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Review article

Agro-industrial waste-derived biochar in sustainable remediation of Arsenic from rice and vegetables for food safety and public health

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ABSTRACT

Arsenic (As) contamination in groundwater, soil, and food crops perturb the environmental sustainability and human health. The geogenic weathering with concomitant up-surge in agro-chemicals application remarkably pollute the environment with this carcinogenic metalloid that adversely influence the food safety, public health, and human well-being. Multiple threats necessitate the need of a sustainable biomass-based technology in As remediation. Present systematic review quests the knowledge gaps in role of 'agriculture-waste/residues-derived biochar' (ARB) to address the As contamination in staple food crops of wide dietary consumptions like rice and vegetables. This discussion follows the standard methodologies to prioritize that elucidation of physico-biochemical mechanisms and molecular biotechnology advances-based scalable deployments of nano-biochar. Nano-biochar possess the potential to fill knowledge voids and mitigate twin environmental challenges. Firstly, restricting the health hazardous practice of biomass burning by valorising agro-industrial-waste, while second being the substitution of harmful chemical methods with bio-based ARB-technologies in As remediation. Results reveal that the nano-biochar modulate oxidative stress tolerance pathways, 'reactive oxygen species' (ROS) capture, phytohormones or signal molecules interactions, and regulatory gene expressions, together potentially leveraging the As remediation. Unlike heavy metals, ARB-driven As remediation is constrained in climate change-impacted paddy agroecosystems by multiple biotic and abiotic factors. Nevertheless, the techno-economic manoeuvring or innovations in nano-biochar can conquer these challenges of As contaminated agro-ecosystems by ameliorating the antioxidant and molecular responses. Likewise, other limitations in biochar-driven As remediation and their addressal through future research on efficient feedstock selection, ARB-production methods, enzymatic pathways, functional nano-composites, and machine learning are critically discussed to potentially deal with pervasive As pollution. Therefore, deploying nano-biochar can help achieve public food safety, environmental sustainability, and 'climate-resilient-smart' sustainable agriculture, together catalysing the United Nations-Sustainable Development Goals (UN-SDGs). In future perspective, the scalable deployments of nano-biochar can be strengthened by encouraging participatory approaches among stakeholders like scientists, farmers, regional consumers, and policy makers for sustainable As remediation.

1. Introduction

Arsenic (As) contamination in groundwater and rice fields is now widely recognized as global concern, perturbing food safety/-security, environmental sustainability, 'planetary public health', and human well-being [1–5]. In respect of abundance in earth crust, though this metalloid is ranked 20th among the all elements, the expanding As-contamination range at global scale is a matter of serious ecological and human health risks [6]. In historical perspective, prior to the advent of techno-economic industrial revolution, the geogenic sources, such as weathering of rocks were considered tro be prime contributors of As contamination [7]. In human health perspective, As is classified as class I carcinogen as per 'International Agency for Research on Cancer' (IARC), with potential public health risks. In current scenario, As is ranked as first hazardous metalloid at global scale, as per the Priority List of the 'Agency for Toxic Substances and Disease Registry (ATSDR)', in view of its carcinogenic, teratogenic, and mutagenic potential [1,6].

Environmental As contamination is either driven by modern intensive agriculture or industrial pollution that result in groundwater contamination [8]. In addition to groundwater, As pollution adversely influenced land, or its fundamental component soil that support agro-biodiversity, especially, those of 95% food crops [4,9]. Moreover,

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ubiquitous As occurrence remarkably resulted in land degradation, with significant adverse influence on soil biogeochemistry and microbial dynamics [10].

According to the global study of Hou et al. [4] on global metal pollution in agriculture systems, about 14–17% of croplands are metal/As-contaminated. Unfortunately, these metals-As-polluted global agricultural landscapes are densely populated, encompassing human population in the range of 0.9 and 1.4 billion. Considering this grim scenario of soil degradation, 'The United Nations (UN) Food and Agriculture Organization (FAO)' predicted alarmingly that 90% of world soil resources will be at serious ecological risk by the time-frame of 2050 [11,12]. Consequently, this global land degradation scenario stressed the non-renewable soil-resources in agroecosystems, which enforced the need to raise the global food production by 35–56% [2]. Indirectly, such toxic metals-As-driven geographical area expansion of marginal non-arable degraded land can adversely influence the socio-economic aspects of global sustainability indicators, by endangering the human well-being and livelihood of about 1.3 billion people [4,13].

Considering the multitude of As-based harmful effects, there has been an urgent call from United Nations (UN) to remediate-As from contaminated landscapes, fostering soil eco-restoration to help achieve the 'Sustainable Development Goals (SDGs)', for climate change-resilient-green earth, and planetary public health [6,14–17]. Nonetheless, in remediation perspective, the widely practiced chemical technologies like 'precipitation, ion exchange, membrane filtration and reverse-osmosis' were not sustainable and imposed secondary environmental pollution [18]. In this respect, activated carbon (C) though seemed to be promising chemical tool [19], however, lack of economic feasibility restricted its up-scaled deployments in As contaminated farmlands. These constraints of chemical technologies, prioritized the need of biomass or C-based clean phytotechnology for green As remediation [3,20]. To this end, the quest of cost-effective and eco-friendly biomass-based adsorbents, such as agriculture-waste biochar, a recalcitrant C-derived from O_2 limited pyrolysis, received wide attention for As remediation, thereby, augmenting the effective implementation of associated UN-SDGs [15,21].

The critical evaluation of past studies revealed that environmental challenges of As-contamination are not uniform, across the global agricultural landscapes [22] For instance, 'Machine learning' (ML)-driven mapping of global As pollution indicated the high risk regions of southern and central Asia, and South America [5]. In respect of As-affected vulnerable human population, Podgorski and Berg [5] predicted that about '94 million to 220 million people are potentially exposed to high As-concentrations in groundwater, with 94% of it being residents of Asia'. Furthermore, recent decades witnessed that the several countries in South East Asia (e.g., Bangladesh, India, and China) and others like Vietnam, Chile, and Southern America faced the intense As pollution in agroecosystem soil, and groundwater ([23]; Rai et al., 2023; [4,24]). Especially, in Indian scenario, few states such as West Bengal demonstrate high As concentrations in rice (74.17–666.57 μ kg^{-1}) and Fish (830 and 900 μ kg^{-1}), while near-by Jharkhand is also heavily stressed with As contamination [23]. The severity of As pollution in groundwater and agriculture systems, especially paddy fields, in fact accelerated the focused efforts towards its sustainable remediation in such vulnerable agrarian regions [3,6,25].

In another environmental perspective, agrarian-driven global economies like India, the agricultural-waste/-agri-residues or agro-industrial-wastes are produced in the range of 98.4 MT/year to 131.9 MT/year, whose unsustainable management by burning, burying, and land-filling, emerged as severe environmental and public health challenge [25]. This problem of quantitatively huge biomass of left-over agro-industrial-waste management challenges still prevail across the global agricultural landscapes ([26]; [10]). At present, the wide implementation of such un-sustainable practices in managing agricultural wastes perturbed the global agroecosystems, nutritional value, food safety, and human well-being [6,21,22]. Specifically, managing the agricultural waste or agri-residues through burning, in concert with ethno-agricultural practices like 'shifting cultivation (*Jhum*)', widely practiced in South-East (S.E.) Asia (e.g., North-East India, Thailand, and Myanmar), jeopardized the environmental sustainability, besides imposing human health risks [21,27]. In this vein, the burning of agri-residues resulted in depletion of soil nutrients, increased emission of respirable particulates matter (PM; especially, $PM_{2.5}$) along-with other human health-hazardous air pollutants, causing morbidity, or even mortality in case of extreme health risks [21,28]. This environmental challenge of agro-industrial-waste management in association with As contamination, exacerbated the addressal of issues linked with sustainable agriculture, already stressed with global climate change [9,29].

The multiple environmental challenges imposed by As contamination, underscore the quest of clean and green sustainable remediation technology, to mitigate this global problem for human health [15]. For instance, vulnerable "Cancer Villages" of China observed 62–74% reduction in As derivatives [e.g., As(III) As(V), and dimethyl arsenate (DMA)], eventually resulting in 66% reduction in the 'incremental lifetime cancer value' to effectively ameliorate human health [30]. Such mitigations at global scale was fostered by a multitude of physico-chemical methods and phytotechnologies [31].

Interestingly, the problem of agricultural-waste management can be a solution to addressing the problem of As pollution in global agroecosystems, by using their biomass as sustainable feedstock for 'nature-based green solutions (NBGS)'. In this vein, their judicial use in biochar production can also facilitate the sustainable agro-industrial-waste management. To this end, 'agri-residues-derived biochar' (ARB), a Carbonaceous product in global organic waste stream, can be potential option for sustainable As-remediation from agriculture systems and other environmental matrices, however, scantily explored in As-contaminated vulnerable regions [32]. Though ARB production by pyrolysis, offered potential options for removal of wide range of heavy metals (HMs), however, it was constrained by multiple factors in case of As remediation [21,33]. These challenges in As remediation need to be pragmatically explored for suggesting clean and green technology. Further, unfortunately, the studies on As remediation in 'soil-food crop-groundwater' interface were rather scant and not systematically explored in context of ARB or nano-biochar-modulated oxidative stress tolerance pathways [20,32]. This holistic assessment of environmental matrices, i.e., groundwater, soil, and staple food crops can explicitly assess the As-induced toxicity in global agriculture systems. A majority of ARB-applications attempted to decontaminate HMs. However, studies related to its application on the As remediation is inadequately explored in relation to antioxidant response pathways [19,21,24,34]. In recent decade, the studies are on the rise for HMs-remediation, while nano-scale ARB deployments in As removal, largely remain uncovered [19,32,35,36]. Especially, the role of nano-scale ARB in remediating As contaminated 'groundwater-soil-food crops' are insufficiently explored in an interrelated physiological, biochemical, and molecular framework [1,6,24,34]. Among food crops, the As contamination in rice or paddy fields is already heralded as global problem [4,8,37], besides poisoning other edible nutritional stuffs and vegetables [38,39]. Further, rice is widely consumed staple crop in the world after maize, while vegetables intake supplement the human diet with minerals and vitamins [2,40]. There exists unequivocally alarming scenario of As contamination in paddy fields of several countries with public health risks. Nevertheless, the lack of systematic or empirical description on its fate, redox homeostasis, oxidative stress tolerance mechanisms, food crop safety, remediation challenges, and future addressal is rather unfortunate [9,15,19,23,32]. These limitations in elucidating the explicit biotic and abiotic stress tolerance mechanisms of As pollution created several knowledge voids, which need to be filled for food safety, human health, and sustainable agriculture.

Recent studies evidenced that agro-industrial-waste-derived nano-biochar can be a renewable option to remediate-As from environmental matrices, to potentially mitigate human health risks [3,21,24,41]. It is worth noting that elucidation of bibliometrics on As adsorption through multiple ARB-physico-chemical and biological attributes revealed their wide global use in remediation of groundwater-soil-food crops interface Liu et al., 2024 [157]. However, Lin et al. [157] showed that China, United States of America (USA), and South Korea are leading countries in deploying ARB for environmental remediation and human well-being. In this sense, Bangladesh and India, with the highly vulnerable agricultural-landscapes of As contamination, therefore, should urgently prioritize the ARB-technology to safeguard environment and public health [32,37]. This necessitated the need of present discussion to offer systematic review on multifaceted nano-scale ARB-driven As remediation aspects in groundwater, soil, and food crops, with explicit unleashing of oxidative stress tolerance mechanisms. Moreover, unlike traditional physico-chemical methods, ARB technology received more social acceptability or public spotlight, especially in perspective of farmers, agronomists, consumers, environmentalists, and social scientists [21,42]. Importantly, sustainable ARB production can be comparatively more suitable to marginal farmers of developing countries, in view of their cost-effectiveness and eco-friendly nature [43].

Present review therefore attempted to fill the existing knowledge gaps in addressing the problem As contamination in global agriculture systems, especially in groundwater-soil-food crops interface. At the outset, the sources and fate of As in agriculture systems, especially, in staple food crops like rice and vegetables are critically elaborated in a comprehensive way. The issue of food safety is critically examined, specifically in relation to As contamination in rice, wheat, other staple crops, and vegetables. This specific attention pertains to As-eco-toxicity in exposed human population and livestock, with explicit elucidation of physiological, biochemical, and molecular responses. It has already been established that the exposure route in human may be As contaminated drinking water, rice, and vegetables [6]. Also, the livestock relying on consumption of As contaminated agri-residues like straw and contaminated groundwater can be adversely influenced by biochemical toxic responses [23]. This can further impart a negative effect on public health, relying on consumption of milk and meat of As-exposed livestock. Moreover, As contamination can be subsequently transferred to food chain across the multiple trophic levels, thereby imposing serious ecological threats [23]. Henceforth, the major focus of this systematic review was to investigate the As contamination in paddy fields and multitude of physico-biochemical and molecular challenges associated with its remediation. To this end, it has been well-known that agri-residues encompasses a wide range of crop residues, forestry/-agroforestry woody residues, livestock manure, and sewage sludge [32]. Additionally, sewage sludge enriched in humic substances e.g., 'humic acid (HA), fulvic acid, and humin' are already demonstrated to mitigate As toxicity from contaminated agroecosystem soil [44]. In this aspect, Xu et al. [44] elucidated that sludge-amended ARB-As--complexation was chemically mediated through redox functional groups. Therefore, multifaceted physico-biochemical and molecular mechanisms, associated with ARB-driven As remediation is discussed in present perspective to enhance their effectiveness in securing food safetry, environmental sustainability, soil quality, and human health. In this respect, the limitations faced by pristine-ARB, and the techno-economic efficiency of engineered nano-biochar or designer-ARB in conquering these constraints are discussed sufficiently to offer state-of-art knowledge on As-toxicity and sustainable remediation. Last, the major limitations of ARB in As remediation and prospects of nanotechnology, microbial biotechnology, nano-biochar, and functionalized nanocomposites/nano-hybrids are discussed in this systematic review. The holistic aim of this discussion therefore aimed to expand the horizon of As contamination in rice and vegetables of global agriculture systems to safeguard the food safety and public health.

