. [9]. In addition to human health risks, studies on HMs phytotoxicity in food crops can be manifested through oxidative stress of harmful free radicals such as reactive oxygen/-nitrogen species (ROS/RNS) [8]. The human health risks can be manifested through dermal, respiratory, neural, and cardiovascular diseases, manifested through morbidity or even mortality at extremely high HMs exposure levels [1,9] (Fig. 1). In this context, Fig. 1 explain the multiple sources of HMs pollution, exposure routes, and human health risks associated mechanisms, that urgently calls for deploying sustainable treatment technologies. The sustainable solution of the HMs contamination in agriculture systems underlie in the biomass-driven remediation or biobased technology [5,10,11].

Biomass is in fact a broad term which comprises 'continental organic matters, including agri-residues that can derive their origin from forestry/agroforestry, tree food crops, hardwood, solid municipal sludge, agricultural residues, and food waste [11–16]. In recent times, the grim scenario of COVID-19, forcing packaged edible stuffs, further

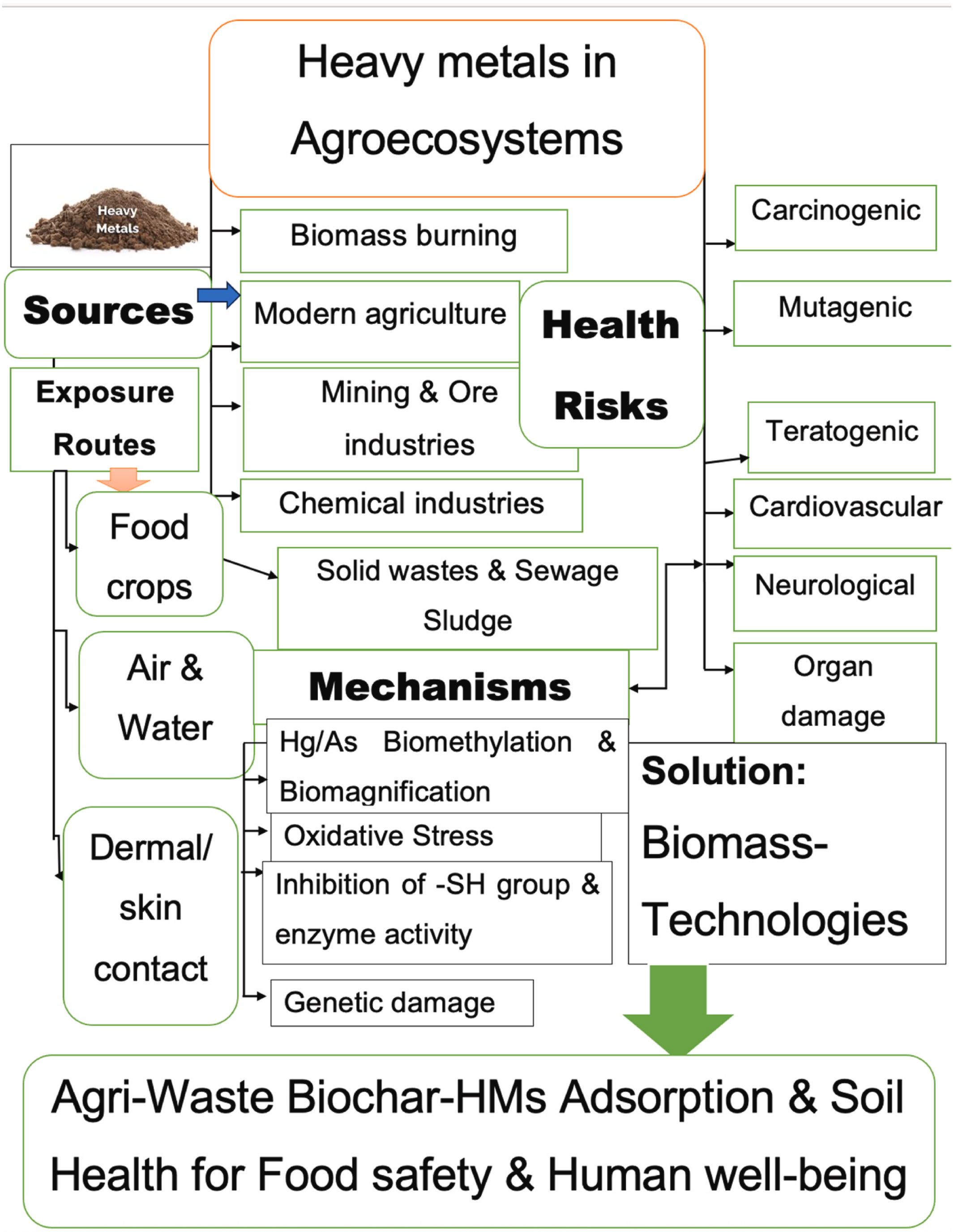

Fig. 1. Heavy metals in agriculture systems: Sources, exposure routes, and human health risks necessitates use of biobased technology mediated through agricultural waste-derived biochar (ARBC) for sustainable future.

exacerbated the problem of food waste [17]. Inadequate disposal of about 80 % of food waste can cause environmental and human health hazards, which otherwise can be a potential biorefinery feedstock [5, 18].In this vein, 'agricultural waste-derived biochar (ARBC)' are bio-based technologies that can accelerate the HMs remediation from soil and food crops [3].

The ARBC-are "carbon rich porous solid" which offers large 'specific surface area (SSA)' and multiple associated mechanisms ([19], b; [20, 21]). Importantly, ARBC is enriched with nutrients such as 'carbon (C)-45–83 %), nitrogen (N)- 0.3–3.2 g/kg%, phosphorus (P)- 0.1–7.99 g/kg, and potassium (K)- 2.64–224 g/kg, that can ameliorate soil fertility ([22]; Khare et al., 2021). Also, ARBC-induced 'cation exchange capacity (CEC)' (10.9–97.3 cmol/kg), 'water holding capacity (WHC)' (41–561 %), and high energy content (15–28 MJ/kg) makes it a promising 'biomass-based sustainable solutions (BSS)' for environmental pollution and issues impending sustainable agriculture (Khare et al., 2021; [21]). The "International Biochar Initiative' (IBI) described" 'ARBC as a solid carbonaceous-residue obtained after the thermochemical degradation of various biomass feedstocks at a controlled temperature, especially, in the absence of air or oxygen. In addition to HMs remediation, the ARBC deployment in agriculture systems act as potential decarbonization technology by 'Carbon Capture, Utilization, and Storage (CCUS)' [6,20]. Also, the extension of ARBC applications in an integrated green biorefinery platforms possess the potential to leverage circular bioeconomy and hence accelerate the attainment of 'United Nations Sustainable Development Goals' (UN-SDGs) ([6,21]; Kumar et al., [23]; 2026).

The rationale behind encouraging ARBC as biobased technology for HMs is ascribed to its biological nature of remediation and biomass valorization, that can effectively conquer the limitations and environmental side-effects of physico-chemical methods, in an eco-sustainable way [3,6]. At present times, limited field-scale applications of ARBC is therefore unfortunate, considering its clear edge over traditional chemical technologies, in terms of both selectivity and sustainability [24,25]. To this end, ARBC can potentially remediate HMs from contaminated soil, however, received less attention in past studies in terms of formulating standardized pre-treatment and thermochemical conversion methods. In this vein, IBI of UN also aims to revitalize soil fertility by using biochar to facilitate sustainable restoration of degraded or marginal lands, especially those contaminated with HMs. Further, the co-benefits of ARBC-driven HMs remediation in decarbonizing both, i.e., natural and agroecosystems, warrant their up-scaled applications to accelerate the efforts towards climate action [21,26]. For instance, application of biochar to soybean reduced the Cd bioavailability, stabilized the rhizosphere microbes, and mitigated N_2O emission by inhibiting its precursor [27]. Therefore, wise applications of ARBC, as biobased technology can potentially improve the environmental and agricultural sustainability by ameliorating the HMs contamination in soil and food crops [28,29]. The global policy platforms like "World Economic Forum (WEF)" though certify the ARBC role in climate change mitigation and sustainable development, however, inadequately explored in global farmlands. In this sense, 'Intergovernmental Panel on Climate Change (IPCC)' has also included biochar or ARBC as 'negative emission technology (NET)' [30]. Notably, the sustainable ARBC production can effectively address antecedent issues such as unwise management of agri-waste biomass that comprise burning of harvested/processed crop residues or left-over remnants in farmlands [21,31]. Agri-waste biomass burning and burial can lead to emissions of environmental pollutants, including HMs, small size fractions of particulate matter (PM) and greenhouse gases (GHGs), imposing serious environmental and human health risks [31].

The widely practiced burning of agri-waste biomass is therefore not sustainable, causing disruptions in agro-ecological functioning, emissions of deleterious PM, GHGs or other air pollutants, nutrient leaching, reduced soil microbial diversity, and pollution induced human health hazards ([32,33]; Neogi et al., 2022; [21]). In this sense, comparative environmental and economic assessment of three widely used agri-residues management practices i.e., 'open burning, fertilizer production, and biochar production' with corn residue, rice straw, and sugarcane leaves biomass revealed that ARBC was best system to contain the emission of air pollutants, GHGs, PM, and black carbon [31]. To this corner, researches opined that solution of coupled or inter-linked problems in agriculture systems i.e., HMs contamination and sustainable management of agri-waste biomass can be addressed with ARBC-applications [34]. In this respect, agri-waste biomass constitute an integral fraction of 'continent's organic waste streams' [16], which can be valorized to biochar, adsorbing HMs from contaminated agro-ecosystems [5,20,29,35].

Despite, the above opinions, in previous studies the potential utilization of ARBC in global agricultural landscapes are either scant or not addressed in the interrelated biorefinery and environmental sustainability framework. The integrated ARBC-based biorefinery platforms can have tight implications to human health, sustainable agriculture, renewable energy, circular bioeconomy, and climate change mitigation [6,36,37]. Therefore, the judicial use of ARBC in HMs remediation from agroecosystems is "multi-win" amendment that deserve urgent focus in terms of guiding techno-economic, environmental, and social policy frameworks for biobased sustainable future [16,20,29,38].

In past decades, 'bibliometric and knowledge mapping analyses' by Liu et al. [39] during 1991–2020, covering 126 countries also revealed that biochar research was not sustained during recent times and unfortunately, those on ARBC further received limited attention. This analysis was mainly attributed to number of publications compiled from 'Web of Science Core Collection' during this time-frame, which can be categorized into 'slow growth period and rapid growth period'. Notably, the knowledge mapping-based delineation of research hotspots advocated the prioritization of ARBC-driven HMs remediation from soil and food crops. The analysis of knowledge domains by Liu et al. [39] further suggested the focused research on modified or designer ARBC in HMs removal from contaminated agroecosystem soil. Though Kamal et al. (2025) opined ARBC deployments as cost-effective and environment friendly remediation approach for HMs remediation from soil-food crop interface, the wide knowledge voids are still exposed [15]. Microbial communities and their distribution in biochar-amended soil have not been well examined, especially with respect to biochar properties like pH, particle size, microporosity, nutrient content, ARBC-microbe interactions, and ion-exchange capacity. This necessitates the need of up-scaled ARBC production, explicit elucidation of ARBC-driven HMs remediation mechanisms, and techno-economic innovations in deployments of designer ARBC to fill these knowledge voids, that are tightly linked with the sustenance of soil fertility, sustainable agriculture, and human well-being [40]. However, studies on ARBC, especially those mediated through coupling of HMs remediation with enhancement in soil fertility and food crops yield are insufficiently elucidated in past studies [16]. Biochar production methods, pretreatment techniques, and biobased technology prospects are further grim in terms of limited explorations of designer ARBC, such as those manoeuvred by engineering or technological modifications with magnetic/nano-scale-particles (NPs) (Xiong et al., 2017; [6,39]). Moreover, sustenance of food security of rapidly expanding human population in limited arable land-uses necessitated the wise use of ARBC as BSS for agriculture and environment (Dhamodharan et al., 2020; Neogi et al., 2022).

Another limitation in previous studies on ARBC-mediated HMs remediation that the confined their quest mostly at laboratory scale [41]. Further, these lab-based assessments were restricted to the ARBC-driven remediation of single metal. On the contrary, at field-scale there can be co-existence of multi-metallic contamination of varying concentrations [41]. These coexisting HMs can compete for binding sites on ARBC, thereby resulting in lower adsorption, when compared to lab conditions. Additionally, varying soil physicobiochemical attributes such as presence of humic acid, allelochemicals or secondary metabolites and root exudates can further complicate ARBC-driven HMs remediation [41].

In light of the abovementioned insights on environmental challenges, present review aimed to elucidate the inadequately explored role of ARBC in HMs remediation from contaminated soil and 'food crops'. To unveil the role of ARBC in ameliorating HMs from soil-food crops interface, standard methodologies were adapted to present state-of-art-knowledge in food safety, soil health, and human well-being. Herein, judicial selection of keywords, search engines (e.g., Sciencedirect and Scopus), and articles uncovering the progress in the field, especially in past couple of decade is prioritized. The present review therefore offers state of art knowledge on ARBC as novel sustainable biochar, especially with no separate land requirements for raising the biomass [15]. Few studies explored the benefits of ARBC in context of food safety and human health, however, were rather scattered to provide holistic information to stakeholders and policy makers. For instance, applications of 10 % sewage sludge derived biochar reduced the rice based dietary consumption of HMs/metalloids (e.g., As, Cd, Co, Cu, Mn, Pb, and Zn) in the range of 22–68 % [42]. Further, it is noteworthy in this sense that about 62–74 % reduction in arsenic (As) derivatives i.e., As(III) As (V), and dimethyl arsenate, resulted in 66 % reduction in the 'incremental lifetime cancer value'. Notably, remarkable reduction in HMs and As ions can mitigate human health risks, as exemplified in ARBC-driven ameliorative healthcare in "Cancer Villages" of China [42]. Though this ARBC-driven HMs remediation was performed at field-scale, however, the findings of paddy fields belonging to highly contaminated soil-rice interface cannot be scalable for other food crops, especially those located in varying agricultural landscapes [43]. To this end, present article attempted to widely explore HMs remediation avenues at varying soil-food crop interfaces by sustainable production, techno-economic functionalization, and up-scaled ARBC utilization in agriculture systems.