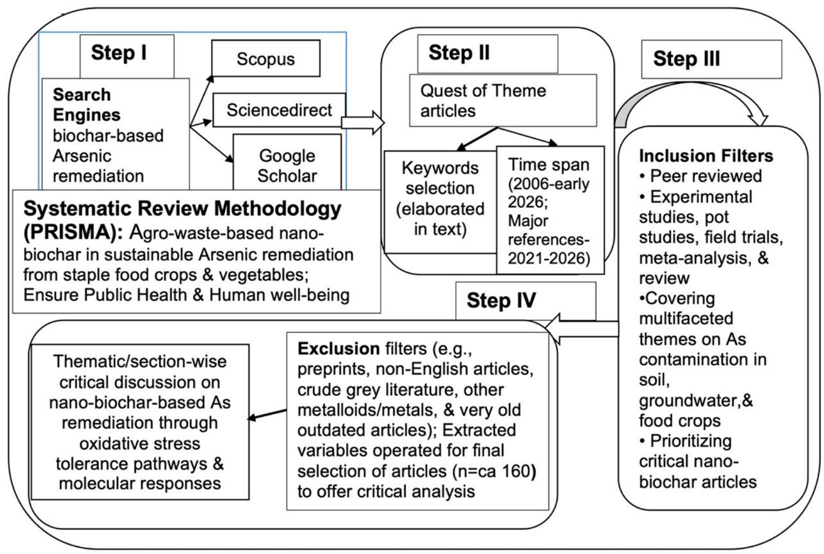
2. Methodology

A comprehensive, comparative, and conclusive literatrure search from selected peer-reviewed articles was done and important studies (of time-frame 2006 to early 2026) were critically analysed for tracking the progress in nano-biochar-driven As remediation. However, in present systematic review, research, meta-analysis, and review articles published during 2021-early 2026 were prioritized to showcase recent advances in agro-industrial waste-derived biochar for As remediation. Inclusion of very recent references reflect the techno-economic developments in biochar-based As remediation. Environmental matrices, especially groundwater, soil, and food crops were given considerable attention during inclusion of literature survey on ARB-based As remediation. The As-induced modulations in oxidative stress tolerance pathways, phytohormones-signal molecules interactions, and gene regulations were top inclusion criteria. Critical analysis on these physico-biochemical and molecular mechanisms, underlying biochar-based As remediation in fact display the recent advances to offer state-of-art knowledge (Fig. 1**a)**. A PRISMA ("Preferred Reporting Items for Systematic Reviews and Meta-Analyses")-inspired flow diagram is shown in Fig. 1a, that concisely describes the methodology adapted in present systematic review. In this review, knowledge gaps were filled through wise selection of high quality articles that include experimental studies, field trials, pot studies, and long-term field research. In this vein, databases used for literature collection included multiple search engines like 'Google Scholar, ScienceDirect and Scopus' with multiple keywords. The keywords were mainly "Arsenic contamination in soil and food crops", "Arsenic contamination in groundwater", "Arsenic contamination and public or human health", "Arsenic remediation and biochar", "Agricultural or agro-industrial waste biochar in Arsenic remediation", "Biochar production methods", "Nano-biochar or magnetic biochar in Arsenic removal", and, "Biochar in Arsenic removal from rice and vegetables", "Arsenic induced oxidative stress tolerance and phytohormones, Silicon, Selenium, and nano-biochar", "Biochar, Arsenic pollution and Sustainable Development Goals" and "Molecular techniques and Artificial intelligence in nano-biochar-based Arsenic remediation". The effectiveness of agro-wastes biochar was performed through comparative assessment of designer/engineered-ARB like nano-biochar and magnetic biochar with pristine biochar. Therefore, non-modified or pristine biochar acted as reference or control to compare the techno-economic innovations in novel nano-composites or functionalized-ARB, that can guide future nano-technology driven biochar research on As remediation. Moreover, exclusion filters were applied to discard studies on HMs or metalloids, other than As, in conjunction with rejection of non-English articles, crude grey literature, and very old or outdated research knowledge. In this review, after exhaustive literature collection on the subject, extracted variables or filters applied for exclusion. These variables comprised biochar feedstock, modification or valorisation methods, locating As in environmental matrix restricted to groundwater water-soil-food crop, staple food crops with rice being focal crop, leafy vegetables, arsenic remediation efficacy of nano-biochar, and biochemical or molecular basis of ARB-induced oxidative stress tolerance. Exclusion filters enabled final selection and in-depth analysis of cited literature (n = ca 160), as shown in Fig. 1a. In brief, the incorporated references comprised proper controls, replication, field validation, arsenic speciation, biochar characterization, and statistical analysis that strengthen this systematic review.

3. Sources, fate, geographical hotspots, and human health hazards of Arsenic

3.1. Sources and fate

Arsenic is considered to be a potential metabolic poison, emanating from natural rocks and percolate to groundwater table *via* storage in soil and aquifers [32,45]. At present time, the anthropogenic perturbations a



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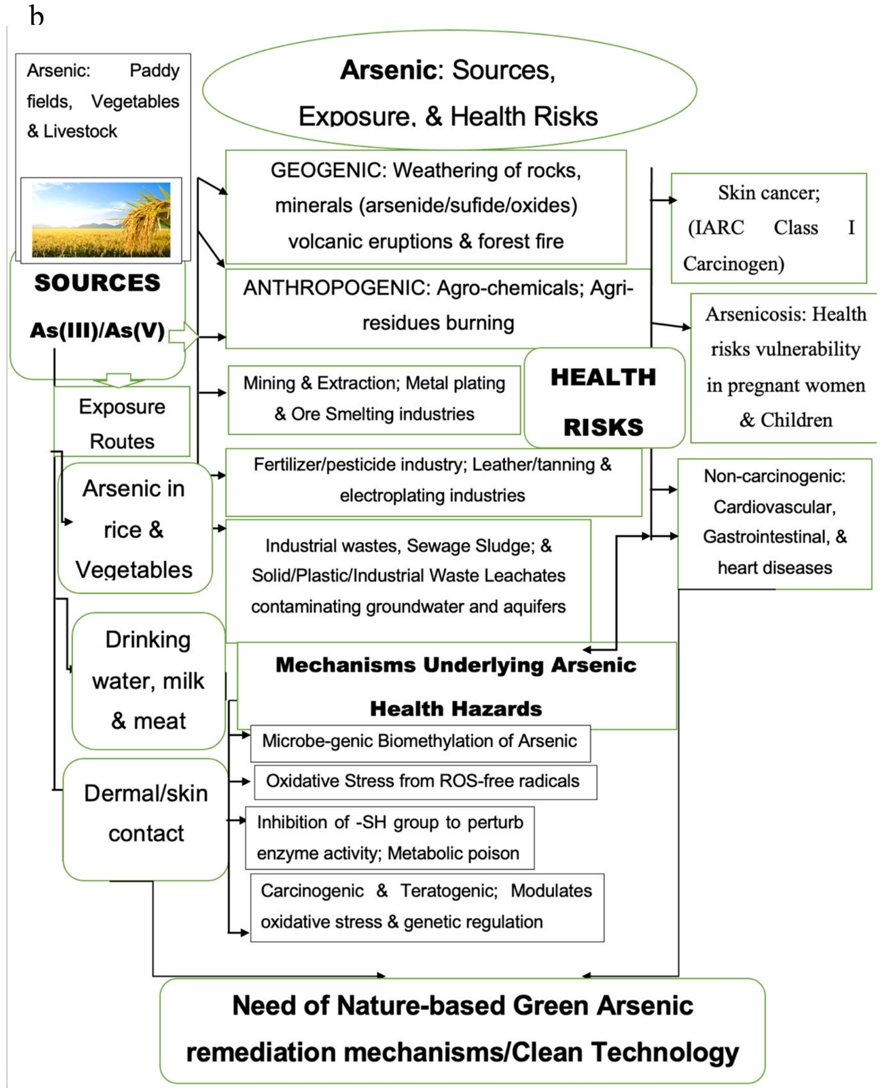

Fig. 1. a-b. Methodology and sources, fate, and health risks of Arsenic contamination **a)** Schematic flow-diagram to explicitly elucidate the methodology adapted in present systematic review; **b)** Geogenic and anthropogenic sources of inorganic-Arsenic [As(III) and As(V)], Exposure routes od As contamination in humans, Mechanisms of hazardous effects, and Public Health risks.

through extensive operation of modern intensive agriculture, relying heavily on chlor-alkali industries derived agrochemicals, like pesticides and fertilizers, in conjunction with metal mining, remarkably added to the natural or geogenic sources of As pollution [7,21]. The As emanating from both geogenic and anthropogenic sources, either tend to mix with clay minerals component or get fixed in soil crystal lattices of agriculture systems [4]. This As-mixing with soil is actively guided by complexation and electrostatic interactions, with SOM (‘soil organic matter’) and ‘Fe-oxohydroxides’ [5,46]. Together these As-intercalation, emanating from either geogenic i.e., weathering of parent rocks/settling of volcanic eruptions on earth surface, or anthropogenic activities based industrial wastes drastically contaminate groundwater-soil-food crops interface in global agroecosystems (Fig. 1**b)**. In this vein, both As pollution sources get potentially mixed with C-soil horizons and during pedogenesis via ‘translocation transformation mechanisms’ effectively join the arable portion of land i.e., O horizon, that is extremely vital for raising staple food crops and vegetables. Also, the regional As-spread in environment can be mediated by the biovolatilization mechanism, forest/wild fires, geogenic, and anthropogenic disturbances [4]. The fate of As contamination in food crops and food chain, especially humans, are discussed in the forthcoming sections and also elucidated in Figs. 2**a and** 2**b**.

3.2. Geographical hotspots of As pollution

Certain geographical landscapes such as those belonging to ‘law-latitude Eurasia’ are widely prone to As contamination, attributed to the considerable anthropogenic perturbations, which is rather tightly aligned with unique climatic and topographic factors [4,17]. The optimum climatic variables such as ‘surface temperature, precipitation, and evapotranspiration’ tends to drive strong weathering or leaching-induced influx, and strong ‘plant-pump effects’ facilitating vertical enrichment, that are the keys to As/other metals-enrichment in the Eurasian region [4,47]. On the contrary uncontaminated metals-As regions, with deep ground frosts and wet climates, demonstrate exactly reverse pattern, restricting HMs/metalloids enrichment [4,47]. Thus, climate and topography can be intimately linked with differential As-enrichment across global agricultural landscapes. In addition to plain landscapes of Indo-Gangetic and Brahmaputra plains, mountain or hilly terrains with variable geological rocks are also faced with As pollution [4]. Notably, in Asian perspective, arable soils of Southern Himalayan regions were observed as potential As pollution hotspots [4].

The ‘metal-enriched corridor’ of Hou et al. [4] comprise Eurasian countries, including ‘agrarian-economy -driven northern and central India’ southern China, South Asia, the Middle East, and Southern Europe, with heightened public health risks. Interestingly, these metal/As-contaminated global corridors are inextricably linked with civilizations, since the time immemorial, like ancient India, Greeks, and the Roman Empire, which extensively used metal smelting and processing tools [4]. Also, Hou et al. predicted that since the nature of metals are persistent or non-biodegradable, these Eurasian countries, underlying in metal-enriched corridor can act as “Keystone Indicator” for the onset of bronze or the Anthropocene era.

Socio-economic indicators and irrigation factors of agroecosystems are inextricably linked with mining/metal-processing geographical landscapes, and in fact act as proxies for metal/As-rich corridors [4]. To this end, Hou et al. [4] noted the maximum As exceedances in ‘southern

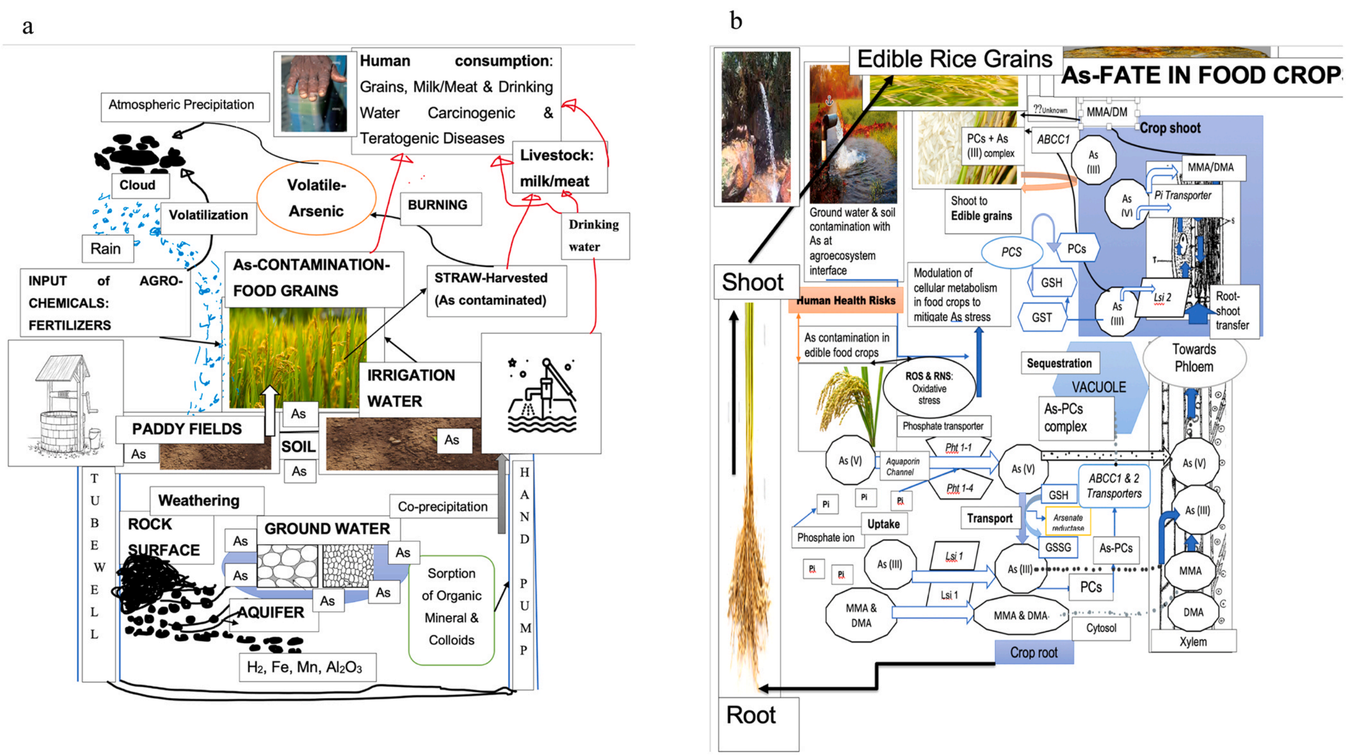

Fig. 2. **(2a-b):** Environmental fate of As in groundwater-agroecosystem soil-food crops interface, eco-toxicity, stress tolerance mechanisms and health risks Fig. 2 **a)** Fate of As-contamination in groundwater-soil and subsequent transfer to food crops and livestock can endanger public health Fig. 2 **b)** Groundwater-soil contamination of arsenic at agroecosystem interface; ROS (Reactive oxygen species) and RNS (Reactive- Nitrogen-species) generation under As stress; biochemical and molecular basis of arsenic stress response; its uptake, transport and sequestration below ground (roots) and above ground (shoots and edible grains). Arsenic-induced ROS and RNS generation and biochemical/molecular basis tolerance mechanism mediated transport and sequestration of As(III)/As(V) below (roots) and above ground (shoots and edible grains) is regulated by transporters (PHT and NIPs). The efflux of As(III) in crop roots is regulated by modulation of rhizosphere chemistry, aquaporin channels, and PC-mediated sequestration inside vacuole and ABC transporters. Further, reduced As-transfer to crop shoots and edible grains is considered as an adaptive strategy for food safety, tightly regulated by Si and PHT-based genes. [Abbreviations: NIPs: Nodulin 26-like Intrinsic Proteins; GSH: glutathione; GST: glutathione S-transferase; PHT: phosphate transporters; GSSG: glutathione disulfide; PC: phytochelatin; PCS Phytochelatin Synthase; MMA: Mono-methyl-arsenate; DMA: Di-methyl-arsenate].

and southwestern China, south and Southeast Asia, West Africa, and central parts of South America'. Surprisingly, Hou et al. [4] observed that these As contaminated soil patches coincides with already predicted areas of high As-concentrated groundwater, as revealed earlier by Podgorski and Berg [5]. This validate the concurrent interrelationship of As contamination between groundwater and soil, which potentially bio-accumulate in food crops, thereby perturbing sustainable agriculture, human well-being, and planetary public health [6].

3.3. Health risks

The burgeoning food security crisis forced a larger fraction of global human population to compromise with food safety or public health and are bound to live in close vicinity of health hazardous metals/-As contaminated agricultural landscapes to consume their staple food crops [4]. The consumption of As contaminated food crops can perturb human health [22]. As stated earlier, IARC classified As in the list of class I carcinogen, whose long-term exposure to high As-concentrations can lead to skin/dermal, lung, and bladder cancer [6]. In addition to cancer, dietary intake of As contaminated food crops can worsen existing non-carcinogenic diseases such as 'ischaemic' heart disease, neurodevelopmental complications, and diabetes [48]. Pregnat women and children of 1–5 years age, with inadequately developed immunity are vulnerable to As toxicity, ascribed to teratogenic or embryo-toxic effects and adverse impacts on immune systems [6]. It is therefore quite evident that As contaminated agriculture systems in these ecologically sensitive countries can significantly perturb food safety/-security and planetary public health (Fig. 1**b)**.

4. Factors and mechanisms impacting ARB-induced arsenic remediation

4.1. Factors influencing ARB-induced As remediation in agroecosystems

Several factors of ARB need to be optimized for effective As remediation in agriculture systems, which is in fact manifested through leveraging of associated physico-biochemical, oxidative stress tolerance, and molecular mechanisms [49–52]. Selecting ARB-dose can favourably modulate the mechanisms underlying As remediation from agriculture systems [53]. For instance, ARB-dose of 3% was observed to be most effective in alleviating labile metals/-metalloids like As, Sb, Ni, and Cr pools, and concomitantly fostered soil health by increasing nutrient, especially C-source, to be potentially utilized by microbes [53]. Importantly, ageing of nano-biochar or ARB in variable soil types can also influence As remediation in environmental matrices. For example, freeze–thaw-technique demonstrated that different ageing processes of 'cerium (Ce)-Mn' nano-biochar in contrasting soil types like red and black can also influence the As remediation [33].

4.2. Chemical Mechanisms

Multiple physico-chemical mechanisms such as ion exchange, surface complexation, electrostatic interactions, and precipitation are associated with As-adsorption onto the ARB surface [54]. The HMs-removal mechanisms can be metals/-metalloids specific, such as for Cd and Pb sorption, cation exchange and precipitation are noted to be the prime mechanisms [55]. Likewise, Cr and Hg adsorption is ascribed to complexation and reduction mechanisms. However, complexation in conjugation with electrostatic interaction facilitated the As-adsorption [55]. Therefore, elucidating the As remediation and stress tolerance mechanisms in food crops can be variable, when compared with other HMs [55,56].

Agro-industrial-waste like grass, rice straw, and wood were applied to remediate mine soil contaminated with As, Cd, Pb, and Zn [16]. Herein, rice and grass-ARB were quite useful in As immobilization, ascribed to the formation of less stable forms of 'Fe-oxide-bound-As', such as goethite and ferrihydrite, which was in tight conjugation with reduction of arsenic ions from As(V) to As(III). Whereas, the general mechanisms of forming dissolved aliphatic- and aromatic-C, sulfur chemistry, phosphate competition, and the electrostatic repulsion was ascribed to removal of multi-metals (e.g., As, Cd, Pb, and Zn) from mine soil [16]. In case of wood-based-ARB, oxygenated functional like hydroxyl (-OH) and carboxyl (-COOH) groups induced the immobilization of Pb-ions into hydroxides and carbonates [16]. In recent perspective, 'Nitrogen (N)-rich *Spirulina platensis*- Ca–N-co-doped ARB (SPCaN-ARB)' resulted in highly porous structure and larger specific surface area (S.S.A.), with increased structural stability in view of Ca-doping [57]. Herein, Choi et al. [57] noted high As-adsorption at variable pH, ascribed to 'electrostatic attraction, surface complexation, and Ca-mediated precipitation'. Together, these studies confirmed the role of chemical interactions in As remediation from soil and groundwater.

4.3. Biological mechanisms

In addition to physico-chemical techniques, biological i.e., plant-microbes interaction was noted to be the major mechanism for ARB-induced As remediation in case of water fern [58]. In this study, biochar applications remarkably increased the biomass of water fern, a potential As-hyperaccumulator from environmental matrices [58]. The underlying mechanism behind the favorable biomass growth of water fern and increased As-phytoremediation was in fact ascribed to increase in "Soil Organic Matter" (SOM content), nutrients like N, Phosphorous (P), and Potassium (K), enzyme activities, and bacterial abundance (e.g., *Streptomyces* by 26.6–54.2%) and *Sphingomonas* (12.3–30.8%) [58]. Metals/metalloids-induced oxidative stress caused by 'reactive oxygen species' (ROS) and methylglyoxal (MG) can perturb the normal metabolic processes of food crops [59]. To counter the As-induced oxidative stress, antioxidant response pathways are catalysed through modulation in the levels of enzymes, osmolytes (e.g., proline), and glyoxalase cycle efficiency [59].

In case of As toxicity in rice, the applications of phytohormones like brassinosteroids, salicylic acid, and jasmonic acid can induce the enzymatic and nonenzymatic antioxidant pathways by modulating the gene expressions [40]. Further, Shaghaleh et al. [40] observed that applications of these phytohormones can remarkably decreases the proline metabolism and Ascorbate-Glutathione (AsA-GSH) cycle to potentially reduce the As-stress in rice. Thus, nano-biochar or ARB-applications can favorably modulate the biological parameters of soil and As-hyperaccumulators to enhance the remediation potential of this hazardous metalloid [42,59].

4.4. Mechanism of Nano-Biochar ARB-driven As remediation in rice

A plethora of mechanisms and factors can influence the efficacy of ARB in As remediation from paddy fields. For instance, ARB-mediated As-adsorption in paddy agroecosystems is tightly regulated by surface functional groups [60]. In this sense, As-immobilization in rice fields are further dependent on the methods of ARB-generation and nature of feedstock selected for producing ARB [60]. For instance, ARB produced from low temperature pyrolysis, effectively increased the S.S.A. and ash content. However, these parameters are of least importance in As-adsorption from paddy soil [60]. On the contrary, ARB resulting from high pyrolysis temperature i.e., > 450 °C get enriched in aliphatic C chains, with intense tendency towards aromatization. Notably, such ARB resemble structural configuration, quite similar to graphene, with increased pore volume, presence of mineral phases (e.g., $CaHPO_4$, $Ca_3(PO_4)_2$, $CaCO_3$), and oxygenated functional groups [60]. Importantly, on ARB surface, these oxygenated functional groups potentially act as electron donor to potentially reduce As(V) into As(III), by offering effective adsorption sites [61,62]. Moreover, ARB, especially those valorised from forestry and agricultural wastes, are endowed with rich contents of lignin, cellulose, and hemicellulose [60]. This makes them suitable feedstock for ARB-production through pyrolysis at high temperature, enabling effective As-adsorption from rice fields [60]. In different microbial biochemistry perspective, As contamination in paddy fields can disrupt functional groups associated with protein molecules, replace enzymes, stimulate release of cell wall degrading cytotoxic compounds, thereby inhibiting the methanotrophs to reduce methane production [63].

The deployment of nano-scale biochar or nano-ARB widely accelerated the As remediation effectiveness in paddy agroecosystems. For instance, 'nanostructured pork bone biochar (NPBB)', pyrolyzed at 400 °C (NPBB400) and at 600 °C (NPBB600) alleviated the As-bioaccumulation in rice roots/shoot tissues, with the simultaneous induction in microbial population of *Ceratobasidium*, *Bacillus* and *Achromobacter* [64]. In this sense, elucidation of Hao et al. [64] on metabolomics revealed that NPBB induced the 'differentially expressed metabolites' in the form of biomolecules, potentially reducing the As-induced phytotoxicity in rice.

Bio-accumulation of As(III)/As(V) in rice and vegetables are mediated by 'nodulin 26-like intrinsic proteins (NIPs)' and 'phosphate transporters (PHT)'; in which 'aquaporin channels and PC'-assisted vacuolar sequestration play a crucial role [65,66]. Importantly, conversion of As(V) to As(III) is obligatory for the mitigation of As-induced oxidative stress in soil-food crop interfaces. In this vein, As(III) is the only ionic form that can effectively conjugate with PCs to be sequestered inside vacuoles, thereby resulting in reduced As-phytotoxicity to food crops [67]. Consequent upon As(III)-sequestration inside vacuole, ABC transporters facilitate efflux from food crops [56,67].