The present review therefore attempts to fill the knowledge gaps by offering ARBC-induced HMs remediation. Another advantage of deploying ARBC-technology is to efficiently reuse and recycle, and hence aid in the sustainable management of globally generated agri-wastes biomass [44]. At the outset, the ARBC-production technologies, including the customized designer ones are critically presented. The sustainable ARBC-technology for HMs-remediation stands on the twin-pillars of physico-chemical and biological mechanisms. Therefore, elucidation of multitude of mechanisms associated with HMs-induced ARBC remediation is pragmatically discussed. The discussion further delves into socio-technoeconomic prospects of innovating and deploying designer-ARBC in leveraging the sustainable agriculture. Especially, a concise discussion is presented on the perspective of deploying magnetic and nano-ARBC to remediate HMs from the soil-food crop interface. The linkage of ARBC-applications as biobased technology with HMs remediation, agri-waste management, soil physico-chemical characteristics, sustainable agriculture, circular bioeconomy, climate action, UN-SDGs, and human health/well-being is critically analyzed to offer state-of-art knowledge. Last, the limitations in techno-economic analysis and "Life Cycle Assessment (LCA)" [21] and future prospects of ARBC as biobased technology is presented. These concluding remarks can be used by policy makers, agriculture scientists, biochar engineers, biomass researchers, farmers, environmentalists, global regulatory institutions, and media for public spotlight. In brief, the present article investigates ARBC's role in valorizing agricultural residues, reducing GHG emissions, remediate HMs from soil-food crops, ameliorate soil quality, together contributing to the attainment of UN-SDGs. Limitations of biochar technology are described in relation to secondary pollution, emanating from leaching of ARBC-impregnated HMs, and possible nanotoxicity by field-scale deployments of nano-biochars. Last, the future prospects are also explored, especially in relation to Artificial Intelligence domain using Machine learning tools to expand the horizon of ARBC-technology in HMs remediation from agriculture systems.

2. Pathways in agricultural waste-derived biochar production

2.1. Production techniques of agricultural waste-derived biochar

Pyrolysis is the process of heating or biomass valorization in temperature range of 300–700 °C under high atmospheric pressure in oxygen limited environment to produce ARBC [36,37,45]. In this respect, the biomass specific selection of ideal operating pyrolysis temperature is necessary for production of sustainable-ARBC to augment agro-ecosystem resilience under the event of HMs stress [37]. It is worth mentioning that the extreme temperature (600–700 °C) can result in production of deoxygenated acidic ARBC with less oxygenated acidic functional groups, high pH, high concentrations of carbonates or other basic cations, thereby adversely influencing the HMs immobilization from agriculture systems [37]. Conversely, the alkaline ARBC has rather well-organized C-layers with high degree of aromaticity.

In this respect, high pyrolysis temperature (600–900 °C) diminishes the number of acidic functional groups like -COOH, with concomitant rise in basic functional groups, and degree of aromaticity [46]. High-temperature pyrolysis can adversely influence the cation exchange and surface chemistry of ARBC due to increased aromaticity and hydrophobicity [47]. Nonetheless, ARBC produced from high-temperature pyrolysis of contaminated sludge and waste biomass can either stabilize HMs in carbonaceous solid char or else volatilize them to efficiently minimize their ecological risks [47,48]. Therefore, high pyrolysis temperature can enhance the safe use of ARBC in adsorption of HMs. However, secondary environmental pollution from volatilization of hazardous HMs/metalloids like Hg, Pb, and As and increased vulnerability towards ARBC-ageing are some limitations of high pyrolysis temperature [47,49]. These limitations is suggested to be addressed by integrations of 'metal organic framework' (MOF) with ARBC [48], however, warrant further research.

On the contrary, operation of moderate pyrolysis temperature (300–400 °C) can result in production of efficient ARBC-based HMs adsorbent with diversified aliphatic groups, cellulose fibers, and organic structures [45]. Another research focused on the pyrolysis of corncob-derived ARBC at different temperature revealed the highest Cd adsorption (85.65 mg g^{-1}) at 350 °C, which was actually mediated through the mechanisms of ion exchange and complexation [50]. Importantly, ARBC-physical activation during pyrolysis for increased HMs immobilization can be manifested through emerging techniques of microwaves, magnetic impregnation, steam, and carbon dioxide (CO_2) [51].

In several agri-residues such as rice husk and corncob, the adsorption of Cr(VI), Cd(II), Zn(II) was noted to be dependent on pyrolysis temperature, which was optimum at 600 °C [46]. In context of elemental (like C,H, O, N) composition of ARBC, 'gradient boosting regression model' can strengthen HMs adsorption studies [52]. The study of Shen et. (2024) revealed that (H-O-2N)/C and pH has profound impact on CEC, thereby play a vital role in HMs adsorption. The traditional wet pyrolysis methods for ARBC-production are energy intensive with involvement of high cost and power per tons of agri-waste to remove their high moisture content, therefore are not resilient in terms of climate change mitigation (Kung and Zhang, 2015; [53]). However, innovation of novel wet pyrolysis methods can result in *Miscanthus sacchariflora* (Maxim.) Hack. based surface functionalized- ARBC, with increased efficiency towards the Cd remediation [53]. Herein, the wet-pyrolysis induced the abundance of COO^- and OH^- functional groups, which resulted in 197mg/g^{-1} Cd adsorption with removal efficiency in the range of 99 % [53]. Ionic surfactants and organic solvents like methanol addition to ARBC can accelerate their HMs such as Cr remediation efficiency [54]. Together, these discussions on pyrolysis driven biobased technology explicitly indicated that in maintaining agricultural sustainability, the influence of pyrolysis conditions and choice of ARBC feedstock is of paramount relevance [37]. Nonetheless, pristine-ARBC have some limitations in extent of HMs remediation, which paved the way for designer-ARBC, with higher efficiencies.

2.2. Designer ARBC production methods

There are several synthetic production methods of designer-ARBC such as impregnation pyrolysis [55]. In this vein, biomass is impregnated into solutions containing transition metal salts that follow a cascade of methods in valorizing agri-waste. Herein, both pyrolysis and magnetization are completed in one step and are tightly controlled by operating parameters such as pyrolysis time, temperature, and inert gas [55]. Co-precipitation is another synthetic method wherein alkaline pH, ranging from 9 to 11, can result in better remediation of HMs, when compared with 'Impregnation Pyrolysis'. Another method i.e., reductive co-deposition is mostly similar to co-precipitation, with difference that there occurs the role of reducing agents (e.g., Sodium and Potassium Borohydride) for reduction of transition metals intercalated with-in biochar [55].

In ARBC-modification, there exist a plethora of approaches to result

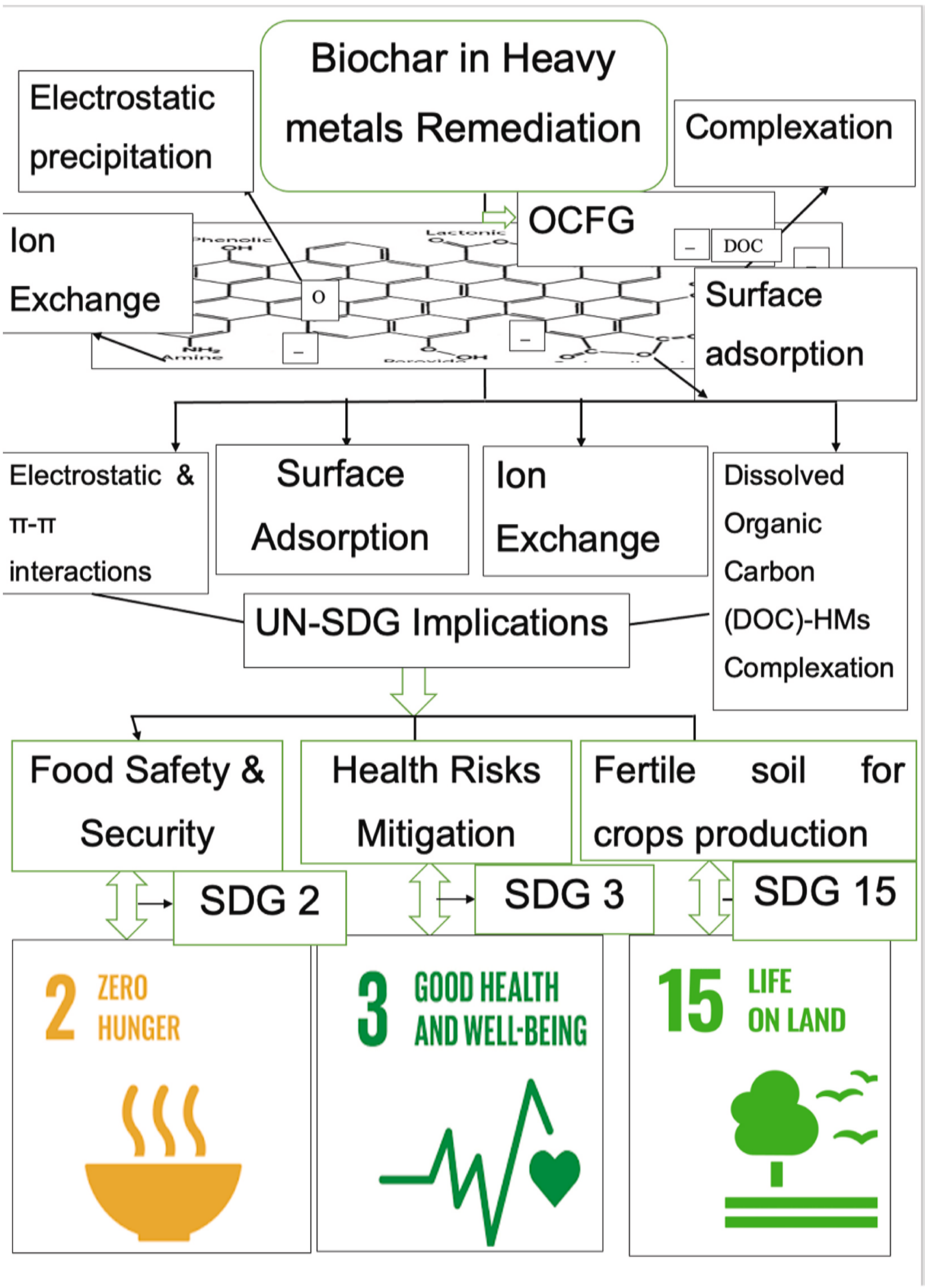

Fig. 2. Mechanisms of agricultural waste-derived biochar (ARBC) in heavy metals remediation and their inextricable linkage with attainment of United Nation (UN)-Sustainable Development Goals (SDGs).OCFG: Oxygen containing functional groups.

in designer biochar with potential HMs removal. Designer-biochar amended with chemicals like HNO_3 can enhance the Cu remediation through creation of more -COOH or other 'oxygen containing functional groups' (OCFG) [56]. Metal impregnated ARBC e.g., 'nano zero valent iron (nZVI) biochar' and 'iron-sulphide biochar' potentially enhance the adsorption capacity of HMs in agroecosystems [57]. Biochar-composites derived from 'Layered-Double-Hydroxides (LDHs)' can increase the HMs-adsorption potential in **a**groecosystems [3]. In this context, LDH based on anionic clay (e.g., hydratocalcite type), in combination with ARBC, resulted in formation of stacked positive layers which can enhance the contaminants' adsorption, though having low partial co-efficients [56]. Furthermore, 'LDH-ARBC-composites' are structurally unique in the sense that their mineral with metal hydroxide layers are positively charged to remove anionic metal contaminants, while the interlayer space consists of anions, which can potentially bind with cationic metal fractions of agroecosystem soil [3,58,59]. However, LDH-ARBC-composites are faced with scalability challenges, as they are pH-sensitive, less stable, with limited regeneration or reusability [60]. Further, at low pH, LDH layers can leach out HMs from ARBC to ambient soil, thereby causing secondary environmental pollution [60].

Nano-ARBC such as wheat straw and rice husk is prepared by mechanical milling, grinding, and sieving with separation when suspended in water/ethanol and eventually exfoliation into a useable form for agriculture systems [61,62]. Chemical modification of ARBC through amination, surface oxidation, sulfonation, microwave treatment, and tailoring with NPs can enhance the ARBC-HMs remediation potential [47]. Separation of ARBC from environmental matrices is difficult and may also cause secondary pollution, which may limit the biochar potential in HMs remediation [63]. Nonetheless, designer-ARBC can address limitations of pristine-ARBC, in view of specificity in their mode of action. The techno-economic innovations in designer ARBC can effectively remediate HMs from contaminated soil and food crops to ensure food safety and public health risks mitigation. In brief, designer biobased technology can effectively catalyze circular bioeconomy and UN-SDGs [23].

3. Mechanism of biochar-driven HMs remediation at soil-food crop interface

Applications of ARBC potentially remediate HMs from soil-food crop interface through multiple mechanisms, though elucidation of explicit mechanism is rather complicated. Therefore, this section delves into the underlying mechanisms associated with ARBC driven HMs remediation from soil and food crops (Fig. 2). Fig. 2 elucidates the intrinsic biochar properties and HMs adsorption mechanisms of ARBC to ameliorate soil health, augment food safety, and human health that align with several UN-SDGs. Remediation of HMs on ARBC surface is facilitated mainly by adsorption, which is guided by multiple chemical interactions [64]. For instance, complexation with oxygenated functional groups and electron-rich domains on graphene-like structures can facilitate Cd adsorption [41].

The ARBC-induced HMs removal mechanisms such as CEC and precipitation can be element (e.g., Cd and Pb)-specific [41]. In this vein, carbonate and phosphate in ARBC can guide precipitation, which was suggested as the main mechanism for biomass driven Cd adsorption. Conversely, Cr and Hg adsorption is ascribed to complexation and reduction mechanisms, while complexation in concert with electrostatic interaction can facilitate As-adsorption [41]. Low pyrolysis temperature enrich ARBC surface function groups, that lead to complexation and electrostatic precipitation of As in agroecosystem soil [41]. In this sense, ARBC-mediated Cr adsorption can be driven by complexation, cation exchange, and electrostatic precipitation. Further, Mohan et al. [65] that ARBC-induced Pb adsorption is mainly ascribed to cation exchange with Ca and Mg followed by minor role of complexation, and precipitation. In this sense, Hg adsorption is facilitated by complexation with carboxylic, phenolic, and hydroxyl functional groups [41].

Agri-waste biochar-induced increase in pH facilitate the appearance of negative charges on ARBC through deprotonation of functional groups like -COOH, which can effectively adsorb positively charged HMs on biochar surface [41]. Electrostatic interactions operate between HMs and ARBC-surface while HMs precipitation driven by phosphate and carbonate ion to form insoluble compound [41]. In this sense cation exchange between HMs and ARBC-surfaced protons like Ca^{2+}. Mg^{2+}, and Na^{+} or alkaline metals. Surface metal complexation is the major As-remediation mechanism with functional groups and π electron rich domain on the aromatic structure of biochar [41] (Fig. 2).