In As-stressed paddy fields, ABC transporters, *OsNRAMP1*, aquaporins, membrane channels, xylem, and phloem loading act in concert to improve oxidative defense [56,67,68]. Another study on As-stress tolerance in rice revealed the vital role of Si-based *OsLsi1/OsLsi2* in lowering the As-uptake in edible rice grains [69,70]. Herein, *OsLsi1/OsLsi2* tightly regulated the As-xylem/phloem loading in rice to address toxicity in food grains. Arsenic-stress tolerance in rice is also mediated through phosphate transporters (PHT) such as *OsPHT1.1* and *OsPHT 1.8* [66]. This As-induced antioxidative defense in rice is also assisted with aquaporins such as NIPs and the Si-influx transporter *Lsi 1/2* (low silicon rice 1/2; *OsNIP2;1*) [56,67,70]. Fig. 2 **(a-b)** explicitly elucidates the fate and As-transfer mechanisms from ground-water-soil to food crops and biochemical/molecular basis of As-stress tolerance.

Aside, from deployments as nano-biochar, nano-scale particles (NPs) in isolation also demonstrated to potentially deal with As-induced oxidative stress [68,71,72]. For instance, application of FeNPs effectively boosted the glyoxalase system, antioxidant responses, photosynthetic pigments, and chelation reactions to alleviate As-stress in rice crops [73]. Concomitantly, FeNPs supplementation to rice potentially downregulated the expression of genes associated with As-uptake, specifically, *Lsi1* and *Lsi2* [73]. In addition to Fe, the use of Silicon (Si) and silica-based NPs as nano-fertilizer was also useful in detoxifying As-induced oxidative stress and phytotoxicity in rice and vegetables [70]. Interestingly, both As(III) and Si use analogous transporters for their uptake in food crops [70]. In this vein, SiO_2NPs upregulates antioxidant enzymes such as catalase (CAT) and simultaneously reduces lipid peroxidation to restrict As-accumulation in food crops [70,74]. Further, in case of rice, SiO_2NPs deployments in paddy fields resulted in alleviation of As-stress, mediated by downregulation of *Lis 1* and *Lis 2* with synchronous upregulation of *OsNIP1;1* and *OsNIP3;3* genes.

Nano-biochar applications like those of 'Nano-ferro-silicon biochar (NNFB)' - γFe_2O_3, and SiO_2 effectively alleviated the As-induced oxidative stress in rice by scavenging 'reactive oxygen species' (ROS) with concomitant reduction in peroxidase (POD) and hudrogen-peroxide (H_2O_2) levels [31]. Besides, biochemical factors, Fang et al. [31] observed that NNFB facilitated molecular modulation of As transporter genes *OsABCC1*, *OsLsi1*, and *OsLsi2* to reduce its uptake in rice, thereby increasing food safety and yield. Variable ARB-doses in conjunction with alterations in water regimes e.g. *via* 'alternate wetting and drying (AWD)' in paddy fields can remarkably influence the bioavailability of As, Si, P, and S in the soil [75]. These 'ARB-AWD' fluctuations potentially modulate the molecular mechanisms, especially those linked with the expression of As transporters. In this sense, Khanam et al. [75] emphasized that ARB-AWD variations enhanced the competitive interactions between As, and Si, and P, thereby, downregulating *OsLSi1*, *OsLSi2* and phosphate (e.g., *OsPT1* and *OsPT2*) associated co-transporters. Importantly, addition of sulphur induced the biosynthesis of phytochelatins (PCs), which in concert with molecular changes reduced the As-concentration, hence producing pollution-free rice cultivars [75]. These ameliorative effects of NPs on As-induced stress and food crops-toxicity, necessitated integration of nanomaterials with ARB to result in novel nano-biochars for food safety and sustainable agriculture [21,71,72].

5. Designer nano/-magnetic biochars for enhanced As remediation in food crops

Pristine-ARB were widely used in As remediation from agriculture systems. Table 1 lists the As remediation studies by using ARB-technology. For instance, rice straw-derived-ARB, from pyrolysis at 600 °C, demonstrated higher adsorption capacity for As (4.51 mg g^{-1}) and Mn (3.61 mg g^{-1}) [76]. This was chemically ascribed to higher S.S.A. (78.17 $m^2 g^{-1}$), in conjugation-with effective electrostatic attraction between metalloids-duo i.e., 'As-Mn', and oxygenated functional groups like -COOH and -OH [76]. The pristine-biochar are although capable of As removal, however, engineered or functionalized nano-biochar composites are more efficient C-phytotechnologies for its remediation [6,57]. The methods for production of pristine and designer-ARB are elaborated in Fig. 3 **(a-c)**. In this sense, pristine or un-modified biochar applications can be constrained by a multitude of abiotic and biotic factors or interactions in case of in agriculture systems, which can drastically limit their As remediation efficiency [77]. In this vein, a metanalyses by Arabi et al. [77], during the time-frame of 2006–2019, validated the potential of biochar in As remediation however, the removal was observed to be impacted by pyrolysis temperature, time, soil organic matter (S.O.M.), and further site conditions of agro-ecosystems. In this respect, the As remediation was found to be effective at pyrolysis temperature > 450 °C, high residence times (>1 hr), low S.O.M. (<3%) [77]. Nevertheless, metanalyses revealed that the pristine-ARB-mediated As remediation was quite challenging than Cr and Ni, therefore advocated the techno-economic innovation of designer or engineered biochar to encourage scalable nano-biochar deployments in vulnerable landscapes [71,72]. Therefore, the efficiency of pristine-ARB in As remediation can be remarkably enhanced through the engineering or customization with nano-scale particles (NPs) [71,72,78].

Meta-analysis of deploying engineered-biochar for As remediation revealed that 'sewage sludge-amended-maize biochars (SMBC)' were observed to be more effective than the pristine ones, especially in relation to their efficiency in decontaminating As-polluted paddy fields [60]. In this respect, designer-SMBC were able to reduce exchangeable-As concentrations in paddy soils, while significantly elevating the Fe- and Ca- bound-As fractions, nutrient uptake, 'cation exchange capacity' (CEC), and S.O.M. contents in paddy soils [60]. Thus, the designer ARB can potentially leverage the As remediation from paddy fields for enhancing global food safety.

5.1. Methods in customizing designer ARB

There exists a multitude of production methods for engineering or customization or maneovoring of ARB, to generate designer or nano-biochar [21]. In chemical modification, both acidic i.e., H_2SO_4, HNO_3 and HCl and basic chemicals like $KMnO_4$ are supplemented during pyrolysis of biochar, to effectively enhance HMs sorption potential [86]. This increased remediation is mediated by increase in S.S.A., surface

Table 1
Efficiency of Agri-residues-derived biochar (ARB) in As remediation and associated mechanisms, unveiled in past studies.

S. No.	Agri-residues feedstock for ARB; operating pyrolysis temperature	Modification/activation method of agri-residue based biochar/nano-biochar	Target HMs	Extent and efficiency of remediation	Mechanism	References
1.	Red oak; Switchgrass; 600^{0}C	Magnetite	As (III)	Maximum adsorption for As is 15.66 mg/g	The Fe present in the magnetite was pyrolyzed to ZVI, facilitating the binding of As (III)	Bakshi et al. [79]; Wang et al. [80]
2.	Sugarcane leaf; 550^{0}C	Nano-size MgO flakes	As & Pb	57 mg As^{5+}/g 103 mg Pb^{2+}/g	As and Pb-remediation was mediated through nanotube like carbon sponge formation and enriched functional groups	Li et al. [81]
3.	Rice, peanut & soyabean Straw;; 750^{0}C	Aluminum-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. [82]
4.	Bamboo; 600^{0}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. [83]; Wang et al. [80]
5.	Rice husk and fruit residues; 450–500^{0}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. [84]
6.	Hickory chips; 600^{0}C	Fe(III) impregnated biochar	As	Higher adsorption potential of 2.16 mg g^{-1} than raw/ unmodified biochar	Fe(III) impregnated biochar induced As-chemisorption	Hu et al. [85]

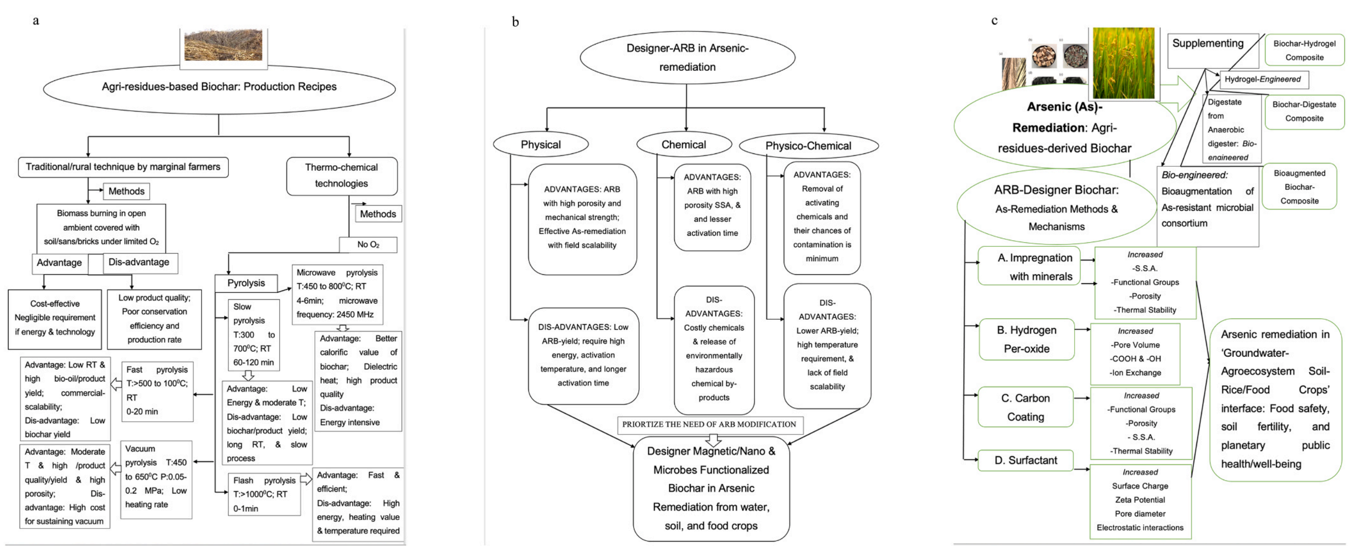

Fig. 3. (a-c). Critical evaluation of different methods in production of pristine and designer-ARB in terms of advantages and disadvantages to standardize the biochar deployments in As remediation from 'groundwater-soil-food crop interface' Fig. 3 **a)** Recipes for producing pristine biochar through thermo-chemical technologies Fig. 3 **b)** Physico-chemical methods and Fig. 3 **c)** other advanced chemical methods in technological innovation of designer-ARB.

complexation/-precipitation, and creation of abundant As-sorption sites. However, for chemical modifications of biochar, the use of certain chemicals such as H_3PO_4 and H_2O_2 are preferred, in terms of environment friendliness, unlike strong acids like HNO_3, which can cause micropore well-degradation and reduction in biochar-S.S.A. Qian [86]. In this sense, H_3PO_4 can decompose aliphatic, aromatic, and ligno-cellulosic compounds and form the polyphosphate cross bridges, which prevent the shrinkage of biochar in agroecosystem soil, especially, during their long-term applications. Amendments of biochar with organic acids, like oxalic acid, induce ligands and proton promoted processes that enhance HMs sorption [21,86]. Efficiency of Fe-impregnated magnetic ARB in As-adsorption can be potentially increased with high concentrations of H_2SO_4 [78].

Agro-industrial-wastes have been widely engineered to result in designer ARB or nano-biochar, with enhanced As remediation efficiency [64]. In this vein, designer ARB such as chestnut shell, on customization with magnetic gelatine, resulted an enhancement in the As-adsorption, from 17.5 mg/g to 45.8 mg/g [87]. In another study, 'magnetic calcium-based-biochar composite (MCBC)' demonstrated high As(V) adsorption potential of 119.7 mg/g, attributed to the mechanism of complexation, electrostatic attraction, and deposition [88,89].

Magnetic or nano-biochar are usually customized with micro/nano-scale Fe/-oxide particles, which have revolutionized the ARB-technology in As remediation from agriculture systems [45,49–51,78]. For instance, magnetic-ARB, when amended with Fe and calcium (Ca), was observed to potentially remove 85% of As(III) and 98% of Cd(II) from contaminated wastewater [159]. In other perspective, it has been elucidated that Fe_3O_4 magnetic particles modified 'cedar sawdust-based-biochar (CSB)' adsorbents, resulted in rapid and simultaneous removal of 20–30% of As, Cd, and Pb from contaminated soil [90]. However, Wan et al. [90] observed that the CSB-induced remediation of metallic contaminants was actually dependent on stability of Fe-oxides [90]. In this sense, another study used MCBC, which demonstrated high As(V) adsorption potential of 19.7 mgg^{-1}, ascribed to the chemical mechanisms of complexation, electrostatic attraction, and deposition mechanism [88,89].