Applications of ARBC induced increase in the HMs immobilization is not only attributed to the modulated pH, soil attributes, and surface functionalities, but also to the abundance of fixed-C and mineral constituents (Yang et al., 2019; [38,66,67]). Thermodynamically, HMs remediation through ARBC is favourable in endothermic reactions. In physical sorption, $\Delta G_0 = -20$ kJ/mol was estimated, while it was noted in the range -400 to -80 kJ/mol in case of chemical sorption [36]. Immobilization of HMs is guided through surface adsorption, OCFG, and cation exchange. HMs cation exchange reactions are dependent on the aforesaid OCFG present on ARBC surface and size of HMs contaminants [36]. Also, mineral contents with-in ARBC can facilitate the precipitation of HMs [45]. In ARBC, surface complexation is considered to be main binding mechanism for HMs removal [64]. Further, in surface complexation, HMs have high affinity for ligands e.g., carboxylic, phenolic, and lactonic, present on ARBC surface, which eventually facilitate their effective immobilization. Also, presence of hydroxyl (OH-) and carboxyl (COO-) as OCFG enhance HMs adsorption potential of ARBC [36]. Similarly, presence of OCFG can reduce the concentrations of hazardous Cr(VI) by converting into relatively less toxic Cr(III) [68]. In this sense, the increase in HMs remediation due to surface oxidation of ARBC is therefore ascribed to enhanced production of OCFG. Also, precipitation mechanism of ARBC removes HMs due to sorption in aqueous phase and subsequent formation of complexes [64, 69].

The soil redox potential is closely related to the chemical forms of HMs in soil [70]. Notably, Wang et al. [70] opined that when the soil redox potential changes, the ARBC-immobilization effectiveness can be significantly reduced, and even the environmental risk of HMs release may be increased. Therefore, the redox potential of HMs/metalloids can remarkably influence the mechanism of adsorption e.g., As with a lower redox potential (As^{3+} and $As^{5+)}$ have higher mobility in soils, than Cr (Cr^{6+} and Cr^{3+}) [71]. In this vein, ARBC with anionic charges can tightly bind with cationic components (e.g., Pb^{2+} and Cd^{2+}) while cationic components can effectively adjoin with anionic metallic components (Gupta et al., 2021). For instance, active oxygenated surface functionalities/moieties on ARBC can convert Cr^{6+} to Cr^{3+}, a relatively less mobile form, therefore mitigating the HMs-induced phyto-toxicity in food crops [72]. Therefore, the ARBC applications in HMs contaminated soil can induce polar functional groups (i.e., amine (NH_2), phenolic (-OH), and carboxyl group (-COOH clusters) which can result in chelation of HMs, resulting in reduced toxicity at soil-food crop interface [73]. Technological innovations in instrumentation or analytical techniques (e.g., 'scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infra-red (FTIR) and X-ray diffraction (XRD) analysis') further confirmed and validated the HMs sorption potential of ARBC ([74]; Neogi et al., 2022).

The oxygen rich-ARBC derived from torrefaction offered effective HMs removal from agricultural wastewater through multiple thermodynamics and sorption mechanisms [6,75]. In this vein, Cr(VI) remediation was attributed to the 'adsorption-coupled reduction mechanism' while surface complexation was ascribed to the Cu(II) removal [75,76]. Further, Pb remediation from contaminated soil was is also augmented by 'urease(enzyme)-induced calcium carbonate precipitation' in conjunction with deploying 5 wt% optimum ARBC-dose, together facilitating Pb^{2+} remediation up-to 98.41 % [77]. In this respect, Bai et al. [77] observed that this ARBC-complex increased the soil pH, consequently, converting free Pb ions to insoluble $Pb(OH)_2$, thus, enhancing its immobilization in agroecosystem soil. Concomitantly, ARBC-complex offered more nucleation sites for urease and porous sites which effectively enhanced the Pb(II) adsorption from contaminated agroecosystem soil [77]. Together, these ARBC-driven HMs immobilization mechanisms act in concert to restrict the their transfer to food crops.

Microbe-assisted immobilization of HMs is in fact guided with electrostatic interactions, van der Waals forces, exopolysaccharides, glycoproteins, high nucleotide e.g., Guanine-Cytosine (G:C) contents, and HMs binding protein i.e., metallothioneins [68]. It is widely perceived that microbial diversity associated with ARBC favourably modulate soil physico-chemical attributes which can enhance remediation potential of HMs/metalloids. For instance, *Bambusa vulgaris* Schrad. ex J.C. Wendl. biomass derived-ARBC was found to be rich in O_2-releasing specimen which can effectively augment the soil remediation process [78].

A plethora of chemical mechanisms in conjugation with activation of microorganisms can potentially reduce Cd transfer in edible part of food grains (Ullah et al., 2024). In this vein, hazardous metalloid i.e., As found to be less mobile in ARBC-conditioned acidic soils, due to its increased adsorption process on iron oxides (Gong et al., 2018). Herein, Fe-modified ARBC offers high SSA and abundant -OH groups that facilitate As adsorption, by forming strong inner-sphere complexes. Therefore, it is crystal clear that soil chemistry, including its elemental or metal-oxides composition, can remarkably influence the efficiency of ARBC in ameliorating HMs remediation from agriculture systems. Also, an indirect mechanism demonstrated that ARBC-associated microbial diversity result in calcite precipitation which can potentially co-precipitate Pb^{2+}, Cu^{2+}, and Cd^{2+}, which in turn get embedded inside the calcite particles [79]. Similarly, ARBC-application was also observed to phytostabilize HMs/metalloids in *Miscanthus* sp. [80]. In this respect, alkaline nature ARBC can mobilize-As better in case of *Miscanthus* thriving contaminated soil when compared with the acidic soil, already modulated with hardwood biomass [81]. Henceforth, the nature of ARBC can also influence the HMs removal from soil and food crops. The secondary metabolites present in ARBC-soil-crop interface can play a vital role in HMs adsorption in agriculture systems [65]. For instance, oak bark contains polyphenolic tannins, flavonoids, and suberin, offering more COO^- and OH^-, facilitating effective binding of Pb [65]. Similarly, in sugar beet tailings and switchgrass, such HMs binding functional groups are derived from complex heteropolysaccharides such as Arabinose, Galacturonic acid, Galactose, and Pectin substances [68,82,83]. As introduced earlier, the HMs/As-induced generation of ROS/RNS can perturb normal cellular metabolism of food crops such as modulation of antioxidant responses. In this vein, antioxidant enzyme activities e.g., 'Glutathione (GSH), Catalase (CAT), Superoxide dismutase (SOD), Ascorbate peroxidase (APX) and peroxidase (POX)', and lipid peroxidation guided through elevated 'malonaldehyde (MDA)' levels is usually increased [84]. Together, these enzyme-driven antioxidant responses combat the HMs-induced oxidative stress in food crops to enhance health safety. Also, decreased cell membrane integrity and electrolytic leakage, Fenton Reaction driven DNA strand breakage, and disruption of genetic material in food crops are other effects of HMs-induced phytotoxicity in food crops [8,84,85]

Agri-residues such as phosphoric-acid pre-treated banana-peel ARBC-mediated HMs adsorption studies are in fact quite complex and 'machine-learning (ML)' in concert with 'deep learning' are being applied for better unravelling of associated remediation mechanisms [86]. In this respect, Jaffari et al. [86] revealed the outcome of FTIR models to unveil the role of factors in conversion of ARBC, which was noted in decreasing order i.e., adsorption conditions (72.12 %) > pyrolysis conditions (25.73 %) > elemental composition (1.39 %) > biochar's physical properties (0.73 %). Therefore, HMs removal is strongly influenced multiple physico-chemical and biological mechanisms, which need to be explicitly elucidated in soil and food crops for environmental sustainability and human well-being.

4. Factors influencing biochar-induced HMs remediation in agroecosystems

Heavy metals adsorption potential of ARBC from agroecosystem depends upon the nature of biomass, high ash content, carbonaceous residues, hetero-carbons, and pyrolysis temperature ([87]; Hasnain et al., 2023). Further, interactions of biotic and abiotic factors with ARBC-amendments or feedstock conditions can influence the effectiveness in HMs remediation from agriculture systems (Hasnain et al., 2023).

In ARBC-production, the selection of biomass as feedstock determines it stability in agroecosystem soil, to act as 'long-term C-reservoir' [88]. Another aspect of paramount relevance is ARBC-application dose, which is very crucial for HMs immobilization and hence imparting optimum effects on staple food crops productivity. For example, 4 % dose of pig biochar can inhibit seed germination of *Brassica chinensis* L. while a lower application dose of 2 % resulted in increased Cd-immobilization [89]. Herein, Chen et al. [89] observed that higher pig-ARBC application doses can result in accumulation of phytotoxic compounds, with drastic shift in pH towards higher side, that can perturb seed germination of *B. chinensis*. Conversely, lower dosage of pig-ARBC promote growth and germination of this food crop by ameliorating soil quality and Cd-immobilization. In this sense, another eleven months treatment study of 4 % ARBC resulted in Cd stabilization, which potentially reduced its concentrations in soil by 67 %, which was quite higher than peat biomass amendment (Van Poucke et al., 2018). Also, alleviation of Pb and Zn-induced phyto-toxicity, mediated through the application of peanut shell-ARBC in the acidic paddy soil was found to be HM-specific (Chao et al., 2018). Moreover, Chao et al. (2018) noted that it was dependent on dose or ARBC-application rate of biochar, wherein 5 % dose was noted as most effective or optimum dose. Further, 'Soil Organic Carbon (SOC)' content can significantly influence the Cd immobilization in *B. chinensis* planted agroecosystems [89].

Residence time influence SSA and pore diameter of ARBC to influence the extent of carbonization, surface OCFG, pore distribution, and mineral concentrations [90]. Importantly, ageing of ARBC can reduce its HMs sorption capacity [91], however, the contrasting reports also exist [49]. To address the ARBC-ageing, intermittent addition of fresh ARBC is required for optimum nutrient cycling in agroecosystems [92]. In this respect, addition of 7 tones/ha bamboo ARBC increased the weed biomass by 65 % and 80 % in 1st and 2nd year, respectively [92,93]. In this vein, aged ARBC showed increased Cd remediation (i.e., ranging from 44-68 % to 59–73 %) than pre-aged ARBC, ascribed to decrease in pH (8.2–10.7 to 7.5–9.7) and induced surface complexation with more numbers of OCFG [93].

Production or pyrolysis temperature of ARBC can also impact the HMs remediation from contaminated agroecosystems [15]. For instance, wheat straw-ARBC produced at low temperature demonstrated higher Zn(II) and Cd(II) immobilization than those produced at higher temperature [94]. Whereas, in the alkaline soil, wheat straw-ARBC produced at high temperature were more effective than those produced at low temperature [94]. Therefore, feedstock type and selection of pyrolysis conditions such as purging gas can remarkably influence the HMs remediation [15]. This was demonstrated in case of 'pulp mill sludge + rice straw-based' ARBC with N_2 and CO_2 being the purging gas for remediation of Pb, Ni, Cd, and Cu [64]. In this vein, Langmuir adsorption model based derivations of Islam et al. [64] revealed the decreasing order of HMs removal as Pb(II) (109.9–256.4 mg g^{-1}) > Ni(II) (40.2–64.1 mg g^{-1}) > Cd(II) (29.5–42.7 mg g^{-1}) > Cu(II) (18.5–39.4 mg g^{-1}) when N_2 was used as the purging gas, which was rather different when compared with CO_2. However, in this study, between both purging gases, N_2 acted as "inert purging gas" (i.e., due to stable triple bond), which was more effective in Pb adsorption for both pulp mill sludge-ARBC and rice straw-ARBC [64]. Whereas, CO_2 may act as "smart purging gas" or activation agent that is effective in enhancing case-specific HMs adsorption [64]. This may be attributed to the fact that CO_2 purging gas can increase the SSA and enhance the ARBC-surface porosity, thereby possess the potential to increase specific HMs adsorption from soil-food crop interface.

Activation of ARBC with physico-chemical factors enhance its SSA, density, and porosity with increase in pyrolysis temperature [95]. In this vein, the yield of rice straw-ARBC was noted higher, when compared with wheat-residues [96]. In this vein, better liming effect, higher ash and silica content, and increased porosity of rice straw-ARBC can result in better HMs remediation for higher food crop yield [97]. Slow pyrolysis with longer retention time produces ARBC with higher average particle size and volatile materials which facilitate formation of pores, increase the pore volume, pore size distribution, and SSA [96]. Together, these factors influence the efficiency of ARBC in HMs decontamination of staple food crops for sustainable agriculture.

Physico-chemical and biological modifications of pristine-ARBC can result in designer ARBC, with increased efficiencies [6]. Designer or engineered-ARBC demonstrated superior efficiency than pristine ones, which was mediated through increase the surface properties and adsorption capacity of HMs [47]. Further, ARBC-functionalization can increase the soil microbial activity and decrease the bioavailability of HMs such as Pb, Zn, and Cd, attributed to increased number of surface OCFG [98].The field of designer-ARBC is unequivocally vital in enhancing the efficiency of HMs remediation, therefore, discussed critically in next section.

5. Designer biochar based heavy metals remediation in agriculture systems

5.1. *Designer ARBC: efficient biobased technology in HMs remediation*

Biomass-waste derived raw or pristine biochar though useful, however, techno-economic innovations, further improvements and modifications to result in designer ARBC [6,56]. These customizations are required to enhance biochar's persistence, novel structural modulations,

Table 1
Designer/engineered Agricultural waste-derived Biochar (ARBC) in Heavy metals/metalloids remediation at agroecosystem soil-food crop interface from agriculture systems.