Customized magnetic-ARB, with modulated Fe and pore space, were found more effective in As(III)-adsorption, especially when coupled with microwave irradiation [91]. Consequently, it results in immobilized or relatively non-toxic form of As-containing mineral crystals i.e., $FeAsO_4$ and Fe_3AsO_7, which can prevent the soil and food crops contamination for human well-being [91]. Mechanism-wise, magnetic-ARB coupled with microwave irradiation facilitated electron transfer, thereby encouraging As(III)-oxidation in soil-food crop interface [91].

Impregnation of either metals such as Magnesium (Mg) or their complex derivatives can also enhance the ARB-effectiveness in As remediation [49–51]. For instance, application of 'Mg-aluminium-modified-biochar (MABs)' effectively slowed the As-migration in conjunction with Pb and Cd in soil, ascribed to immobilization mechanisms of ion exchange and surface-complexation [92]. However, Peng et al. [92] observed that possible field-scale environmental factors, such as presence of organic acids like oxalic acid, effectively decreased the MABs mediated immobilization of As, Pb and Cd, up-to the range of 15.5%–38.5%. In this aspect, the effects of HA in reducing Pb immobilization was higher (89.7%), while on the other corner, HA increased the Cd remediation by 19.5%, thereby manifesting metals-specific effect of organic acids. Also, in this aspect, the application of stimulated rainfall, having pH range of 4–8, resulted in the increased HMs immobilization efficiency of MAB, especially in alkaline conditions [92] (Fig. 3**b-c**).

5.2. Nano-ARB in As remediation from soil- groundwater-food crop interface

Nano-biochars have gained considerable attention in As remediation from soil- groundwater-food crop interface of venerable global landscapes. Nano-biochars are endowed with intrinsic chemical mechanisms to potentially adsorb As in agricultural systems for ameliorating soil fertility, crops yield, nano-sensing, C-sequestration, and climate resilience [29,42]. Nano-biochar formulations can leverage the As remediation by improving soil physico-chemical parameters and crop yields, mediated by better nutrient retention and colonization of beneficial microbial diversity [3,15]. For example, magnetic 'Nano-sized bentonite -amended date palm-derived biochar' (NBDPBC), with optimum application dose of 3%, was noted to be effective in As-decontamination from agricultural systems [93]. In this respect, nanbo-biochar i.e., NBDPBC deployment in microcosm arable soil, contaminated with 100 mg kg^{-1} As resulted a decline in As root concentration by 34–38%, while decrease in shoot, at same As concentrations was noted to be in the range 59% [93]. Therefore, nano-biochar in the form of NBDPBC can be successfully used for As remediation in agroecosystem soil, wherein phytoremediation is effectively driven through the mechanism of phytostablization.

In perspective of aquifer/groundwater recharge technique for safe or As-free drinking water supply, between pristine pine wood-ARB (PWARB) and engineered iron-impregnated magnetic Fe-PWARB in As (V), the engineered magnetic ARB was found to be more effective [45]. In this vein, Kumar et al. [45] indicated that higher As(V) adsorption of Fe-PWARB, compared to one, was ascribed to its facilitated adsorption on magnetic ARB-active sites. Among the different agricultural wastes, orange peel, banana peel, and rice husk-ARB were noted to quickly remove up-to 100% of As (wherein initial concentration was 10 μg/L) from contaminated groundwater [94]. However, in this study, higher As levels of 100 μg/L slightly reduced the As remediation, lying in the range of 90%.

Groundwater As contamination can also be addressed by ARB technology, specifically those derived from ecologically harmful invasive alien plants (IAPs) of marginal or degraded landscapes. For example, the *Lantana camara* L.- residues derived ARB at optimum temperature of 500 °C modulated physico-chemical attributes and surface functionality, enabling As-adsorption capacity of IAP [95,96]. Herein, plant parts adsorbed up-to the extent of 5.47 mgg^{-1}, while lantana leaf-litter-based-ARB demonstrated adsorption in the range of 6.36 mgg^{-1} from As-contaminated groundwater samples that were collected from sensitive or vulnerable Jharkhand state of India [95,96]. In terms of chemical mechanism, *L. camara*-based-ARB demonstrated exothermic As-adsorption, which followed Freundlich isotherm and pseudo-second order kinetics, wherein reusability was sustained up-to five cycles [95, 96]. Therefore, biomass of global IAPs can also be valorized into sustainable biochars for As remediation [97].

Green ARB-based adsorbents such as 'water-hardened magnetic composite biochar sphere (WMBCS)' can be effectively recovered or regenerated by EDTA-2Na with assistance of ultrasound [98]. In this aspect, WMBCS can potentially result in As-decontamination up-to the extent of 5.0–25.6%, simultaneously along-with with the remediation of other HMs to facilitate sustainable agriculture [98]. In this perspective, functional magnetic-ARB, enriched with Fe and increased pore space was found more effective in As(III)-adsorption, when coupled with microwave irradiation [91]. In this vein, effective As-ion by magnetic-ARB is in fact guided by immobilized form of 'As-containing mineral crystals ($FeAsO_4$ and Fe_3AsO_7)', which can have an intricate implication in ameliorating As-toxicity in edible crops for increased food safety. In this vein, Zhang et al. [91] elucidated that magnetic ARB-facilitated electron transfer to encourage As(III)-oxidation at soil-food crop interface [91]. In another study, Lanthanum-modified biochar (La-ARB) at dose of 1 g/kg was found effective in As remediation from rice, wherein La can impart roughness to ARB surface by forming La-OH groups and 'La-O-As complex' [49–51]. The La-ARB-induced As remediation in rice was mediated through modulation in increased soil physico-chemical attributes like pH, CEC, and SOM, in concert with Fe-plaque sequestration, thereby stabilizing the bioavailable As species [49–51]. Thus, bioengineering or nano-engineered-ARB from crop-residues, woody agroforestry/-forestry plantations, sewage, and livestock waste can easily complement the As remediation in groundwater-soil-food crop interface for enhancing environmental health and human well-being [10].

5.3. Alleviation of As-induced Oxidative Stress in rice and food crops by using SiNPs-melatonin functionalized Nano-Biochar

The ARB-functionalized with Silicon (Si) NPs are cost-effective nano-biochar options in mitigating As-induced phytotoxicity in staple food crops and vegetables by modulating their ROS-induced anti-oxidant responses [31,32,49–51]. Rice-residues are rich in Si, therefore offering potential applications in ARB technology to mitigate As-driven oxidative stress in paddy fields. For instance, applications of 'rice straw-derived-ARB, impregnated with Silicon (RSBC-Si)', effectively mitigated As-induced oxidative stress with significant ($P < 0.05$) increase in plant growth, biomass accumulation, gas-exchange characteristics, enzymatic/non-enzymatic anti-oxidative defence [99]. In line with modulation in morphological and biochemical antioxidant responses, Alwutayd et al. [99] elucidated RSBC-Si-induced alteration in gene expression, enhancement in cellular fractionation, decreased proline metabolism, and altered 'ascorbate-glutathione (AsA–GSH)' cycle, in case of rice crop seedlings.

In barley crop, higher dose i.e., 20 mg $kg^{-1}$of As-induced phytotoxicity and oxidative stress was effectively mitigated through immobilization by SiNP-functionalized-ARB [100]. In this study of Naeem et al. [100] 'cotton shells-derived biochar (CSBC)' increased barley yield by 51%, while its SiNPs-amended version ameliorated productivity up-to 71%, thereby confirming the increased efficiency of nano-biochar. In this vein, best nano-Si-formulated ARB treatment was recorded to enhance the grain yield by 94%. This nano-biochar or CSBC-induced barley yield was ascribed to better operation of photosynthetic processes and ameliorated antioxidative responses. Therefore, CSBC, amended with SiNPs can effectively perform As-immobilization and reduce its phytotoxicity in barley plants [100]. As stated, CSBC-nano-biochar potentially reduced oxidative stress, mediated through reduction in 34% H_2O_2 and 48% monoaldehyde (MDA) content. On the contrary, Naeem et al. [100] observed CSBC-nano-ARB driven enhancement in As-stress tolerance in barley crop, manifested through elevation in POD and Ascorbate peroxidase (APX) activity by 92% and 46%, respectively. In brief, the holistic nano-biochar driven As remediation in soil-barley crop interface resulted in low human health risk (HQ < 1), thereby enhancing food safety to effectively mitigate human health risks.

The soil amendment with nano-biochar (1% w/w) and foliar spray of melatonin (100 μM) on *Glycine max* L. (Soybean remarkably reversed the multitude of As-induced oxidative stress pathways or ROS-driven adverse influence on physico-biochemical parameters [52]. In addition, the synergy of 'nano-ARB- melatonin' effectively enhanced the Soybean growth attributes, in conjunction with metabolic attributes like photosynthetic efficiency, and nutrients uptake. Further, Gulsah et al. [52] noted that this 'nano-ARB-phytohormone' synergy combated the As-toxicity by increase in proline (34%), starch (23%), and sucrose (19%) contents, which acted in osmo-protection and As-stress tolerance in selected food crop. Similarly, exposure of As and ROS-induced oxidative stress in Soybean was effectively reversed by the supplementation of 1% w/w nano-biochar, *via* modulating MDA and H_2O_2 levels, though explicit anti-oxidative stress tolerance or biochemical defence mechanisms are yet to be elucidated [101]. Magnetic biochar, especially those impregnated with Fe, remediated As-contamination in saline soil, mediated through mechanisms of 'complexation with iron oxides, redox transformation, and adsorption' [49–51]. Therefore, nano-biochar improves food crops safety for planetary public health, fostered by modulation of As-induced oxidative stress tolerance pathway, redox homeostasis, and phytotoxicity [31,52,101].

Nanobiochar derived from amendments of agricultural waste with titanium oxide nanoparticles (TiO_2-NPs) reduced As accumulation in rice grains through remarkable alleviation in oxidative stress [8]. This As-induced elevation of oxidative stress tolerance pathways were manifested in rice through decreased electrolytic leakage, with synchronous reduction in MDA and H_2O_2 levels. Functionalized nano-biochar modified with chitosan reduced As concentrations in paddy soil by 21% and in rice grain up-to 43%, which is attributed to restricted As-mobility mediated by cell wall binding and Fe plaque formation [3]. Interestingly, in this study of Li et al. [3], natural ageing of nano-biochar elevated As-sequestration, that was guided by Fe in case of rice.

5.4. Microbial functionalization

In context of ARB-functionalization with microbes, peanut shell-ARB, immobilized with Proteus alimentorum strain TY6 and Pseudomonas aeruginosa strain K7Pb, duly encapsulated with 'polyvinyl alcohol-sodium alginate' was sustainably used for As remediation, that can be sustained even up-to eight cycles [25]. Therefore, ARB-encapsulated bacteria was noted to be better in As-adsorption, when compared with biochar immobilized with 'free cell bacterial consortium. Microbe-assisted ARB efficiency in reducing As(V) and Fe (III) was observed higher when compared to pristine biochar [102–104], In this vein, [102–104] observed that increased abundance of microbes such as *Geobacter*, played a crucial role in As(V) reduction, while another bacterium i.e., *Clostridium* was found effective in Fe(III) reduction [102–104].

The applications of 'zero-valent-iron (ZVI)' to amend pristine biochar, effectively reduced the As-bioavailability by 64.2%, when compared with control [88,89]. However, nano-remediation was remarkably influenced by soil physico-chemical attributes, especially S.O.M., as the removal was mediated through formation of 'As-Fe-SOM' complexes [88,89]. Thus, the agroecosystem soil, deficient in SOM, compromised the As removal up-to the extent of 289.8%, which can be attributed to increased contents of fulvic acid and hydroxyl (-OH) ions. However, the increase in Fe(III) concentrations and abundance of As (V)-reducing bacteria such as *Bacillus* and *Ammoniphilus*, under the event of endogenous SOM depletion, effectively acted as defence wall to restore As remediation [88,89]. Applications of nano-biochar, such as Fe-Mn-impregnated ARB can induce synchronous As, thallium and vanadium immobilization up-to the extent of about 70% [160]. This customized-ARB-induced As removal was ascribed to elevated pH induced 'Fe–Mn (hydr)oxides'-driven immobilization, oxidation of contaminants, and most importantly, the increased availability of adsorptive-sites on nano-biochar [160].

Microbe interactions such as those of *Shewanella oneidensis* MR-1 was demonstrated in case of on As-retention in Fe (hydr)oxide-based ferrihydrite – and goethite-enriched biochar (F-ARB and G-ARB) [6]. Further investigations during flooding-drying/anaerobic-aerobic fluctuations conditions in pak-choi seedlings revealed that stable As-passivation was observed in case of G-ARB. This research on effectiveness of G-ARB by Wang et al. [6] in variably flooded, either aerobic and anaerobic or oxidized/reduced conditions was useful in real-time monitoring of As-adsorption, in the fluctuating environmental conditions. Moreover, microbe-G-ARB interactions was crucial in devising sustainable agronomy practices in terms of standardized irrigation strategies and site-specific crop cultivation for augmenting sustainable agriculture under the event of As-stress [6]. The integration of AgNPs with microbial inoculum such as *Bacillus subtilis* can effectively capture ROS to favourably modulate the antioxidant responses under the event of As stress in wheat, besides ameliorating morphological growth parameters and crop yield [36].