S. No.	Agri-residues feedstock for biochar; operating pyrolysis temperature	Modification/activation method of agri-residue based biochar/nano-biochar	Target HMs	Extent and efficiency of remediation	Mechanism	References
1.	Sugarcane Bagasse/ Chip; 600 °C	CNTs modified biochar	Pb	Highest efficiency among other adsorbents	CNTs modified agri-residues biochar demonstrated high SSA, pore volume, & thermal stability	Inyang et al. [99]; Rajapaksha et al. [45]
2.	Red oak; Switchgrass; 600 °C	Magnetite	As (III)	Maximum adsorption for As is 15.66 mg g^{-1}	The Fe present in the magnetite facilitated the binding of As (III); pseudo 2nd order was best fit and Langmiuir model demonstrated better adsorption potential of As	Bakshi et al. [100]; Wang et al. [47]
3.	Peanut hull; 600 °C	H_2O_2	Pb, Cu, Ni, & Cd	Engineered biochar enhanced Pb remediation from 0.88 to 22.82 mg g^{-1},equivalent to commercial-scale activated C	Increased abundance of Oxygenated-functional groups (especially-COOH) on hydrochar surfaces	Xue et al. [101]
4.	Sugarcane leaf; 550 °C	Nano-size MgO flakes	As & Pb	57 mg A^5 $^+$/g 103 mg Pb^2 $^+$/g	As and Pb remediation through nanotube like carbon sponge formation and enriched OCGG	Li et al. [102]
5.	Rice, peanut & soyabean Straw; 750 °C	Al-modified	As (III)	Increased adsorption by Al(III) from 445 to 667 mmol kg^{-1}	Inner-sphere As(III) complexes with Al hydroxides on increased biochar surface	Qian et al. [103]
6.	Saw dust; 500 °C	Amino-modified	Cu	Engineered biochar enhanced Cu remediation	Engineered biochar with amino (-NH_2) can better complex with Cu with high stability constants for HMs- NH_2 complexes	Yang and Jiang [104]
7.	Bamboo; 600 °C	nZVI nZVI + HNO_3 nZVI + H_2O_2	As (V) & Ag^+	109.1 mg As^{5+}/g; 1217 mg Ag^+/g	Reduced surface free energy and HNO_3 & H_2O_2 driven decrease in reactivity of nZVI	Wang et al. [105]; Wang et al. [47]
8.	Rice husk; 450–500 °C	Polyethylenimine-modified	Cr	Designer-ARBC noted highest adsorption potential (435.7 mg g^{-1}) than raw/pristine biochar (23.09 mg g^{-})	Amino (-NH_2) moiety enhance chemical reduction of Cr to increase its adsorption	Ma et al. [106]
9.	Cornstalk; 500 °C	nZVI + HCl	Cr (VI)	Highest adsorption of Cr (VI) 35.29 %	Nano/engineered biochar facilitated more adsorption of Cr (VI) than pristine biochar	Dong et al. [107]; Wang et al. [47]
10.	Bamboo, sugarcane bagasse, hickory wood, and peanut hull; 600 °C	Chitosan-modified biochars	Pb, Cu, Cd	Increased remediation of three HMs	Effective HMs-chitosan binding resulting in increased adsorption of Pb, Cu, and Cd	Zhou et al. [108]
11.	Oak wood and oak bar; 400–450 °C	Magnetic biochar	Cd and Pb	Increased adsorption of Cd and Pb	Magnetic biochar induced enhanced binding of HMs	Mohan et al. [109]
12.	Rice husk and fruit residues; 450–500 °C	Fe(III) impregnated biochar	As (III) & As (V)	Increased adsorption of hazardous As	Tight interaction of As ions with FeOH and $FeOH_2^-$	Samsuri et al. [43]
13.	Rice hull; 450 °C	ZnS nanocrystals (NCs)	Pb(II)	Maximum adsorption: 367.65 mg g^{-1}	Better magnetic separation & 10 folds higher Pb adsorption than traditionally produced magnetic biochar	Han et al. (2016)
14.	Hickory chips; 600 °C	Fe(III) impregnated biochar	As	Higher adsorption potential of 2.16 mg g^{-1} than raw/ unmodified biochar	Fe(III) impregnated biochar induced chemisorption of As	Hu et al. [110]
15.	Pinewood; 600 °C	Magnetic biochar	Pb(II) & 696 mg/ kg	Increased As remediation than pristine biochar	Magnetic particles i.e., γ-Fe_2O_3 particles potentially acted as adsorption sites for As (III)	Wang et al. [111]

application-oriented outcomes like HMs immobilization efficacy, engineered functionality, and remediation potential [45,56]. In relation to agri-wastes also, pristine-ARBC are less effective in soil HMs remediation, ameliorating soil-food crops health, and augmenting sustainable agriculture, when compared with designer/engineered biochar [6]. Therefore, technological advancements in terms of pre-treatment and production pathways (i.e., chemical, physical, impregnation, magnetic, and nano-scale approaches can remarkably increase the engineered functionalities of ARBC for enhanced applicability in HMs remediation from polluted agroecosystems [45]. Especially, magnetic and nono-chars are quite effective in terms of improving ARBC-engineered functionalities, associated physico-chemical characteristic, especially in terms of structural configurations and surface chemistry for enhanced HMs-sorption potential from soil and food crops. In this sense [63]. ARBC-induced HMs adsorption can be manoeuvred by engineering or technological modifications such as carboxylation, amination, and magnetization to potentially leverage their high-end application fields (Xiong et al., 2017). Customized or designer-ARBC can better adsorb HMs than pristine or raw biochar, ascribed to improved surface chemistry i.e., pH, CEC, OCFG, and high SSA [6,63]. Indeed, techno-economic innovations in designer-ARBC production are envisioned to help achieve maximum HMs remediation for food safety, soil health, and sustainable agriculture [45] (Table 1).

Application of chemically amended-ARBC with hydroxyapatite and zeolite in paddy fields increased Cd and As-immobilization [112]. Herein, the increased Cd and As adsorption was ascribed to covalent

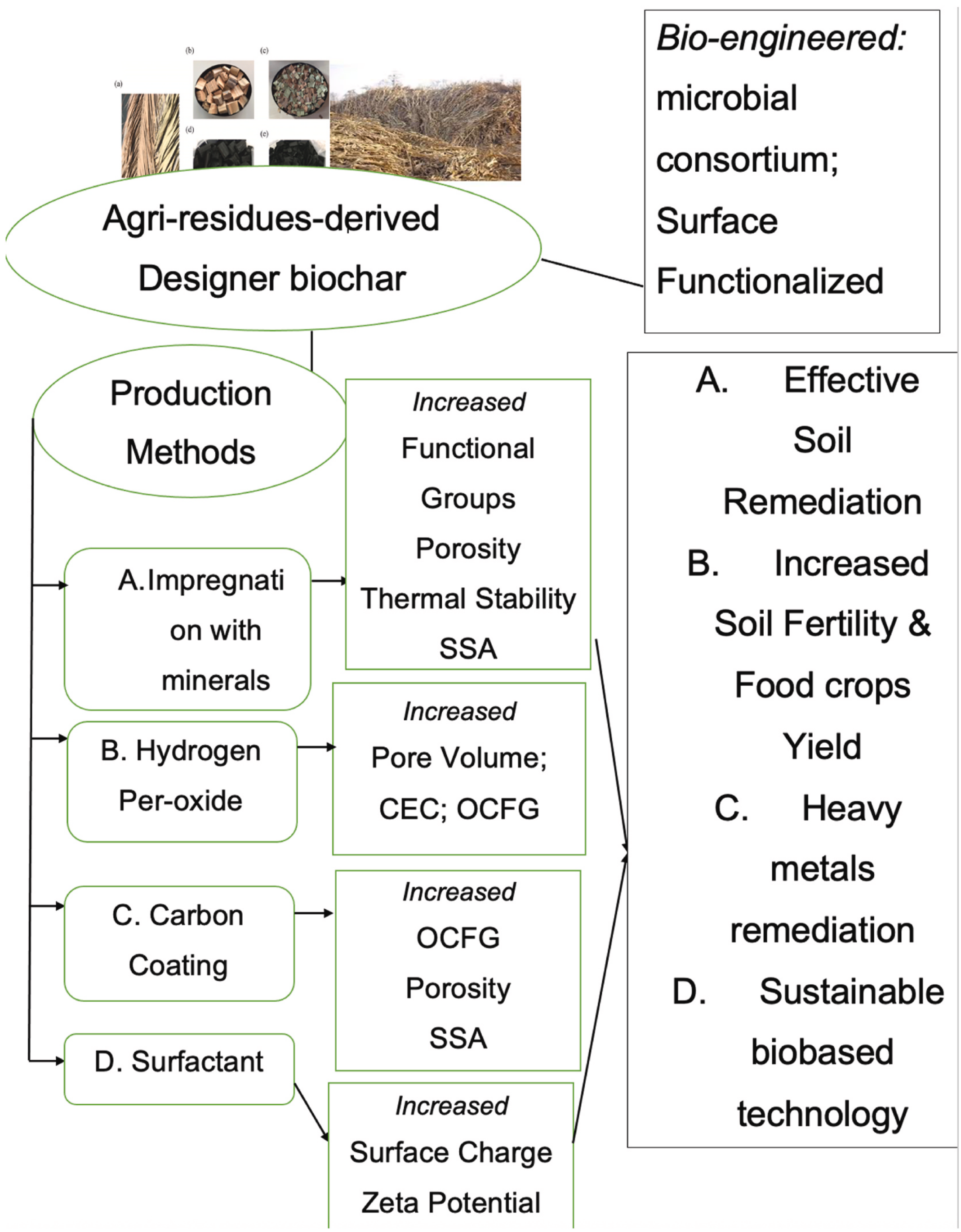

Fig. 3. Designer/engineered Biochar with higher efficiencies for heavy metals remediation in agriculture systems (agroecosystem soil-food crops interface): Customization of crop/tree residues for manoeuvring of agricultural waste-derived biochar (ARBC). OCFG: Oxygen containing functional groups.

HMs binding with surface OCFG like -OH, -COOH, -*Si*-O-Si, and CO_3^{2-} to produce carboxylates, silicates, and carbonates-HMs complex to facilitate 'As-Cd duo' immobilization in paddy fields [112]. Further, compost amended-ARBC though activated As, and Cu but effectively decreased the Cd and Zn (Wang et al., 2020). The interaction of rice straw-ARBC with metal oxides such as γ-Al_2O_3 can remarkably influence the immobilization of Zn in contaminated soils [113]. In this respect, Al released from γ-Al_2O_3 was adsorbed along with Zn on ARBC surface to form Zn-Al silicate, in place of Zn-Al LDH on the γ-Al2O3 surface [113].

The modified-ARBC can also favourably modulate the growth, development, and physiology of food crops in agriculture systems. In addition to Cd remediation, S-Fe biochar also increased rice growth and chlorophyll content, thereby augmenting the rice productivity with concomitant mitigation of human health risks [114]. In this vein, amendment of agroecosystem soil with 5 % cornstalk-ARBC increased the root dry weight of *Beta vulgaris* L. by 267 %, while Cd-bio-accumulation was increased to 206 %, and the Cd concentration in leaves and roots increased by 36 % and 52 %, respectively [115]. Though the maize-based biochar remediated soil or organic-bound Cd through bio-accumulation in *B. vulgaris*, however, its dietary intake should not be allowed near experimental sites to abate human health risks. The production pathways of designer biochar that upgrade the ARBC-physico-chemical attributes to facilitate HMs remediation and enhance soil-food crops health are shown in Fig. 3.

5.2. Studies on designer ARBC for HMs remediation: magnetic and nano-engineered

Several studies confirmed the superior efficiency of designer-ARBC in HMs remediation than pristine or raw biochars. For instance, coconut shell-ARBC, when physico-chemically modified with diluted HCl and ultrasonication, was found to be more efficient in HMs remediation (Cd (increase by 30.1 %), Ni (57.2 %), and Zn (12.7 %)) [116]. Further, coconut shell-ARBC also significantly contributed to soil biological activities by increasing maximum bacterial number by 149.43 % [116]. Biochar composites or designer-ARBC improves the surface functionalities, which enhance the adsorption potential of HMs, however, a concomitant decrease in porosity is observed through leakage of pores [56]. Importantly, tailored-ARBC derived from microwave-assisted catalytic pyrolysis supplemented with K_3PO_4 have high CEC, which significantly decrease the bioavailability of HMs [117]. Herein, Mohamed et al. [117] recorded customization of designer ARBC resulted in extraction of Pb by 408 mg/kg, Ni 15 mg/kg, and Co 148 mg/kg). In this respect, ARBC by decreasing HMs availability can increase the nutrients availability in agroecosystem soil, food crops growth, and productivity [117].

5.2.1. Magnetic ARBC

Another important facet of designer-ARBC is magnetic biochar, demonstrating a remarkable role in remediation of HMs contaminated soils in agriculture systems [63,118]. Magnetic fabrication methods of biochar address the limitations imposed by separation and recovery problems faced with deployment of non-magnetic HM sorbents [119]. In this sense, 'Fe-enriched activated-ARBC' was observed to be effective in reducing Pb and Sb leaching, especially in low TOC soil [118]. Crop residues based magnetic-ARBC undergoing alkaline (i.e., NaOH) pre-treatment, effectively destroyed lignocellulosic structure and hence facilitated the impregnation of Fe and P to potentially increase the SSA and porous structure [120]. For instance, NaOH pre-treatment followed by Fe-Co composite and H_3PO_4 acid increased the Pb^{2+} and Cd^{2+} adsorption capacities of cotton straw-ARBC, however, rice straw-ARBC was recorded with relatively higher HM remediation potential [120]. Also, magnetic-ARBC is derived from the operational magnetic field, with supplementations of Fe oxides such as Fe(O), γ-Fe_2O_3, Fe_3O_4, and $CaFe_2O_4$, that can remarkably increase the HMs remediation potential [55].

Magnetization process can transform ARBC into magnetic materials. Magnetic-ARBC can address the constrain of separation in powdered biochar and also restrict the secondary pollution emanating from their long-term use [63]. In this vein, 'magnetic (Fe_3O_4) biochar -microbe--biochemical composite' demonstrated to enhance the Cd (II) remediation which was 230 % higher than raw or pristine ARBC. Herein, the -NH_2 and -OH functional groups linked with *Bacillus* sp. K1 enhanced removal efficiency of Cd(II) (25.04 mg g^{-1}) and As(III) (4.58 mg g^{-1}), ascribed to coupled effects of competitive binding and synergy. Moreover, magnetic ARBC has more OCFG, high selectivity for contaminants, and increased separation and reuse efficiency [55].

Magnetic biochar resulting from wet fast pyrolysis of magnetite (Fe_3O_4) precipitating on Douglas fir-ARBC was observed to effectively remediate Pb and Cr in a more cost-effective way [121]. Herein, Fe_3O_4 modified Douglas fir-ARBC was observed to more effective biobased technology for HMs removal, when compared with traditional adsorbents like activated-C. Further, magnetic poultry litter-ARBC was noted to be more effective in Cd, Pb and Zn remediation that further restricted their leaching to increase the paddy crop yield, when compared with the eucalyptus-ARBC [122]. In HMs remediation from soil-food crop interface, the designer-ARBC, especially those derived from impregnation of magnetic particles can be more effective than pristine biochars. In this sense, Fe-modified magnetic-ARBC resulted in synchronized removal of As, Cd, and Pb. The contamination of agroecosystem soil with Antimony (Sb), a metalloid categorized as priority pollutant can be immobilized by wheat straw-based-ARBC, mediated through increase in microbial activity [123]. Thus, techno-economic innovations of magnetic-ARBC are promising field to decontaminate HMs at soil-food crop interface and accelerate the efforts towards achieving human well-being, sustainable agriculture, and UN-SDGs.