5.5. Macrophytes-based designer biochar in Arsenic-remediation

Macrophytes possess remarkable potential in ameliorating As pollution from multiple environmental matrices, ascribed to their oxidative stress tolerance pathways [105]. Emergent wetland plant e.g., Reed (*Phragmites* sp.)-straw-derived ARB on subsequent modification with goethite demonstrated to be effective in As(V)-adsorption [106]. In this respect, As(V) remediation was mediated through chemical mechanism of ion exchange, electrostatic interaction, and precipitation. Furthermore, As(V) adsorption was mainly ascribed to the process of reduction [106]. Another emergent macrophyte, *Eleocharis dulcis*-derived ARB, metal-impregnated with Cu, produced composite/-functionalized bio-derivative, that resulted in better AsO_4^{3-}-adsorption [107]. This remediation was chemically demonstrated by Ud Din et al. [107] through Langmuir isotherms and Ho and Mckay's plot, while adsorption mechanism was well elucidated by the Clark model. Another agri-residue in the form of fruit waste i.e., pomelo peel-derived ARB, enriched with colloids demonstrated As(III)-adsorption (1732 mg/kg), in later stages of remediation [108]. Nonetheless, this delayed As(III)-remediation was noted to be quite higher than antecedent As(V)-adsorption up-to 75.7 mg/kg. In this aspect, high As(III)-adsorption by colloidal interface was in fact ascribed to higher electron donating capacity of 8.26 $\mu mol_{e-}/g$, which was remarkably higher than those of residual fraction (0.88 $\mu mol_{e-}/g$) [108]. Therefore, HMs remediation phytotechnologies can be augmented with ARB-supplementations.

6. Arsenic-contamination in global paddy fields and biochar-driven remediation

Arsenic contamination in groundwater, paddy soil, and rice crops is now widely recognized as global challenge, in view of possible human health concerns ([1,23]; [6]). In this sense, Asian countries contribute to about 75% of global rice production, a staple food crop, widely influenced by As contamination in 'Groundwater- soils' interface of paddy fields [4,37,109]. An important study by Rahman et al. [23] in highly As-contaminated zones of Bangladesh revealed that 40 mg $Askg^{-1}$ in soil resulted in 0.570.02 $mgkg^{-1}$ As in rice grains, which may cause 0.20–0.35 $mgday^{-1}$ intake of As, considering the daily consumption of rice to be lying in the range of 400–650$gday^{-1}$. In this vein, the As-toxicity was demonstrated to be of heightened human health risks in view of direct high dietary intake of rice grains and indirectly by adverse influence on livestock due to consumption of As-enriched-straw, contaminating milk and meat (Rahman, 2008). Therefore, As contaminated rice, milk, and meat can pose serious threats to human health.

Exposure of rice to As contamination has remarkably impacted it's agronomic or plant growth traits, photosynthetic processes, and yield, manifested through ROS-mediated oxidative stress [110]. The quest of NBGS is still on the rise to address this As-challenge in cost-effective and environmentally sustainable way [21]. Considering the wider consumption of rice in many countries as staple food crop, the ARB or their engineered derivatives can be a NBGS to As contamination in paddy fields ([23]; [43]). For instance, the application of P-loaded-ARB can reduce the As contamination in rice fields by conversion of hazardous Arsenite (ion AsO_3^{3-}) to less toxic form Arsenate (ion AsO_4^{3-})) [43]. Notably, Iron (Fe) plays a vital role in As-immobilizing capacity of soil, however, ferro-lysis may escalate its levels due to release in paddy fields [111]. Manganese oxide-modified-ARB was observed to reduce As-concentration in brown rice while concomitantly increasing the food crop growth and productivity [112]. In another study, bismuth (Bi)-amended wheat straw-ARB regulated the ferro-lysis process in a paddy fields by promoting the reduction of Fe-oxides and facilitating arsenic-adsorption, mediated through additional micropores and increased S.S.A. Zhu [113].

6.1. Challenges in biochar-based As remediation from paddy fields

Arsenic is found to be less mobile in ARB-conditioned acidic soils due to increase in As-adsorption process on Fe-oxides [114]. Furthermore, in environmental media, chemical processes or mechanisms like precipitation, adsorption and coulombic or ion exchange; and Lewis acid-base interaction can act in concert or independently, in order to remove As (IIII)/As(V), however, their selective removal is still a challenge [115]. In this perspective, the selective As(V)-removal is further complicated in view of its comparable chemical affinity with phosphate [115].

Several studies confirmed that Cadmium (Cd) and As are widely observed to co-exist, especially in paddy fields, which on subsequent bio-accumulation in tissues of rice food crop can impose serious human health risks [71,72,116]. Therefore, the As-contamination, especially in paddy fields, are often exacerbated by co-existence of Cd as 'As-Cd' duo, wherein both toxicants are hazardous to public health [71,72]. Therefore, past As-contamination in paddy fields is usually accompanied with Cd pollution, however, both evidenced to possess distinct or opposing geochemical and chemical characteristics. The co-existence of As-Cd underscored the need of combined remediation, which is rather challenging. Interestingly, in this vein, ARB-induced pH causing liming effects can result in effective Cd-immobilization, but adversely influence As removal [71,72], underlying the basis of co-remediation challenge.

Application of 2% dose of 'calcium-enriched eggshell-corncob biochar (CECB)' was found to be a potential strategy for alleviating As and Cd transfer from the paddy soil to rice grains, thereby increasing the food crop yield and maintain the food safety [117]. In addition, CECB mediated modulation of rhizospheric-soil pH and induction of Fe-plaque formation in paddy roots also restricted the As-Cd transfer from soil to rice shoot and edible grains [118]. Among diverse ARB e.g., 'mushroom, soybean straw, sewage sludge, peanut shells', and rice straw, soybean straw-based ARB resulted in the maximum As-reduction (88%) in paddy fields [119]. In this study, Li et al. [119] observed the potential role of 'dissolved organic matter' (D.O.M.) in restricting the mobility and bio-accumulation of As-Cd duo in rice fields.

In quest of NBGS to these twin metals/-metalloids contamination, simultaneous removal of Cd-As were attempted with 'rice-straw-derived pristine biochar (RSPB), 'magnesium (Mg)-loaded rice-straw biochar (MRSB)', and ZVI [49–51]. Herein, descent reduction in As-concentration of rice grains were observed in RSPB (35.4%), MRSB (33.1%), and ZVI (29.1%). In another study conducted by [49–51], Cd concentrations noted a decline in the proximity of 46.1% with RSPB, 90.3% by MRSB, while ZVI resulted in its complete (100%) elimination. Herein, it is clear that As remediation depicted an interesting reverse trend, whereas pristine biochar i.e., RSPB, resulted in better As removal than nono-biochar i.e., MRSB and ZVI.

Conversely, the trend was quite predictable in [49–51] studying o Cd remediation, wherein deployment of nano- biochar like ZVI and MRSB resulted in about 2-fold higher Cd-removal, than pristine i.e., RSPB. Furthermore, in case of As remediation from porewater, [49–51] noted decrease in As-concentrations with MRSB (51.6%) and ZVI (87.7%), however, no such reduction was observed with pristine RSPB. On the other side, ZVI induced an increase in 'Dimethyl-arsenate (DMA;

$C_2H_7AsO_4$)' concentrations in pore water by 4.9, while in rice grain, it was increased by a factor of 3.3 [49–51]. Therefore, the PRSB amended with MgO and ZVI remarkably modulated As, DMA, and Cd translocation in rice crop. Molecular basis revealed that As(III)-removal was importantly guided by increased Si-mediated supressing of *LSi* genes, DOM, Fe-plaques, and Cd in porewater [49–51]. Further, [49–51] observed that ZVI mediated elevation in Fe levels, also enhanced rice growth/biomass by ameliorating the photosynthetic processes.

The nano-biochar such as those amended with 'hydroxyapatite, zeolite, biochar (HZB)' on application to paddy crop potentially reduced Cd concentrations and its subsequent bio-accumulation in rice tissues, which was significantly greater than that of As-sequestration [116]. The decrease in Cd and As concentrations was attributed to their adsorption mediated through oxygen containing functional groups (e.g., -OH, -COOH, -Si-O-Si and CO_3^{2-}), eventually producing carboxylates, silicates, and carbonates, which together tends to effectively immobilize HMs or metalloids [116]. The co-contamination of As-Cd in paddy fields was remediated in soil porewater by pristine rice straw(SC), Magnesium functionalized SC (Mg/SC), and ZVI mediated through divergent pathways, and to differential extent [49–51]. In this vein, As in pore water was reduced up-to the extent of 51% by Mg/SC, while a comparatively higher fraction of 87.7% was noted with ZVI. In this sense, [49–51] observed that As-Cd remediations were tightly linked to levels of As(III), Si, DOC, Fe-plaque, and porewater-Cd.

Nano-biochar such as magnetic Fe-amended-ARB are observed to be particularly effective in addressing As-Cd coupled remediation challenge [120]. This nano-biochar was noted to be effective in As removal by 43.1%, with slightly better Cd (53.7%) remediation from flooded paddy fields, when compared with the upland field In this vein, Wei et al. [120] further revealed that this coupled remediation of differentially stable As and Cd in agriculture systems was attributed to the production of Fe-plaque, which effectively enhanced their passivation, therefore, bearing tight implications towards food safety.

In addition to As-Cd, coexistence of the 'As-Sb' duo also imposes a techno-economic challenge in paddy fields, which need to be pragmatically addressed for sustainable rice production. Magnetic or nano-biochar such as Fe-functionalized-ARB, when applied at optimum dose of 1.5%, can simultaneously remediate twin-metalloids i.e., As and Sb from mine contaminated soil [121]. In this vein, exposure of metalloids-duo i.e., As-Sb can concomitantly increase the enzyme activities, especially, those of acetyl-β-glucosaminidase and urease [121]. In addition to enzyme activity, microbial diversity, specifically, those belonging to Proteobacteria and Actinobacteria is remarkably increased, when compared with pristine biochar. In this respect, Li et al. [121] also noted Fe-functionalized ARB mediated amelioration in soil physico-chemical properties such as pH, electrical conductivity, CEC, SOM, and Fe can together synergize positive modulation of enzyme activities and bacterial composition. In light of above discussion, it is quite evident that As remediation that is of serious concern in paddy fields, faced with above-mentioned challenges. Especially, it is worth noting that As contamination is more challenging in flooded paddy fields, attributed to reductive-dissolution mechanism of Fe-associated minerals [122].

Nano-biochars like magnetic-NPs supplemented with 'graphene-loaded biochar', reduced the As (i.e., Na_2HPO_4-extractable As) concentrations in soils by 9.9%, attributed to increased S.S.A., number of 'Fe-O' bond, electrostatic attraction, and complexation (as 'Fe–O(H)–

As/Sb') [123]. In this respect, Gao et al. [124] importantly observed that this magnetic nano-biochar was most effective in As remediation (i.e., Pristine biochar- 8.2% *vs* FeBG- 16.4%) than co-existing Sb-metalloid. In addition, Gao et al. [124] noted an increase in enzyme activities of sucrase (9.6%), and leucine aminopeptidase (7.7%), in conjugation with π-π electron donor-acceptor coordination. However, besides decreasing the bioavailability of twin metalloids i.e., As-Sb, negative impact of FeBG on soil physicochemical properties as well as enzymatic activities were observed, which necessitated the need to elucidate the long-term effects of nano-biochar, especially in case of up-scaled or commercial applications [123].

The co-contamination of As and Sb is ameliorated up-to the extent of 100% with ZVI and Fe-modified biochar, when compared with pristine biochar [125]. This efficient metalloid-duo-remediation was ascribed to chemical mechanism of surface sorption and co-precipitation on Fe-complexed phases. However, in case of As-Sb duo, this coupled As-Sb remediation was tightly regulated by soil-conditioning [125]. Ameliorations in soil health, mediated by high moisture content, with 100% 'water holding capacity (WHC)' and rich organic matter layer potentially facilitated solubilization and complexation mechanisms in case of twin-metalloid, manifested through formation of As/Sb- DOC complexes [125]. This nano-remediation can effectively reduce the As-Sb duo bioavailability in soil-crop interface of agriculture systems.

6.2. Climate change exacerbate As contamination in rice

The pragmatic evolutions through modelling of As contamination in paddy fields, faced with the concurrent effects of climate change, specifically, global atmospheric carbon dioxide (CO_2) and elevated surface temperature, indicated alarming signals, especially in context of food safety and public health [6]. Further, predictions of Wang et al. [6] stated that if concurrent effects of climate change maintain status quo, there will be sharp increase in As-bio-accumulation of rice grains, with projected 'cancer burden' in 'tens of millions', by the year 2050, in tandem with increase in severity of non-carcinogenic heart diseases.