5.2.2. Nano-ARBC in HMs remediation of staple food crops

Agricultural waste-derived biochar, modified with NPs can unequivocally enhance the HMs-removal from soil-food crop interface (Table 1). For instance, the amendment of biochar with TiO_2NPs was demonstrated to increase the Sb remediation from soil- *Sorghum bicolor* (L.) Moench interface and also enhanced chlorophyll contents of the food crop [124]. In this study, Zand et al. [124] observed that combined application of ARBC and TiO_2 NPs enhanced the remediation of Sb from agroecosystem soil, which was allocated for raising raising *S. bicolor* [124]. Another study observed that wheat straw-nano-ARBC increased the immobilization of Pb, Cd and Cr, with concomitant improvement in the growth of maize seedlings [125].

Nano-ARBC can effectively reduce the levels of extremely health hazardous HMs such as Hg which has demonstrated propensity towards the microbes-induced process of biomethylation [47]. In this vein, 0.5 % *w/w* biochar amendment decreased Methyl-Hg levels by in edible brown rice grains by 82–87 %. [47]. Further, during co-application of Se and ARBC, Se was crucial in decreasing net MeHg production in rice grains, while ARBC reduced its bioavailability in the soil which can be attributed to presence of organosulfur compounds [47]. In another case, dose of 2.5 % rice-straw nano-ARBC with 1.2 % lime reduced the concentration of Pb by 84.33 %, increased rice yield by 53.38 %, and decreased the translocation of Pb in brown rice plants [126].

The incorporation of NPs in engineered-ARBC can also such as graphene and nano zero-valent iron (nZVI) decreased Cu-content in the range of 65 % [127]. Co-application of nZVI and ARBC with mass ratio of 1:1 was considered to be optimum in stabilizing Cr (VI) up-to the extent of 100 % Cr (total) by 92.9 % in field soil conditions (Su et al., 2019). Likewise, Cr, Cd remediation was also observed to increase three times, when nano-ARBC was coupled with ZVI/nano a-hydroxyl iron oxide through effective complexation, mediated by Fe(III) induced increase in the OCFG [128].

Biochar modified with Fe-phosphate-NPs and sodium carboxymethyl-cellulose enhanced the Cd-immobilization efficiency in soil (by 81.3 %), crop-belowground (44.8 %) and aboveground parts

(70.2 %) of cabbage-mustard farmland [129]. Thus, nano-ARBC can increase the soil fertility, growth, and development of single and multiple crop systems after the HMs remediation in an eco-sustainable way. In this sense, nano-hydroxyapatite amended ARBC also remediated Pb contaminated soil to restore fertility, thereby minimizing its transfer to plants by 31.4 %, attributed to decreasing the bio-available HM fraction [130]. Nano-ARBC derived from chitosan and zerovalent Fe(ZVI) on amendment with poultry manure resulted in Cr(VI) reduction by 45 % reduction, which was in fact 55 % higher than the traditional manures [131]. Therefore, nano-ARBC can potentially reduce Cr(VI) into relatively less toxic Cr(III) in agroecosystem soil, thereby restricting its transfer to staple food crops [131].

Surface modified ARBC application with Fe (III), and activated-C to maize-soil interface increased maize height by 20 %–59 %, alleviated Cr stress, increased Cr(VI) removal by 72.9 %–96.34 %, enhanced nitrification and denitrification, and facilitated NO_3-N transfer from roots to shoots [128]. On the contrary, nano-ARBC modified with nZVI resulted in phytotoxic effects to maize, as it significantly decreased maize height by 65 % [128]. Nanotoxicity of nZVI in maize can be attributed to overaccumulation of ROS that may cause oxidative stress in food crops [8]. Co-application of Silicon oxide (SiO_2)-rich-ARBC with Fe-based-NPs such as nZVI increased the Cr(VI) removal potential, mediated through the mechanism of reduction and co-precipitation [132]. Another study noted that 8 g of surface modified-ARBC on impregnation with nZVI completely immobilized Cr(VI) (i.e., up-to the extent of 100 %), while total-Cr was reduced by 91.94 % (Su et al., 2016). This nano-ARBC eventually found to raise the productivity of food crops. In this sense, Su et al. (2016) noted that Cr was successfully converted to Fe-Mn oxides and organic matter and the extrapolation of this experiment increased the growth of cabbage-mustard plot, along-with positive influence of ARBC-nZVI on soil fertility. Nano-ARBC can also enhance the rice crop productivity, however, need to be adequately monitored for environmental implications on long-term use to mitigate chances of nano-toxicity in agriculture systems [133]. Also, nano-ARBC resulting from amendment of nano-hydroxyapatite increased the immobilization rate of Pb in the soil by 74.8 %, thereby reducing its bioavailability in soil [130].

Nano-ARBC impregnated with sulphur and Fe decreased the exchangeable Cd in paddy fields by 29.71 %, 18.53 %, respectively, along-with imparting favourable effects on microbial diversity [113]. Further, Hua et al. [123] also observed that the co-application of nano-ARBC can induce Sb-oxidation genes. Further, in perspective of nano-ARBC, sulphur-modification of rice husk-based biochar increased its Hg^{2+} adsorptive capacity by ~73 %, thereby facilitating the green HMs remediation approach [134]. Also, 'S-biochar' along with the 'S-Fe biochar', effectively reduced bioavailable-Cd at soil-rice crop interface by increasing pH to potentially reduce the Cd accumulation in brown rice mediated by increased formation of Fe-plaque [114]. Herein, Fe-plaque facilitates several Cd-immobilization mechanisms, ascribed to synergistic effect between iron Fe and sulphur. Biochar amended with sulphur has high adsorption affinity for Hg than pristine-ARBC, resulting in formation of stable HgS precipitate [47,135].

6. Biochar modulates soil fertility to enhance HMs remediation face

6.1. Nature of feedstock and soil physico-chemical attributes

Past studies revealed that the ARBC-applications demonstrated remarkable potential in the remediation, revegetation, and restoration of HMs contaminated agroecosystem soil ([136]; Oliveira et al., 2017). Designer magnetic-ARBC can also be deployed to ameliorate soil chemistry for HMs remediation (Table 2). Amendment of agroecosystem soil with ARBC can favourably modulate pH, SOC, essential nutrients, and microbial diversity, or their symbiosis with food crops [137,138]. Together, these ameliorations in soil physico-chemical characteristics can remarkably improve soil health, besides enhancing HMs remediation [139]. Therefore, this biobased technology of deploying ARBC can enhance soil fertility, in concert with enhanced HMs decontamination, to safeguard food safety and public health. In this respect, 'tuning' the ARBC for tailored application in soil-food crops interface can enhance the agroecosystem health by acting as better source of macro and micro-nutrients, inextricably linked with soil fertility (Oliveira et al., 2017). For instance, co-application of magnetic-ARBC and ryegrass better stabilize the SOC pool and eventually produced magnetized spheres to potentially adsorb Cr (24.12 %), Ni (23.30 %) and other HMs/metalloids (Cu, Zn, As, and Cd ranging 9.98 %–22.01 %) [138]. Together, magnetic and ryegrass ARBC induced enrichment factor which was noted in increasing order i.e., Zn > As > Cr > Cu > Ni > Cd. Thus, ryegrass coupled magnetic-ARBC can be efficient in HMs amelioration, especially in multi-metallic conditions, prevailing in major agriculture systems.

Among HMs, Cd is ubiquitous in most global agricultural landscapes and impose serious health hazards on dietary intake of contaminated food crops [150]. However, ARBC-co-application with the compost

Table 2
Agricultural waste-derived Biochar (ARBC) in Heavy metals/metalloids remediation from agroecosystem soil.

S. No.	Agri-residues feedstock for biochar; operating pyrolysis temperature	Biochar dose	Target HMs & Initial soil concentration (mg/Kg)	HMs remediation (%)	References
1.	Rice Straw; 500 °C	20 t ha^{-1}	Cd(II) & 3.09 mg/kg	97.1 %	Zhang et al. [140]); Wang and Wang [69]
2.	Wheat straw; 550 °C	40 t ha^{-1}	Cd(II) & 3.13 mg/kg	93.6 %	Bian et al. [141]); Wang and Wang [69]
3.	Rice Straw; 300 °C	5 %	Pb(II) & 2.0 mg/kg	100 %	Jiang et al. [142]); Wang and Wang [69]
4.	Bamboo; 400 °C	1.5 %	Cd(II) & 50 mg/kg	87.4 %	Mohamed et al. [143]
5.	Eucalyptus wood; 500 °C	2 %	Cd(II) & 1.4 mg/kg	80 %	Li et al. [144]
6.	Soybean stover; 700 °C	20 %	Pb(II) & 696 mg/kg	90 %	Moon et al. [145]
7.	Tree bark; 400 °C	10 %	Cd(II) & 5950 mg/kg	>99 %	Venegas et al. [146]
8.	Woody biomass, (*Gliricidia sepium*) ; 900 °C	5 %	Ni, Cr, Mn	93 % (Ni); 97 % (Cr), & 92 % (Mn)	Herath et al. [147]
9.	Sewage sludge	8 %	Ni (13.35 mg/kg); Cu (7.6 mg/kg); Cd (4.3 mg/kg); Pb (26.8 mg/kg); Zn (48.5 mg/kg)	Ni (99.7 %); Cu (97.9 %); Pb(99.9 %); Zn(99.9 %);	Mendez et al. (2012)); Wang and Wang [69]
10.	Chicken manure; 550 °C	5 %	Pb(II) & 1000 mg/kg	93.5 %	Jin et al. [148]
11.	Sugarcane straw; 700 °C	5 %	Zn(II) 2027 mg/kg; Pb (II) 3688 mg/kg; Cd (II) 6.09 mg/kg	54 % (Zn); Pb (50 %); Cd (56 %)	Puga et al. [149]; Wang and Wang [69]

reduced the Cd and Zn bioavailability in multi-metal contaminated wetland soil through modulation of physico-chemical attributes such as enhanced soil pH, total organic-C, and water-extract organic-C [137]. Pertaining to Cd remediation from soil-food crop interface, walnut shell-ARBC was noted as an effective tool, demonstrating high Cd immobilization stability, ascribed to precipitation and complexation mechanisms [151].

The individual effects of husk/straw/stalk-based ARBC may not be efficient adsorbent, therefore their combination with hardwood-ARBC is advocated in HMs, especially, Cd contaminated agriculture systems [152]. Interestingly, pertaining to HMs remediation mechanisms in case of both the varying ARBC from feedstock i.e., hardwood and rice husk adsorbents, Khan et al. [152] observed that both electrostatic and non-electrostatic mechanisms led to Cd remediation. However, it has been observed that hardwood-ARBC induced non-electrostatic mechanisms which operated more effectively in case of rice husk-ARBC [152].

Agricultural waste-derived biochars induced OCFG, O/C ratio, and organo-mineral complexes in pores, which were together responsible for immobilization of Pb, Cu, Cd in soils, ascribed to the mechanism of co-precipitation and complexation [139]. Notably, desorption experiments during field biochar ageing experiments of Chen et al. [139] noted that effects of HMs toxicity fade or slow over ageing time in increasing order i.e., $Pb^{2+} < Cu^{2+} < Cd^{2+}$, therefore, can be safely used in long-term field experiments. In this aspect, Pb toxicity diminishes faster than Cd and Cu due to variations in binding efficiency, as desorption rate for Pb was 0.08 %, followed by Cu (0.20 %) and maximum value of 13.15 % in case of Cd [139]. For instance, co-application of rice straw-ARBC and lime was able to remediate the Pb-contaminated acidic soil by raising the soil pH in brown rice [126]. Likewise, application of eucalyptus wood-ARBC in conjunction with the sewage sludge also raised the soil pH to remediate Pb, Cd, and Zn, by decreasing their bioavailability [13].

Designer ARBC can remarkably ameliorate the soil quality to enhance the food crops yield and HMs remediation to secure the public health [21,69,146]. In relation to soil physico-chemical attributes, designer ARBC potentially modulate soil pH, CEC, SOC fractions, and nutrient-use [21]. Further, applications of ARBC to agroecosystem soil can enhance soil aggregates stability, WHC, and porosity, while reduce bulk density through the alleviation of soil compaction [69].

6.2. Soil biological attributes: ARBC-microbe interactions

Ameliorations in biological attributes such as those mediated through microbial consortium supplemented-ARBC can potentially reduce the HMs phytotoxicity in food crops [153]. Interestingly, ARBC pores act as congenial habitat for beneficial soil microbes such as symbiotic mycorrhizae and bacteria, wherein their metabolic requirements such as SOC, SOM, and nutrients are fulfilled with-in biochar-surfaced micro-habitats ([154]; Oliveira et al., 2017).

Microbe-ARBC interactions positively modulated the formation and protection of soil aggregates and nutrients uptake, inextricably linked with HMs stabilization [155–157]. For example, microbe (*Pseudomonas* sp. NT-2) assisted maize ARBC increased the soil pH, thereby resulting in enhanced HMs immobilization than the ARBC devoid of bacterial inoculation [153]. In this vein, a recent three-year field experiment demonstrated that ARBC ageing increased soil alkalinity by raising its pH [139].

Microbes supplemented-ARBCs have shown profound impacts on immobilization of HMs in agroecosystem soil and food crops [38]. For instance, the saw-dust ARBC supplemented with Hg(II)-volatilizing *Pseudomonas* sp. strain, DC-B1 can potentially enhance the Hg remediation from agroecosystems' soil and simultaneously enhance the growth parameters e.g., increased root length in case of *Lactuca sativa* L. (i.e., lettuce) [89]. Similarly, in *Hordeum vulgare* L. microbe-assisted-ARBC resulted 3.11–17 fold decrease in Zn, Mn, Cr, Cu, Pb, Ni, and Cd content, which was importantly higher than the control i.e., ARBC-applications without microbial supplementations [158]. Further, Chen et al. [158] calculated the decrease in HMs in separate treatment wherein 'ARBC only was recorded a decrease by 1.78–9.23 fold, while 'Microbes (bacterial strains only)'-based decontamination was recorded 1.79–5.30 fold, which was lower reduction in HMs concentrations than their co-application (3.11–17 fold) [158]. Thus, bioaugmentation with bacteria-loaded ARBC can restore microbial community and soil functions after potential HMs immobilization in agriculture systems [38].

Mine soils amended with willow and ryegrass-ARBC can also influence the microbes-assisted phytoremediation of Pb, Zn, Ba, As, and Cd [159]. In this vein, Zn Al LDH composites were also noted in Fe and Mn remediation from acid mine drainage [3]. In addition to HMs immobilization, ARBC-application exerts positive influence on microbial activity, biomass, community composition, and microbial C-use efficiency [50,93]. Also, ARBC-amendment of agroecosystem soil can influence the microbial diversity such as those of reducing bacteria to enhance ARBC-based HMs remediation and nutrient assimilation [93,156]. In this vein, Shannon and Simpson diversity and abundance of microbial diversity especially those belonging to groups Proteobacteria, Bacteroidetes, Rhodocyclaceae (class Betaproteobacteria) and Geobacter (class Deltaproteobacteria); and Actinobacteria increased with the application of S and Fe-loaded biochar applied to paddy fields for Cd immobilization [113].

Microbes-assisted-ARBC can effectively ameliorate the HMs contamination in food crops. Rice husk ARBC on inoculation of phosphate-solubilizing bacteria enhanced the Pb remediation by 24.11 % [89]. In this vein, Chen et al. [89] affirmed that ARBC-induced Pb remediation was due to multitude of mechanisms like stable pyromorphite formation, increased P contents, and positive modulation of pH. Recently, 5 % dose of maize straw-ARBC, loaded with *Trichoderma harzianum* phytostablized the 'Cd–Cu'duo in contaminated agroecosystem soil, mediated by their decreased mobility, bioavailability, and revitalized soil enzymatic activity [15].

The field-scale ARBC-deployments in agroecosystem soil may act as an effective liming agent to regulate soil pH, reduces soil bulk density, improves soil aeration and WHC [41]. Together, these soil quality ameliorations can potentially regulate nutrient transport and assimilation in microbes, thereby establishing an inextricable 'soil-biochar--microbe' interactions [41]. Importantly, signal molecules in 'ARBC-microbe' interaction prevailing in agroecosystem soil regulate 'cell–cell recognition, cell signalling and cross-talk' in soil microbes. In nutshell, stable or recalcitrant C-pool of ARBC can be influenced by chemical and microbial decomposition, together resulting in biochar ageing (Gul et al., 2015).

Biochar aging can alter its physico-chemical characteristics which potentially influence ARBC-microbe interactions. The study by Venegas et al. [146] noted that ARBC ageing caused minor changes in the physicochemical properties of biochar in agroecosystem soil, however need to be temporally monitored. However, the effect of ARBC ageing on agriculture systems and food crops yield is tightly linked to spatial variations in soil types and physicobiochemical characteristics [146]. Interestingly, another study observed that ARBC-environmental ageing can also increase their HMs remediation efficiency, which is tightly regulated by adsorption and microbial interactions [49].

6.3. Symbiotic/functional microbes-ARBC interactions modulate oxidative stress enzymes

Symbiotic association of microbes such as fungi are deeply linked with roots of food crops, therefore, their supplementation into ARBC can reduce HMs toxicity in agriculture systems [160]. In this sense, Liu et al. [160] noted that inoculation of arbuscular mycorrhizal fungi (AMF)--supplemented ARBC resulted in synergistic effects on Cd immobilizations in maize. Furthermore, favourable modulations were noted in yield of maize, manifested by 79.1 % increase in biomass growth with elevated SOD by 50.06 %, POD (67.19 %), and CAT (58.04 %) [160]. Also, in this vein, AMF supplementation in ARBC can increase the fungal population which can further enhance the microbe-assisted remediation of HMs.

Individual effects of rice stubble compost and rice stubble-ARBC in combination with AMF on pea crop was assessed for HMs removal [161]. In case of soil irrigated with municipal/sewage wastewater and among all formulations 'rice stubble ARBC + AMF' demonstrated maximum remediation [161]. Herein, co-application of ARBC with AMF demonstrated removal of Pb(35 %), Cd(50 %), Ni(43 %), Cu(43 %), Co (52 %), and Zn(22 %) from wastewater irrigated soil. Importantly, in food grains HMs concentrations were further reduced in case of Pb(93 %), Cd(76 %), Ni(83 %), Cu(72 %), Co(71 %), and Zn(57 %), when compared with control treatment [161]. Further, in this study of Farhad et al. [161], soil enzymatic activities were also noted an increase such as urease (78 %), CAT (156 %), POD (62 %), phosphatase (123 %), β-glucosidase (235 %), and fluorescein diacetate (96 %). This elevation in soil enzymes is due to 'Biochar-AMF' interaction and together they act in concert to elevate soil nutrients and concomitantly alleviate HMs stress [161]. Moreover, these enzymes are crucial for soil nutrient cycling and the breakdown of SOM, tightly linked with soil fertility. Therefore, the rice-ARBC in concert with AMF can address the problem of HMs-contamination in soil to sustain agroecosystem and human health.

In another study, ARBC when inoculated with bacteria and functional microbes, resulted in enhanced Cd and Cu immobilization through increased urease and CAT activity in the HMs contaminated soil [35]. In this vein, ARBC co-application, derived from maize straw, cow, and poultry manure with *T. hazianum* and *B. subtilis* improved the Soybean yield after increased Cd remediation [35]. In this study, microbe-assisted ARBC imparted synergistic effects in reducing the Cd bioavailability through the dual mechanisms of immobilization and adsorption. Concomitantly, Haider et al. (2021) noted that this 'ARBC + microbial consortium' improved Soybean growth by strengthening the antioxidant or oxidative stress tolerance potential. Henceforth, Soybean performance driven by microbe- ARBC interactions was in fact ascribed to increased biomass, photosynthetic activity, nutrient contents and activity of antioxidative enzymes. Also, in biochemical oxidative stress tolerance aspects, ARBC minimized the ROS levels and Cd content in Soybean [35].

7. Agri-residues-based biochar for HMs immobilization in agriculture systems

7.1. Role of ARBC-driven HMs remediation in food crops

The role of ARBC-driven HMs remediation operate through diverse chemical mechanisms in soil-food crop interface is subject of utmost attention in agriculture systems, in view of their inextricable linkage with human health and sustainable agriculture [37] (see Table 2). In this perspective, a meta-analysis of 74 articles before 2016 was performed with 1298 independent observations which revealed that the average decreases of HMs-uptake i.e., Cd (by 38 %), Pb (39 %), Cu (25 %) and Zn (17 %) was estimated in different staple food crops [158]. In this vein, the largest decreases in HM-concentrations was noted in food crops raised on coarse-textured soils, amended with ARBC, having high pH values [158]. Maize is widely used staple food crop, susceptible to Cr and Cd toxicity, visualized in terms of increased oxidative stress, reduced photosynthesis, and decreased growth parameters, adversely influencing crop yield [37]. To abate this, Spent mushroom substrate-ARBC remarkably revitalized the growth parameters, chlorophyll content and sustained yield of maize mediated through potential remediation of Cr-Cd duo [37].

Biochar applications at the red soil-cabbage interface alleviated the exchangeable Al^{3+} with concomitant increase in soil pH and available nutrients [162]. In agriculture systems, one of the major impending is that leachates of HMs in contaminated agroecosystem soil can be toxic to the soil, food crops, and groundwater [6,163]. Nonetheless, application of sugarcane-ARBC to mining soils increased the mobility and chemical fractionation of HMs, thereby reducing the Cd (57–73 %), Pb (45–55 %) and Zn (46 %) concentrations in the leachate [163]. In this aspect, soil amended with sunflower-poultry manure compost, rice husk ARBC, and groundnut shell ARBC enhanced the stress tolerance as well as Pb phytoremediation potential (i.e., in the range of 420–2100 mg/kg) of planted *Moringa oleifera* Lam at low or moderate concentrations [164].

Amendment of ARBC with 3-mercaptopropyltrimethoxysilane increased the adsorption of CH_3Hg^+ and Hg^{2+} through the thiol-(SH-)-modification and surface complexation [165]. Interestingly, corncob ARBC can simultaneously remediate As and Cd, with favourable modulation of the soil microbial diversity [166]. In this vein, Shen et al. [166] observed that ARBC in conjunction with the biochar-mineral composites can remarkably enhance HMs remediation potential of contaminated soil. Further, the biochar component of MgO modified corncob ARBC increased the Pb adsorption through 'cation-π interaction' and surface adsorption [166]. Moreover, Shen et al. [166] also noted that the coated MgO exerted synergistic Pb-remediation effects through the mechanism of precipitation.

Peanut shell waste-ARBC resulted in effective adsorption of chromium(VI) from environmental matrices in the range of 79.35 % [167]. Application of ARBC increased the proportion of acid soluble fraction of Cd and Cu, thereby facilitating their remediation from the agroecosystem soil [150]. In this aspect, biochar-struvite-composites resulted in efficient Cu remediation, with concomitant reduction in the abundance of 'antibiotic-resistance genes (ARGs)' in agroecosystem soil [150]. In this respect, the ARGs were mainly hosted by dominant bacterial groups such as Firmicutes and Actinobacteria. In another study, the co-pyrolysis of the rape straw-ARBC, amended with orthophosphate, acted as novel adsorbents for remediation of Cd, Pb, and Cu [59]. In this respect, the decreasing order of HMs remediation i.e., Pb > Cu > Cd was either guided directly by the phosphate and -OH groups-enabled precipitation and complexation, or indirectly by modulating the soil pH and available P, which eventually facilitated the HMs stabilization [59]. In addition to chemicals, organic manure-ARBC modified with H_2O_2 can enhance the HMs remediation, attributed to increased number of oxygen and -COOH group contents (Wang et al., 2020).

Field experiments have shown that Cd, Cu and Pb were less labile in the agroecosystem soil, when amended with sugarcane bagasse-ARBC, consequently decreasing their bioavailability in the edible part of *Brassica chinesis* (common name-pak choi) [168]. Herein, the decreased bioavailability of Cd, Cu, and Pb was tightly linked with the increase in soil enzyme and microbial activity. Application of wheat-straw-ARBC to seedling bed of *Solanum melongena* L. or eggplant increased the crop growth and productivity, with concomitant reduction in the Cd concentration or bioavailability. The increased reduction in Cd concentrations in eggplant parts i.e., roots, shoots and the fruits was noted in the range of 12.2 %, to 18.5 %, when compared with traditional seedling method devoid of ARBC [150]. Similarly, Li et al. [150] further assessed that amendment of eggplants' seedling bed with wheat-straw ARBC by increasing the rhizospheric pH to 8.83 which induced Cd-immobilization to decrease the Cd bio-accumulation factor from 0.36 to 0.32. Herein, the increased Cd immobilization in ARBC amended seedling bed of eggplant is also ascribed to up-regulated biochemical mechanism of Phytochelatin synthesis.

7.2. Chemical kinetics of ARBCs-induced HMs phytoremediation

Besides, biochemical and molecular basis of ARBC-driven HMs remediation, the role of chemical kinetics in elucidating adsorption models is another important facet, which need to be explored in soil-food crop interface [3] (Table 3). In this vein, palm tree leaves-ARBCs were characterized through several techniques and revealed high C-content (78.5 %), SSA (21.6 m^2/g), and surface oxygen content (15.7 %), which made it an efficient adsorbent for HMs [169]. In this respect, Freundlich maximum adsorption uptakes for Pb (79.2 mg g^{-1}) and Cr

Table 3
Chemical kinetics and adsorption models associated with agricultural waste-derived biochar (ARBC) in Heavy metals remediation from agroecosystem soil-food crop interface.

S. No.	Agri-residues feedstock for biochar	Heavy metals	Mechanism (Optimization process) & Models	Adsorption/Remediation	References
1.	*Prunus armeniaca* stones	Pb, Cd, Ni	Relying on percentage of adsorbate removal and equilibrium adsorption capacity, q_e; Dependent on biochar dosage, pH, and initial contaminant concentration	Mono-layer adsorption i.e., 179.476 (Pb), 105.844 (Cd) and 78.798 (Ni) mg^{-1} Up-to 95 % heavy metals remediation; Engineered biochar was 5 times lower in cost-effectiveness than activated carbon	Turk Sekulic et al. [170]; Osman et al. (2022)
2.	Woody residues (20 % spruce +80 % pine)	Pb	Increased SSA and OCFG act as binding sites for Pb remediation through complexation and electrostatic attraction; *Optimized variables:* pH, mixing time, biochar mass, And initial concentration of Pb & Central composite design	Mild air-oxidation increased SSA and induced adsorption by OCFG which was augmented by optimization in case of Pb up-to 7.9 mg g^{-1}	Bardestani et al. [171]
3.	Agri-residues biochar from *Lolium perenne*, *Mis-canthus x. giganteus*, *Fraxinus excelsior*, *Salix viminalis*, *Picea sitchensis*	Zn	*Optimized variables*: %Zinc adsorbed, biochar yield and feedstock composition Taguchi design	Among six feedstocks, *Lolium perenne*-derived biochar and its extracted fibre demonstrated greatest Zm adsorption (83.27–92.96 %) under the event of slow pyrolysis	Hodgson et al. [172]
4.	Sugarcane bagasse	Zn, Cu, & Ni	*Optimized variables*: initial adsorbent bed height, initial solute concentration, liquid flow rate, and airflow rate & Central composite design	Zn: 87.56 %; Cu: 88.89 %,& Ni: 84.31 % Optimization increased the extent of adsorption and % removal of HMs	Biswas et al. [173]
5.	Sugar beet shreds	Cu	*Optimized variables*: Concentration of the inlet solution, adsorbent dos-age, and pH of the inlet solution & Box–Behnken design	Cost-effective adsorption of Cu	Blagojev et al. [174]
6.	Shells of *Pistacia* sp.	Pb	*Optimized variables*: Biochar dosage, initial concentration Pb, initial pH, reaction temperature, residence time & Artificial neural networks (ANN)	Levenberg–Marquardt algorithm revealed effective adsorption of *Pistacia*-derived biochar which was further effective with ANN	Yetilmezsoy and Demirel [175]; Osman et al. (2022)
7.	Leaves residues of jackfruit, mango, and rubber plants	Cd	Cd adsorption *via* mass transfer, intraparticle diffusion, and chemical adsorption. *Optimized variables*: pH, initial Cd concentration, biochar dose, contact time, and temperature; pseudo-second-order kinetic model & ANN in concert with genetic algorithm	Freundlich isotherm model demonstrated biochar induced Cd-adsorption and reduced its toxicity in bioassay experiment on red blood cells than contaminated samples	Nag et al. [176]
8.	Sawdust of white spruce (*Picea glauca*), canola (*Brassica napus*) and wheat (*Triticum aesti-vum*) straw	Pb	*Optimized variables* Feedstock type, pyrolysis temperature, steam activation & Principal component Analysis/Multiple linear regression model;	Adsorption of Pb 109 mg g^{-1} was elucidated by pseudo-second order kinetic model revealed the sustainable HMs remediation through agri-residues based biochar	Kwak et al. [177]
9.	Rambutan (*Nephelium lappaceum*) peel	Cu	*Optimized variables*: Contact time, tempera-ture, biochar dosage, initial copper (II) concentration; & ANN), adaptive neuro-fuzzy inference system (ANFIS) & multiple linear regression (MLR)	Accurate and cost-effective adsorption of Cu from Rambutan peel-derived biochar	Wong et al. [178]; Osman et al. (2022)

(51.9 mg g^{-1}) was observed with reusability that sustained over five cycles [169]. This was mainly attributed to the chemical mechanisms of complexation, precipitation, and ion exchange. This findings are again relevant to treat HMs contaminated agroecosystem sites through applications of ARBC.