It is widely suspected that climate change can exacerbate the As contamination of ground water and food crops, manifested through elevated CO_2 concentrations and ambient temperatures [6]. However, the effects of increased CO_2 and surface temperature is rarely explored in paddy fields, which is tightly linked with human well-being. In this vein, Wang et al. [6] elucidated that agriculture systems that are faced with As contamination, under the event of interacting effects of climate change as manifested by elevation in CO_2 concentrations and surface temperature, can remarkably enhance the As-reductive dissolution, with profound influence on rice crop-yield and human nutritional security.

Importantly, Wang et al. [6] observed that both individualistic and synergistic effects of elevated CO_2 and temperature substantially impacted soil biogeochemistry, realised through alterations in physico-chemical and biological (e.g., microbial root exudates release/decomposition) paddy-soil attributes. Notably, such physico-biochemical modulations resulted in a paradigm shift in abundance of microbial genes, along-with reduced redox potential, which potentially guided reductive dissolution of iron-oxyhydroxides with concomitant reduction of arsenate to arsenite. Together, these factors increased As contamination in rice grains that jeopardize the food safety and human well-being. At molecular scale, the concurrent effects of CO_2 and temperature shifted the abundance of '*arsC* genes' to increase six-fold, especially, during vital 'rice-grain filling' stage, which is tightly associated with reduction of As(V) to As(III) [6]. Therefore, future studies on As remediation should incorporate the interacting effects of climate change for environmental stewardship and human well-being.

6.3. Designer/ engineered biochar in As remediation from paddy fields

Pre-treatment of natural adsorbents with chemicals such as Fe and aluminium (Al-) oxides can accelerate the As-biosorption [21]. In context of As remediation, 'layered double hydroxides' (LDH) ARB-composites are structurally unique, as their interlayer space consists of anions, which can potentially bind with cationic As (III) and As (V) at soil-food crop interface in paddy fields [126]. Activation of agri-residues like chestnut shell-based-ARB with magnetic gelatine was found to enhance the As-adsorption from17.5 mg/g to 45.8 mg/g [87]. Modified Fe/Mn-oxides amended-ARB were demonstrated to reduce As-uptake by rice by forming Fe-plaque in the belowground roots of rice, which was actually ascribed to the Fe minerals-dissolution in food crop-rhizosphere [127–129]. Interestingly, presence of abundant silicate groups in rice guided the As-adsorption mediated by transformation of Fe(II) to Fe(III) on neutral ARB surface [62,129,130]. Chemically, this Si is vital to effectively compete with As-binding sites, thereby impeding the As-uptake in rice. Importantly, mechanism of Si-uptake was regulated through expression of Si-transporters, in order to mitigate As-induced phytotoxicity in paddy fields [60,127,128]. In this sense, manganese oxide (MnO)-modified maize straw ARB also reduced As in paddy fields by modulating redox conditions, through enriching surface charge of Fe, Mn, and Al oxides and hydroxides [112].

Nano-scale Fe amendment of oil palm fibre-derived ARB with ZVI, remarkably reduced the As-bioavailability through chemical complexation in paddy agroecosystems [102–104]. In this vein, As-complexation by 'conversion of soluble Fe into amorphous iron oxyhydroxides phases' was microbes(*Geobacter* and *Desulfosporosinus*)-assisted, inducing oxidation of Fe(II) [102–104,131,132]. In case of rice, 'ARB amended with zeolite (ARBZ)' enhanced the As-adsorption/complexation, mediated through increase in soil Ca-contents [133]. In this vein, Gu et al. [133] elucidated that ARBZ-induced Ca-levels in agroecosystem soil effectively increased formation of 'Ca-As bound complexes', thereby, effectively reduce As-exchangeable fractions. Such designer-ARB also demonstrated to enhance As-adsorption at soil-crop interface, owing to rich abundance of oxygenated-functional groups, which can covalently bound to soil-As fraction to potentially restrict their subsequent uptake in food crops [128].

The challenges associated with Fe-minerals-reductive dissolution mechanism in flooded paddy fields was effectively addressed by 'magnetic bamboo-based ARB (MBARB)' produced from variable pyrolysis temperatures i.e., 300, 450 and 600 °C [122]. Herein, most effective MBARB-driven As-immobilization was noted to be optimum at temperature of 450°C in case of flooded paddy fields. Concomitantly, increased As-immobilization in rice fields was also attributed to paradigm shift in bacterial community composition, manifested through modulations in α diversity of 'electroactive bacteria (EAB)' [122]. In this aspect, previous studies observed that EAB belonging to Geobacteraceae, Xanthomonadaceae potentially induced the formation of amorphous Fe-oxides, which eventually resulted in As-passivation or stabilization as 'As–Fe-DOM' complex [122,134].

Among designer/modified ARB, ZVI coating is widely investigated, in view of Fe being the potential element for As removal from aqueous solutions [21]. Therefore, Fe-amended-ARB are particularly effective in As remediation (43.1%) from flooded rice fields [120]. This As remediation in paddy fields is actually mediated through increased production of Fe-plaque, which potentially enhanced the As-passivation in rice farmlands [120].

In paddy fields, As-adsorption can be effectively facilitated by co-application of FeNPs and ARB that can efficiently alleviate 61% metalloid concentrations in the rice grain [102–104]. In another perspective, modification of ARB with FeNPs and other nano-materials can remarkably enhance the As-adsorption potential [125,135]. In this sense, magnetic particles-fortified nano-ARB from Douglas fir, resulted in pH dependent As removal [135]. Herein, highest removal of As(III) and oxidized As(V) in concert with subsequent ionic transformation was observed at an optimum pH value of 3. In this respect, Rodrigo et al. [135] opined that As(III) adsorption is facilitated *via* its conversion to As (V), in anoxic conditions of paddy fields with As (V)/AsO_4^{3-}, wherein remediation process was noted to be endothermic, exhibiting Langmuir adsorption capacity of 6.33 mg/g at 25 °C.This was further corroborated by a recent study on magnetic-ARB from pine-cone, duly impregnated with Fe-salts such as $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$, which effectively reduced the As-bioavailability (up-to 12.14 mg g^{-1}) in soil and groundwater of paddy fields [136]. Herein, this As remediation at paddy soil-groundwater interface was in fact facilitated by its chemical fixing or transformation as stable complex, mediated by active functional groups on ARB-surface. Furthermore, Khan et al. [136] elucidated that in terms of chemical mechanism, 'outer-sphere complexation' between As(V) and 'Fe, O, NH, and OH' of pinecone-magnetic-ARB was in fact were the prime reasons for As(V) adsorption [136].

In paddy fields, 'FeONPs-doped-rice-straw-derived ARB (FRSARB)' was observed to be more effective in reducing the bioavailability of As (43.9–57,3%) at soil-crop interface, when compared with pristine biochar [137]. Concomitantly, the FRSARB resulted in enhanced biochemical or antioxidant responses, in concert with the nutrient enrichment at paddy soil-crop interface [137]. Fig. 4 explains the ARB-mediated As-detoxification in paddy fields to mitigate public health risks and environmental sustainability.

6.4. Arsenic remediation in other food crops and vegetables

Sustainable As remediation from agroecosystem soil, mediated by nano-functionalized/composite ARB can be inextricably associated with raising of pollution free safe crop cultivars for increased food safety and human nutritional security ([68], b; [71,72]). For example, composite-ARB, derived from amalgamating steel-slag and corncob, effectively ameliorated the growth of *Abelmoschus esculentus* L. or Okra by mitigating As-induced oxidative stress [138]. The antioxidant responses in Okra were guided by induction of potential ROS-scavenging mechanisms, well supported with biochemical modulations by elevated or activated osmolytes accumulation, glyoxalase system, thiol and PC-contents. Few studies observed the food safety and positive ARB-implications to ecosystem's trophic levels, without any significant enhancement in yield or food productivity [139]. In this sense, a study on application of orchard prune residue-derived-ARB observed potential As-immobilisation into soil pore water [139]. However, Beesley et al. [139] noted that subsequent As-transfer in tomato roots and aboveground plant parts was remarkably reduced, restricting the risks of food chain transfer. Nevertheless, no effects of biochar amendment was noted in biomass yield of tomato, while nutrient contents were reduced, except in case of treatment of biochar with NPK [139].

Arsenic-toxicity in green leafy vegetables such as spinach can be alleviated through Silicon (Si)-amendments in contaminated soil that potentially induce the antioxidant enzymes, with concomitant ROS capture, less electrolytic leakage, and reduced MDA levels [39]. Selenium (Se)-amendment in case of *Capsicum annuum* L. or edible bell pepper varieties was demonstrated to reduce As toxicity by modulating morpho-physico-biochemical processes, thereby safeguarding ion-uptake and photosynthetic processes to sustain the crop yield [38].

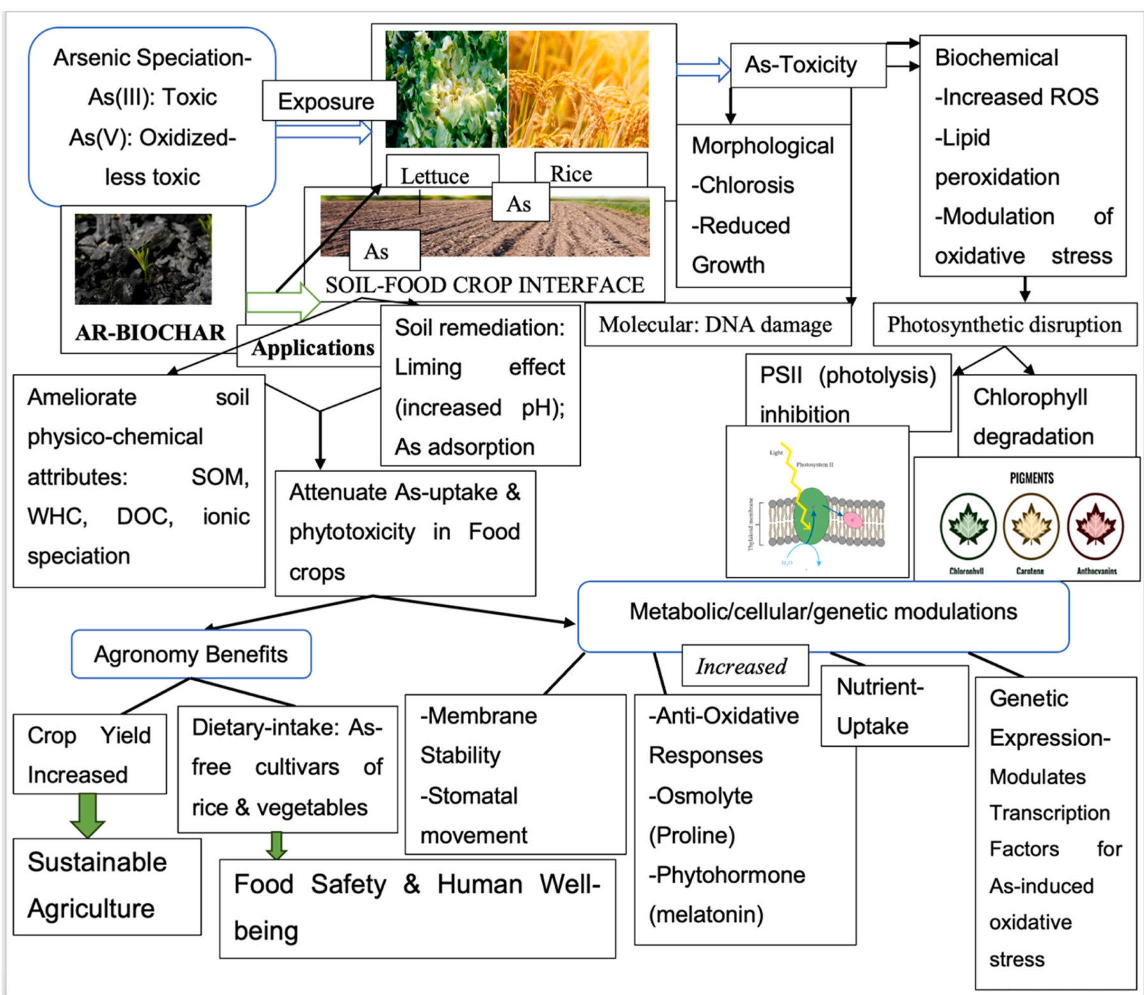

Fig. 4. The explicit and holistic elucidation of ARM-mediated soil conditioning and phytotoxicity alleviation in food crops (specifically, rice and vegetables). The reduced phytotoxicity in food crops are manifested through biochemical, cellular, and genetic mechanisms to offer agronomy benefits, inextricably linked with food safety, public health, and sustainable agriculture.

Past studies have shown that rice-husk-based ARB-applications can effectively remediate As(III) and As(V) [84]. In this vein, 'Corncob-based-ARB (CARB)', effectively remediated the co-existing As-Cd, ascribed to S.S.A., higher porosity, and organic matters [140]. Further, CARB positively modulated the soil microbial diversity and fertility of yellow and cinnamon soil [140]. Co-application of ARB with oyster-shell waste resulted in decrease of exchangeable-As fractions, from 105.8 to 54.0 mgkg^{-1} in highly contaminated soil with 15,000 mgkg^{-1} As [141]. In this study, '2%ARB- oyster-shell waste' was observed to be the most effective dose in reducing the As-concentration in pore-water by 62.3% [141].