Wheat straw-ARBC pre-treated with H_2O_2 and optimum microwave power of 500–600W enhanced its inherent physico-chemical properties in view of remarkable increase in SSA (190.35 m^2 g^{-1}) and porosity/pore volume (1493 cm^3 g^{-1}) [179]. Together, these ameliorations enhanced adsorption capacities of Pb^{2+}(190.21 mg g^{-1}), Cd^{2+} (57.56 mg g^{-1}), and Cu^{2+} (65.16 mg g^{-1}) through dual chemisorption mechanisms, i.e., surface complexation, which was effectively coupled with precipitation. Herein, adsorption process revealed best fit with pseudo-second-order kinetic and Langmuir isotherm models.

Globally, the practice of 'ethno-medicinal plants' (EMP) is an age-old practice wherein traditional knowledge on plants is used in primary health-care [180]. In this vein, residues from EMP-based alkaline ARBC showed intricate interrelationship between its physicochemical properties, pharmaceutical residues, and adsorption performance with rich higher lignin content [181]. This study of Yan et al. (2024) noted EMP-ARBC driven effective Pb remediation in the range of 29.30–38.65 %, attributed to the mechanisms of precipitation, ion exchange, complexation, and enrichment of OCFG. Herein, HMs adsorption was in accordance with pseudo-second-order models, while adsorption isotherms followed Langmuir model [181]. Further, biochemical supplementations of Glycine and Alanine-amended rice husk-ARBC increased the Cr, Cu, Ni, and Pb adsorption potential [182]. Herein, Langmuir isotherm indicated monolayer sorption following pseudo second-order kinetics models revealed HMs adsorption in the range of 21 %–30 %, when compared with pristine rice-husk ARBC.

Magnetic-ARBC was more effective than pristine coconut shell and bamboo-ARBC resulting in Cu(II) adsorption, following the Langmuir kinetic model (R^2 = 0.982), up-to the extent of 371.50 mg g^{-1} [183]. Notably, the magnetic-ARBC has alleviated the Cu-uptake and phytotoxicity in lettuce [183]. Reduced Cu phytotoxicity in food crops was ascribed to multiple mechanisms such as enriched OCFG such as -OH, -COOH, C=O, and Fe–O, soil organic matter (SOM), and physico-chemical interactions such as 'chemical precipitation, ion exchange, and metal-π complexation' [183]. Recently, Wibowo et al. [3] observed the efficiency of 'montmorillonite (MMT) and ZnAl LDH composite-biochar' in remediating Fe and Mn from acid mine drainage. Interestingly, the elucidation of chemical kinetics further revealed that adsorption isotherm in case of biochar followed 'Dubinin–Radushkevich model', while biochar composites stick to the Redlich–Peterson model. Moreover, Wibowo et al. [3] confirmed the pseudo-second-order model, with chemisorption being the dominant mechanism. In brief, the study on chemical kinetics of ARBC-induced HMs adsorption can better elucidate their remediation efficacy from soil and food crops (see Table 3). Thus, ARBC-driven HMs remediation from agroecosystem soil can be elaborated with outcome of chemical kinetic studies to expand the horizon of food safety, sustainable agriculture, and human well-being.

8. Biobased HMs remediation technologies: catalyzing UN-SDGs

8.1. Food crop safety and enhanced yield augment SDGs

The sustainable utilization of ARBC in HMs remediation from soil-

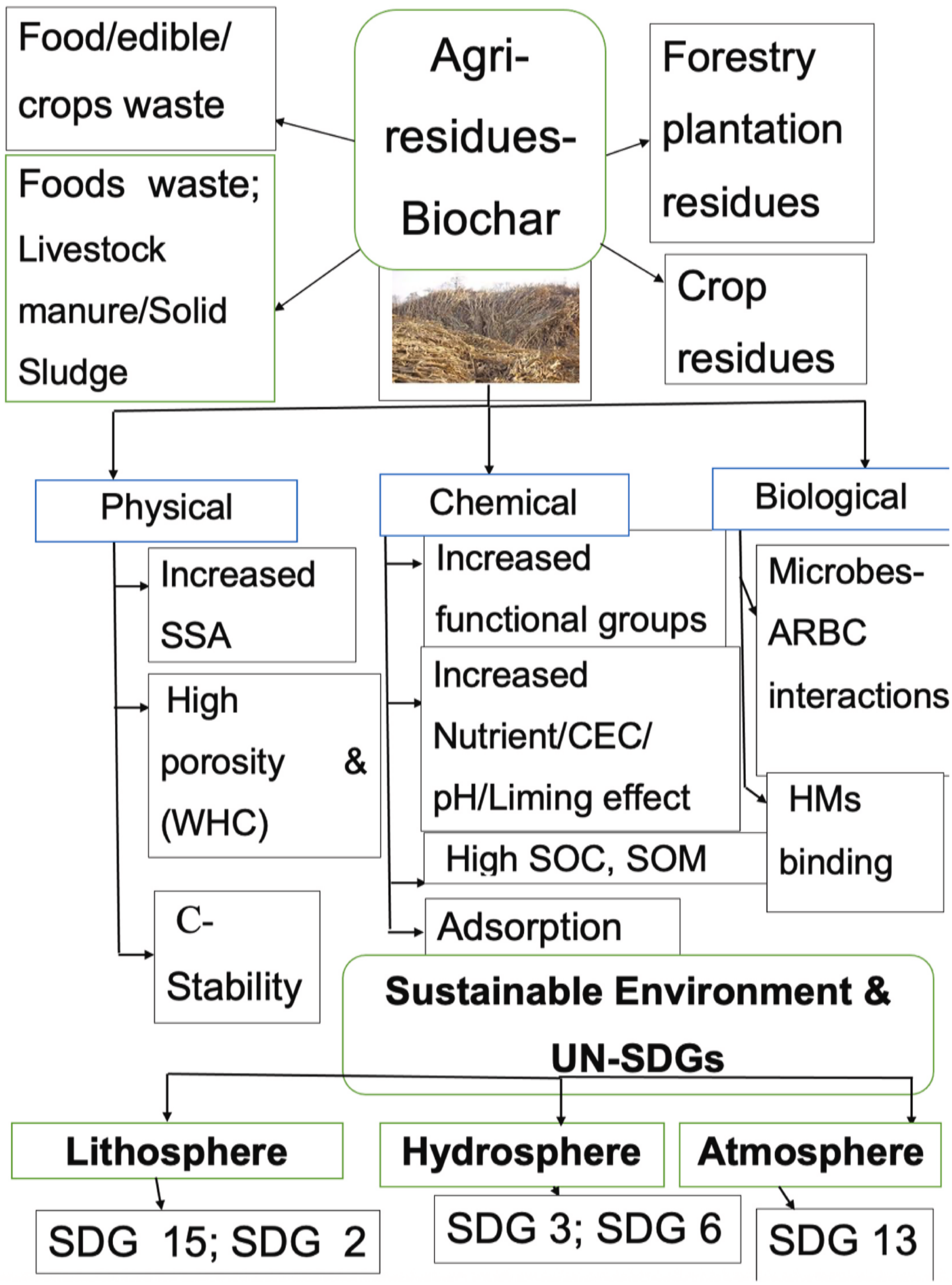

Fig. 4. Multitude of physico-chemical and biological attributes of agricultural waste-derived biochar (ARBC) contributing to metals remediation at soil-food crop interface and their linkage with environmental sustainability/sustainable agriculture (mediated through environmental ameliorations in biosphere comprising lithosphere, hydrosphere, and atmosphere) and achievement of United Nation (UN)-Sustainable Development Goals (SDGs).

food crops interface is essential to mitigate human health risks and attain sustainable agriculture [139] Fig. 4 represent the vast array of biomass options from agriculture and forestry ecosystems that result in ARBC production. Further ARBC are endowed with physico-chemical attributes and biochar-microbe interaction that can ameliorate soil fertility and HMs removal. Importantly, these ARBC-mediated ameliorations in biosphere align with several SDGs linked with food safety and security, climate action, public health, and human well-being. To this end, ARBC can be potentially applied to address the problem of multi-HMs contaminated agriculture systems, with an explicit motive to increase the food crops yield [139]. In his meta-analysis on HMs uptake by ARBC, Nikoh et al. (2022) noted reduction in HMs and As concentrations in contaminated soil. Herein, the decrease was recorded in the range of 3.03 % for Pb followed by 25.8 %–26.2 % (for Cu and Cd) while maximum of 41.5 % was recorded in case of As, offering better food crops yield.

Recent advances in nano-technology and molecular biology has remarkably revolutionized the HMs remediation from soil-food crops interface, plant growth attributes and yield, with higher efficiencies. For instance, the integration of NPs with ARBC mitigates phyto-toxicity in barley, tobacco, onion, wheat, and spinach, ameliorates plant growth, biomass accumulation and sustain the agricultural productivity ([184, 185]; Hasnain et al., 2023). Furthermore, the applications of ARBC-NPs microaggregates is cost-effective or sustainable way to synergistically ameliorate Cd toxicity by increasing nutrient availability and enriching microbial communities (Hasnain et al., 2023). Also, ARBC, on being amended with ZnONPs, improved the plant growth and development of food crops like maize [186] and wheat [187] in Cd contaminated soil. In addition to NPs, the co-application of phytohormones and microbes along-with ARBC can also ameliorate the growth and productivity of food crops in HMs stressed soil (Hasnain et al., 2023). Concomitantly, modulation of physio-biochemical/genetic attributes such as phytohormone dynamics, genetic regulations, and structural transformations can also escalate HMs remediation from agriculture systems to enhance the yield of food crops [188].

In addition to increasing the crop yield, the deployments of biomass-based designer-ARBC technology in agriculture systems is inextricably linked with several UN-SDGs [10]. In arid or drought susceptible regions, designer biochar can restore the HMs degraded or marginal lands into arable ones, therefore can be tightly linked to 'Life on Land' i.e., SDG 15. It is worth mentioning that SDG 15 'seeks to protect, restore, and promote the sustainable use of terrestrial ecosystems' for the environmental and human well-being (Figs. 2 and 4). The sustainable-ARBC technology can also result in HMs free food crops which is closely linked with human health, thereby help achieving the SDG 3 'Good Health and Well-being' [8]. Also, biobased ARBC applications in agroecosystem soil can remarkably enhance the abiotic, especially HMs stress tolerance in food crops, ascribed to its intrinsic properties of enabling increased nutrient cycling, porous structure, soil aggregates stability [189]. Simultaneously, ARBC can decrease the bulk density, ameliorate soil physico-biochemical attributes like pH, CEC, and soil enzyme activity in conjunction with growth of beneficial microbes, consequently, alleviating pollutants stress to ameliorate soil fertility. This ameliorative effects of this biomass-driven ARBC technology on soil health can augment food security to SDG 2 'Zero Hunger'. Also biobased technology is advocated to act as potential NET by global regulatory instutions like IPCC and WEF. Thus, sustainable ARBC technology facilitates C-neutrality to help attain SDG 13 'Climate Action' (Fig. 3). Together, these biomass-based ameliorative ARBC-effects on food crops yield can facilitate sustainable agriculture and human well-being that align with UN-SDGs.

8.2. Human health risks mitigation and UN-SDGs

Pollution free food crops cultivars raised on ARBC-driven HMs decontaminated soil can be safely consumed by residential society, therefore, inextricably linked with human health risks mitigation [139]. Therefore, the discussion in this section on biobased technology driven HMs remediation align with UN-SDG 3 'Good Health and Well-being'. Safe food crop production can be ensured by the ARBC-applications, which not only ameliorated soil quality but also reduced HMs transfer in edible plant parts of food crops in decreasing order i.e., edible grains (36.1 %, 33.6–38.6 %) > shoots (31.1 %, 29.3–32.8 %) > roots (27.5 %, 25.7–29.2 %) [139]. Herein, the ARBC-driven reduction in bioavailability of HMs at soil-food crop interface was ascribed to increased SSA and C-contents, which can potentially mitigate the possible human health risk implications *via* restricting trophic level food chain transfer.

Metals Fe-Mg-modified-bimetallic peanut shells-ARBC at 3 wt% were also demonstrated to remediate Cd, Pb, and Cu by reducing their mobility in agroecosystems, consequently, enhancing *Spinacia oleracea* L. (spinach) biomass and food crops yield [190]. This increase in spinach biomass was mediated through increased photosynthesis by 22 %, transpiration elevated up-to 21 %, stomatal conductance by 103 %, and elevated intercellular CO_2 levels by 15.3 % [190]. Together, these physico-biochemical changes alleviated HMs-uptake to potentially mitigate phytotoxicity and oxidative stress *via* modulating oxidative stress tolerant enzyme i.e., APX, SOS, and CAT levels in spinach [190]. Thus, elements modified-ARBC can immobilize HMs to reduce their concentrations in plant parts (e.g., in Roots: Cd by (34.1 %), Pb (79.2 %), Cu (47 %); Shoots: Cd by (56.3 %), Pb (43.3 %), Cu (54.1 %) that can potentially restrict their transfer to edible food crops [190]. In totality, these factors together enhance safer food crop production to augment food safety/security and safeguard human health.

Besides, ARBC-driven HMs remediation and enhancement in soil fertility, the human health risks are also mitigated due to dietary intake of pollution free food crop cultivars. To this end, ARBC-induced human health hazards mitigation was evidenced by estimation of prescribed health indicators in wild edible mushrooms [191]. In this respect, several health indicators such as 'estimated daily intake (EDI)', 'Target hazard quotient (THQ)' 'hazard index (HI)' and 'Incremental Lifetime Cancer Risk (ILCR)' are devised [9,191,192]. The risk for chronic systemic effects is considered acceptable if the resulting HI value is less than 1. However, if the HI value equals or exceeds 1, it indicates possible long-term consumption risks associated with adverse non-carcinogenic health effects. In this sense ILCR is vital index that assesses the risk of cancer development and its value exceeding 10^{-4} indicate a potential carcinogenic risk, while an ILCR value below 10^{-6} is considered negligible [191].

These health indicators can facilitate human health risks assessment in healthcare or biomedical sector to connect it with UN-SDG 3. These health indicators and their limit is described below-

$$\text{`}EDI = \frac{\text{MC x IR x EF x ED}}{\text{ET x BW}}\text{'}$$

where, MC is the element content in food crops (mg/kg in dw), IR - food ingestion rate (6.6×10^{-3} kg/person/day). EF - exposure frequency (365 days/year), ED - exposure duration for an adult (70 years), ET - averaged exposure time (365 days/year × 70 year or 25550 days/year), and BW- mean body weight of consumers (60 kg). In this context, another health indicator i.e., 'Target hazard quotient (THQ)' was used to evaluate the potential health risks of human consumption following the equation.

$$\text{`THQ} = \frac{\text{EDI}}{\text{R}f\text{D}}\text{'}$$

where, R_fD is the oral reference dose of the HMs in mg/kg/day.

The HI is calculated by adding up the THQ values for each food type assessment element. In such cases, there is the potential for harm due to non-carcinogenic health effects. The HI is calculated as below-

$$\text{HI} = \text{THQ}_{\text{Cu}} + \text{THQ}_{\text{Zn}} + \text{THQ}_{\text{Mn}} + \text{TH}_{\text{Fe}} + \text{TH}_{\text{Ni}} + \text{TH}_{\text{Pb}} + \text{TH}_{\text{Cd}}$$

For instance, in study of Nawab et al. [192], agroecosystem ARBC-deployment not only remediated HMs, but also reduced the extent of human health risks. In this vein, human health indicators such as the 'THQ' and 'HI' were noted <1 (except for Cd), whereas 'ILCR' is a vital index that assesses the risk of cancer development due to exposure to carcinogens through consumption of food stuffs also decreased in case of all ARBC types [192]. Another meta-analysis assessed the health implications mediated by ARBC-induced HMs reduction in the overall daily dietary intake by 12.5 %, THQ by 30.0 % while ILCR decreased by 30.6 % in the biochar amended agroecosystem soil. In this respect, the adsorption, ion exchange, and amelioration of soil physico-chemical characteristics were the underlying mechanisms for biostablizing HMs in contaminated agroecosystem soil (Nkoh et al., 2022). Evaluation of health risk indicators revealed that spinach leaves were not safe for human dietary consumption as evidenced by health risk indices such as HI > 1 while ILCR values was also recorded on higher side, ranging from 0.0085 to 0.0119, thereby exceeding the cancer risk threshold [193]. Therefore, the ARBC deployment in agriculture systems can remarkably reduce the human health risks, manifested by decontamination of HMs at soil-food crop interface. To summarize, agricultural waste can act as an important feedstock for biochar, renewable energy, and integrated biorefinery platform to leverage circular bioeconomy, UN-SDGs, and environmental sustainability [10,23].

9. Limitations and future prospects

The sustainable ARBC-applications can address the ecological, environmental, and human health repercussions of biomass burning, burying, and land-filling of globally generated agricultural waste. Unlike phytoextraction, ARBC-assisted phytostablization tend to stabilize HMs and metalloids in roots or rhizosphere regions of food crops [194]. This aspect should be adequately dealt with caution in future to control or restrict the chances of HMs bioavailability in edible root/rhizomes and tuberous food crops. Also, scant studies suggested to investigate the dust/PM matter emissions from up-scaled ARBC-applications for mitigating possible environmental and human health risks (Gerald et al., 2019). Besides few constraints, the ARBC can still be promising BSS to manage the agriculture waste, address HMs remediation, and guiding sustainable soil eco-restoration. These limitations are summarized here as below-

A *Screening clean ARBC-feedstock and biomass quantification*

Feedstocks like rice-husk and sugar-beet-pulp associated with ARBC-production, if raised on HMs contaminated sites, offer higher chances for their subsequent transfer to agroecosystem soil. Consequently, such ARBC amendment can contaminate food crops like spinach with HMs like Fe, Zn, Cd, Pb, and Ni [193]. In this respect, spinach leaves were not safe for human dietary consumption, as evidenced by health risk indices, such as HI > 1, while relatively higher ILCR can impose cancer risk in local people, especially those which are regularly consuming this food crop, as an integral part of their daily dietary intake. Therefore, adequate caution should be taken to select the ARBC from uncontaminated soil for pyrolysis to produce safe ARBC for agro-ecosystem applications. This can effectively mitigate human health risks and simultaneously sustain food safety/-security.

The database collection or quantification of biomass resources, especially from agriculture and forestry sector should be quantified in legal policy perspective of each country to explicitly assess their potential in biorefinery, bioenergy, and circular bioeconomy sector [11, 23]. In this respect, the recent European Union legal framework encouraged increased share of biomass resources as per "The Renewable Energy Directive (RED) III" which can effectively foster biobased technology and policy initiative [11]. Similar initiative should be promoted at various continental and national scale to accelerate the fulfillment of UN-SDGs [10].

B *Artificial intelligence (AI)- Machine learning (ML)*

The exploration of artificial intelligence (AI) in elucidating the interaction of ARBC with HMs, specifically ML and deep learning tools are gaining popularity [195]. Also, AI-based ML can be vital in terms of explicating the role of specific feedstocks, several variables, ARBC-intrinsic attributes, and influence of reaction conditions in HMs remediation [86,195]. The abundance of wide variety of agri-waste biomass suitable for valorization, the AI/ML tools can screen the most potential ones for ARBC production [196]. Further, a vast array of ARBC and soil physico-chemical attributes operating in multi-HMs remediation are mediated by plethora of mechanisms, that urgently need the AI or ML facility for standardizing the pathways [196,197].

Notably, ML can predict the attributes that potentially influence HMs remediation to a greater extent, therefore facilitate techno-economic modification and functionalization for optimized operation [196]. For instance, biochar properties (53.1 %) were more observed to be more significant for HMs remediation than soil properties [197]. In this sense Sun et al. [197] also noted that among multiple factors influencing ARBC-efficiency in HMs remediation, biochar dosage and pH were more important parameters. Importantly, the HMs adsorption mechanisms can also be elucidated by ML techniques and in this perspective HM/biochar concentration ratio and ARBC-Carbon content were identified as the key deciding parameters [198]. In this vein, Palansooriya et al. [199] predicted through ML tools that the N-content in the ARBC (0.3–25.9 %) and biochar application rate (0.5–10 %) were most vital attributes that can remarkably influence the HMs immobilization. Notably, ML-based 'Feature importance analysis' predicted that HMs type in multi-metallic contamination and ARBC-feedstock were determining parameters in metal adsorption [196]. Nonetheless, further AI/ML-driven analysis is warranted to delve into mechanism of ARBC-driven HMs remediation in agriculture systems.

C *Elucidating toxic effects of nano-char on beneficial microbes*

Maneuvering of physico-chemical properties in designer-ARBC can be suitable approach to raise their efficiency in varying soil and food crop systems. Nevertheless, ARBC tailoring with certain materials like C-based NPs like graphene (C_{60}) can diminish soil microbiota and impose toxicity to agriculture systems [55]. Therefore, 'ARBC-HMs-microbe interactions' need to be pragmatically examined in agriculture systems to remove hazardous elements in an eco-sustainable way [200].These limitations further prioritize the need of adequate caution in up-scaling of ARBC technology, without causing significant perturbations to global agricultural landscapes. Therefore, nano-toxic effects, impact assessments, risk analysis, and management options are necessary for long-term scalability of designer ARBC. Designer ARBC, especially colossal or field-scale deployments of nano-char need explicit 'Life Cycle Assessment' (LCA) and adoption of green chemistry principles to mitigate the possibility of nano-toxicity in agriculture systems to safeguard environmental and public health [201]. Henceforth, in terms of public spotlight, the up-scaled industrial applications of designer ARBC are still in their infancy [6,55].

D *Sustainability constraints*

The cost-effective ARBC generation pathways promote sustainable agriculture, aligned with 'water energy food (W-E-F nexus)' and UN-SDGs throughout the 'cradle-to-grave' LCA [6,202]. Despite few limitations, the customization of biochar to techno-economically innovate designer-ARBC is receiving global research attention to enhance its functionality through ameliorated physico-chemical attributes e.g., 'surface properties, pH buffering capacity, and presence of desired OCFG (Neogi et al., 2022; [3]). In addition to above-mentioned SDGs, agri-waste act as potential renewable biomass resource for bioenergy production and storage can help attain 'UN-SDG 7' 'Affordable and

Clean Energy' [6,21]. Therefore, exploring renewable energy production and storage is an important prospect of agri-waste biomass or ARBC to augment SDG 7 and SDG 13, that need urgent focus in future studies.

E *Designer-ARBC driven secondary pollution and nanotoxicology*

During scaled-up application of ARBC in agriculture systems, the stability of biochar in terms of their propensity towards release of Volatile Organic Carbons (VOCs), polyaromatic hydrocarbons (PAHs) and HMs should be adequately assessed to mitigate the harmful secondary environmental pollution [49,146]. Though the influence of designer biochar ageing on HMs remediation is not clear, further researches are warranted to explicate their environmental behaviour at temporal scale, especially in spatially distinct soil types, in order to mitigate the nanotoxicity and secondary pollution [49]. Moreover, the soil redox potential is closely related to the chemical forms of HMs in soil [70]. Notably, Wang et al. [70] opined that when the soil redox potential changes, the ARBC-immobilization effectiveness can be significantly reduced, and even the environmental risk of HMs release may be increased. Especially, the long-term implications of nano-ARBCs deployment necessitates the explicit elucidation of NPs behaviour and environmental fate to restrict possible nanotoxicity [69,146].

The environmental release of NPs from nano-biochar can impose severe eco-toxic effects on food crops, soil quality, and human health [24]. Thus, adequate caution need to be taken at field-scale applications of nano-ARBC to safeguard environmental sustainability, sustainable agriculture, food safety, and public health [25]. In this respect, the elucidation of ARBC-stability, its reuses and post-treatment co-benefits of spent biochar need to be analyzed in up-scaled agroecosystem-level applications [49,69,146].

F *Techno-economic and Life Cycle Assessment*

The explicit evaluation of LCA is essential to validate environmental sustainability paradigm of ARBC as green HMs adsorbent in soil remediation [203]. However, LCA of agri-waste biochar is complicated by varying ARBC production pathways, lack of explicit HMs assessment mechanisms, complicated fate and dynamics in soil, and inadequate quantification of C-stocks to elucidate their role in C-sequestration and climate change mitigation [203].

In recent study, analysing the ARBC techno-economic and LCA of biomass journey from biochar production by hydrothermal carbonization, transportation, to agroecosystem's soil application, demonstrated its feasibility as an eco-sustainable technology [21]. In this vein, the 88 % stable ARBC-C-fraction resulted in effective C-sequestration of 1.7 $tCO_2eq\ t^{-}$, reducing GHGs emission by $tCO_2eq\ t^{-1}{}_{biochar}$, thereby certified the utility of biobased technology potential in CCUS to accelerate climate action efforts, that is well aligned with SDG 13. Additionally, Gamaralalage et al. [21] noted that cost-effective in-situ ARBC-production, favourable modulation of nutrient dynamics to ameliorate soil heath, value-added product co-benefits in an integrated biorefinery framework, together encouraged field-scale applications of agri-waste biochar. This study of Gamaralalage et al. [21] further affirmed the economically beneficial cost-benefit assessment, techno-economic feasibility, and LCA suitability of up-scaled-ARBC applications in agroecosystems, that ensure sustainable agriculture and human well-being. Importantly, these techno-economic and LCA-based favourable indicators of biobased technology are tightly linked with GHGs mitigation, UN-SDGs, integrated biorefinery platform, and circular bioeconomy [21,23,204].

Notably, there exists paucity of studies which utilizes large scale production of designer-ARBC and their deployment at field-level. Field scale applications of ARBC can catalyze biomass-driven CCUS for environmental decarbonization and HMs remediation at soil-food crop interface [119]. Therefore further investigations would be crucial to validate the field applications of designer-ARBC in global agricultural landscapes. In this vein, HM-specific design of tailored biochar with detailed chemical characterization and LCA can effectively enhance the scalability of ARBC amendments in future prospects.

The expanding horizon of designer-ARBC, especially fabricating magnetic and nano-chars can effectively augment the pace in removal of pollutants, achieving sustainable agriculture, attaining UN-SDGs, biorefinery, boosting C-sequestration mitigating GHGs emissions, co-production of renewable bioenergy, and circular bioeconomy (Neogi et al., 2022). Nonetheless, safe disposal of ARBC, issue related with ageing, and associated contaminants is a challenge for its wide use in agriculture systems. This can be addressed in an environmentally sustainable way by concentrating future researches on biorefinery to help strengthen planetary public health, soil eco-restoration, and human health/well-being.

10. Conclusions

Traditional practice of agricultural waste biomass burning is observed as non-sustainable approach, in view of GHGs and hazardous air pollutants emission, causing perturbations to the environment and human health. Moreover, the higher chances of secondary environmental pollution from conventional physico-chemical technologies envisioned the ARBC-use with dual advantages of HMs remediation, coupled with sustainable management of agricultural waste, mediated through biomass valorization. In perspective of HMs remediation, multiple mechanisms and ARBC-physico-chemical characteristics facilitated the HMs remediation from agroecosystems in an economically feasible and eco-sustainable way. The potential of ARBC in nourishing soil characteristics, water resource conservation, and restricting transfer of HMs to food crops was remarkably increased by customizing it as designer ARBC, with higher efficiencies. In this prospect, the ARBC manoeuvred with magnetic and NPs demonstrated better potential in HMs remediation, when compared with pristine biochar. However, the potential of ARBC in decontaminating HMs contaminated soil-food crops was tightly regulated by abiotic and biotic factors operating during ARBC production, that need to be standardized. Further, the ARBC-scalability and stability in long-term application need to be explicitly studied in terms of biochar ageing-induced leaching of HMs, VOCs, PAHs, and other contaminants back in to environment to mitigate secondary pollution. To this end, techno-economic ARBC-innovations can equitably trade-off between C-derived in biomass through photosynthesis and sequestered recalcitrant-C in ARBC for amelioration of soil fertility in concert with HMs remediation. Sustainable biobased technology in terms of designer ARBC deployments can hence aid in eco-restoration of HMs contaminated soil to raise HMs pollution free edible cultivars of food crops. However, field scale applications of designer ARBC, especially nano-biochar should be adequately monitored to help mitigate nanotoxicity in the multiple environmental matrices. This agri-waste biomass-valorization driven ARBC technology can therefore enhance food safety, soil health, and human well-being, that align with several UN-SDGs. Nonetheless, the farmer's and public acceptance for ARBC applications necessitates the concrete implementation of institutional, national, and global policy support, education and awareness in agrarian countries, adequate technoeconomic and LCA studies, with judicial incorporation of green chemistry principles. Also, increased financial incentives either in the form of subsidized biochar or pilot facilities in rural regions can effectively up-scale this biomass-based sustainable valorization technology from 'lab to farmlands'. Integration of socio-technoeconomic approaches in up-scaled ARBC technology with integrated biorefinery platforms can strengthen circular bioeconomy to foster climate action, pollution free food crop cultivars, and environmental sustainability to help achieve UN-SDGs.

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Declaration of competing interest

There is no competing interest.

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