6.4.1. Composting

Under the face of drought stress, 7.5 wt% of 'cow manure-enriched rice straw-derived ARB (CMRSARB)' ameliorated soil physico-chemical properties [95,96] These soil characteristics were 'porosity, water holding capacity, soil respiration, CEC, AEC, and nutrient contents. On the contrary, [95,96] noted that CMRSARB applications in agroecosystems decreased soil bulk density, mobile-As (35.7%), bio-available (45.3%), and leachable (56.5%) As-fractions. Consequently, the CMRSARB induced growth of edible Bengal gram and coriander plants by 62–188%, increased biomass accumulation with synchronous increase of 90–277% in terms of length, and hence increased their yield, compared to pristine-ARB [95,96]. In this aspect, food safety of Bengal gram and coriander plants was manifested through reduced As-bioaccumulation (i.e., in range of 49–54%) in their plant parts. Thus, CMRSARB can mitigate As-induced phytotoxicity for increased food security in long-term, if validated pragmatically across variable soil types and climatic conditions. Also, the co-application of biochar with compost, each with a dose of 3%, enhanced the activity of soil enzymes such as dehydrogenase, b-glucosidase, and urease [53]. Therefore, composting can be integrated with biochar technology for sustainable agriculture.

6.4.2. Microbes functionalization

Arsenic-free safe food crop/agricultural production like *Ipomoea aquatica* L. or water spinach can be facilitated by the application of functionalized-ARB, with supplementation of *Bacillus aryabhattai* (B10) and sodium alginate [71,72]. In this sense, [71,72] observed that 'edible wetland plant-B10' co-application improved rhizosphere-associated beneficial-functional microbes, metalloid-resistant genes, CEC, and SOM to enhance As-Cd immobilization. The beneficial implications of this result were noted as vital strategy for safe food crop production for healthy human diet. Another study on microbes-functionalized-composite ARB, such as *Bacillus* sp. K1 loaded onto Fe_3O_4 magnetic biochar potentially adsorbed As up-to 4.58 mg g^{-1} while Cd-removal was in the range of 25.04 mg g^{-1} [142]. This microbe-assisted functionalized-ARB-driven remediation was ascribed to multiple mechanisms, such as microbe-based functional groups e.g., $-NH_2$ and -OH, formation of type B ternary surface complexes, competition, and synergy effects [142]. Besides bacteria, endophytic fungi also synergistically stimulated efficacy of biochar in enhancing As-bio-accumulation in the range of 49.91%–134.60% [142]. Together, these physico-chemical and biological attributes of soil restricted HMs bio-accumulation in edible vegetable like water spinach and food chain, thereby resulting in safer food crop production for healthy human diet [71,72].

In another study on food safety in As contaminated Amazon soil, located in proximity of gold mining tailings was also found to be ARB-mediated [143]. Herein, As-phytotoxicity was reduced in edible leafy vegetable i.e., lettuce by the application of *Euterpe oleracea* Mart. (açaí palm) seed-based-ARB. In this vein, Dias et al. [143] elucidated that As-free lettuce production was in fact manifested through ARB-driven increase in soil fertility, elevated nutrient accumulation, and higher vegetation indices. Importantly, co-contamination of As-Cd was effectively addressed in lettuce by applications of Rice-straw-based Fe_3O_4-ARB (Cd-99.62%; As-62.39%) and pyrite FeS_2-ARB (Cd-81.73%; As-55.54%%), wherein over-all remediation efficiency was higher in case of Fe_3O_4-ARB [144].

7. Limitations and prospects

7.1. Biochar Ageing

Biochar ageing reduced the immobilization efficiency of HMs by MAB- 5 [92]. Although, Peng et al. [92] noted that freeze-thaw-ageing enhanced the HMs-immobilization efficiency of MAB-5, which could slow down the vertical migration of HMs. Nevertheless, similar insights in context of As remediation are not explicitly elucidated, especially under the event of aged-ARB in varying soil types.

7.2. Standardization of environmental factors

Several environmental factors can influence the effectiveness of As remediation, that need to be optimized. For instance, As-immobilization by ZVI-embedded-ARB was observed to be dependent on multiple environmental factors like high temperature, soil moisture, amendment doses, and variable physico-chemical characteristics of soil [145]. Therefore, the ARB-induced As removal can be influenced by various abiotic factors in field, farms, or agroecosystem soil, which need to be investigated for optimizing the remediation efficiency.

Biochar based 'biogenic iron (oxyhydr)oxides (BIOS)' can potentially adsorb the As(V) as bidentate binuclear complex, and the abiotic factors such as DOC did not influence the binding mechanism of metalloid. However, interaction of DOC with As(V) was observed to be influenced by the pyrolysis temperature applied in BIOS production, which necessitated the need of pragmatic study for such interactions to be unveiled. Explicit studies on such interactions can be vital in elucidating the fate of As in aquatic ecosystems, agroecosystem soil, and groundwater [146].

7.3. Augmenting Phytoremediation

The literature on As phytoremediation through wetland plants and aquatic macrophytes are widely evidenced and popularized in recent decades [58,147,148]. However, the biochar-induced augmentation in phytoremediation of potential As-hyperaccumulators can further leverage the efficient innovation of pollution phytotechnologies [19]. Nonetheless, the coupling of ARB with phytoremediation is still an unexplored field of study, that is ripe for scientific investigation. In this sense, an important example of *Pteris vittata*, a water fern, can be cited, which has been widely identified as potential As-phytoremediation tool, whose removal efficiency was further strengthened by supplementation of biochar [58]. In this aspect, Biochar + *P. vittata* combination increased the available As-uptake by 3.80% (at 2% dose application rate) and 8.01% (at 5% application rate), attributed mainly to increasing biomass accumulation in hyperaccumulator water fern [58]. Therefore, ARB-optimum dose needs to be standardized for maximizing the phytotechnology, with increased efficiencies. However, such studies integrating the ARB with As-phytotechnologies are few, which necessitates the need further studies to potentially maximize the sustainability paradigm in As remediation.

7.4. Organic As remediation still an enigma

Inorganic As remediation is prioritized in rice and vegetables, however, the fate of organic As in food crops, and their remediation is inadequately explored [149]. These biomethylated organic-As are more hazardous to environment and human health than inorganic Arsenic [149]. Nevertheless, relatively less is known about the interaction of ARB with methylated/-thio-arsenate compounds and their remediation, especially, in case of rice and vegetables [19,149].

Although Wang et al. [6] elucidated the effects of inorganic As, the organic As-fractions like DMA and 'Dimethyl-mono-thio-arsenate DMMTA' in paddy fields are scantily explored. This study of Wang et al. [6] revealed that organic As i,e., DMA and DMMTA are exceedingly toxic, which gets generated after microbes-induced process of bio-methylation. In this aspect, these organic As-fractions are reported to be 3–10 times more cytotoxic than soil-bound inorganic fractions of Arsenic [123], Despite these hazardous impacts of organic-As, their fate in agriculture systems and phytotoxicity-driven health hazards is still an enigma, that need to be resolved in future researches (Fig. 2b). Also, the explicit mechanism of MMA (Mono-methyl-arsenate) DMMTA and DMA-bound eco-toxicity and their effective remediation should be explored more, in view of their high cytotoxicity than inorganic-As [49–51] to secure food safety, public health, and human well-being.

8. Future prospects

8.1. Elucidation of interactions with other contaminants

Critical analysis on state of art knowledge in present perspective revealed that future studies on ARB-mediated As remediation should address competitive uptake/interactions of other contaminants [60]. In this vein, phosphates, silicates, sulphates, and organics act as contaminants to potentially alter the redox conditions and soil pH during crop growth stages/flooding/wet/dry seasons in rice or paddy fields. Further, in this sense, the interaction of other soil amendments such as fertilizers and irrigation is also vital in amelioration of As-stress in food crops [60].

8.2. Abridging nanotechnology and biotechnology advances with ARB valorisation

In this aspect, modification with thiol-functionalized/nano-scale customized-ARB can help achieve sustainable As remediation from agriculture systems [21,60]. The empirical tracking of progress in nano-biochar and microbes-functionalized-nano-ARB should be prioritized to address the constraints in As remediation at soil-food crop interface of agriculture systems. Therefore, sustained efforts on techno-economic innovations in upscaled ARB technology is warranted, which may be possible by integrating it with recent advances in nanotechnology, 'NPs-phytohormones-Plant growth regulators-ARB' synergy, omics, sustainable agronomy, crop breeders, transgenics, and biotechnology [52,56,68,71,72,150]. Incorporation of biotechnological advances in genome editing, especially with CRISPR/Cas ('Clustered Regularly Interspaced Short Palindromic Repeats/CRISPR-associated proteins'), RNA interference (RNAi), metabolomics and proteomics can remarkably increase the As remediation to boost nano-biochar technology for pollution free safe crop production and climate-resilient smart agriculture [9,10,15,34]. Nevertheless, for scalable nano-biochar applications in As-contaminated agroecosystems, the assessment of nano-toxicity and long-term ecological repercussions are necessary for food safety, public health, and SDGs [15]. Moreover, in future perspective, the role of citizen science, artificial intelligence (AI), especially ML should be deployed more frequently to explicitly elucidate the As-adsorption mechanisms in contaminated agroecosystems [4,5,26].

8.3. Elucidating trophic level transfer or other stress tolerance mechanisms and general management options

Pragmatic studies on further elucidation As-fate in agriculture systems, with the exploration of explicit mechanism across their transfer in food chain of trophic levels, need to be assessed for accurate assessment of ecological health risks [23]. Since the priority As-polluted sites are identified in several studies, Zheng et al. [151] advocated the plantation of edible crops, which are poor in As-bio-accumulator efficiency, unlike rice and leafy vegetables. This can be a an effective 'avoidance strategy' to minimize the public health risks.

The complex and intricate processes linked with nano-biochar ageing in variable soil types of distinct geographical landscapes need to be studied for optimized As remediation [3,33]. Elucidation of nano-biochar ageing processes therefore need to be prioritized in future studies for sustainable As remediation in vulnerable global agro-ecosystems. Also, in future researches, attempt should be directed to raise the food crop cultivars with better anatomical adaptations and oxidative stress tolerance to effectively mitigate As stress for increased food safety [35].

8.4. Expanding nano-biochar or ARB-feedstock range

The selection of agro-industrial-wastes or novel feedstocks such as bamboo species and their amendments with nanomaterials like ZnONPs can augment the sustainability paradigm of nano-biochars in As remediation [24,29,59]. The integration of NPs can leverage the As-mitigating antioxidative, biochemical, enzymatic, and stress tolerance pathways. The increased number of studies on exploring the prospects of IAPs and bamboo biomass in producing ARB can facilitate the As remediation in rice and other food crops [45]. The ARB-feedstock selection of is very crucial step and need to be further standardized in As remediation from agriculture systems, including paddy fields. It is worth mentioning that Si-rich Rice straw and Bamboo sp., N-rich macrophytes like water hyacinth and algal biomass, Fe-rich sewage sludge, and P-rich livestock manure-based-ARB can be more effective in As remediation from food crops, ascribed to structural analogy and high binding affinity of Si, N, and Fe [49–51,57,70]. This research progresses can safeguard food safety/-security, soil, and human health to accelerate the attainment of UN-SDGs (Fig. 5).

8.5. Investigating As contamination-climate change nexus interactions

The implications of climate change in the form of rising temperature, CO_2, and floods can further exert a profound impact on soil biogeochemistry, in tandem with paradigm shift in microbial dynamics [6]. Together, these factors can further exacerbate the As-toxicity in 'groundwater-soil-food crops' interface. These interrelated factors should be investigated in nexus-perspective to simultaneously address As contamination in agroecosystems and sustain climate-resilient-smart agriculture.

8.6. Scalable deployments of Nano-biochar for pollution free climate resilient food crops

Nano-biochar can be effective in As contaminated agricultural landscapes if field validation, scalability, and long-term ecological impacts are explicitly assessed [42]. For instance, a recent study by Emamverdian et al. [24] revealed that the technological innovations in quest of novel nano-hybrids (SiO_2+TiO_2 NPs) can remarkably enhance As removal by boosting antioxidative stress response pathways and increased phytochelatin synthesis, while simultaneously alleviating the damage to photosynthetic or other metabolic apparatus. The techno-economic innovations in nano-biochars and nano-enabled agrochemicals/nano-fertilizers can be a potential tool in enhancing the As remediation for improving food crops resilience and public health safety [24,152, 154–158]. The techno-economic innovations in functionalized C-based nano-biochar composites such as Chitosan can address both abiotic stressors such as thermal/drought and metals-driven oxidative stress, in conjunction with biotic stress like pathogens and pests attack, thereby help develop climate change-resilient smart food crops [3,20].

8.7. Encouraging regulatory measures and participatory approach with farmers

The scalable nano-biochar can result in sustainable As remediation, if

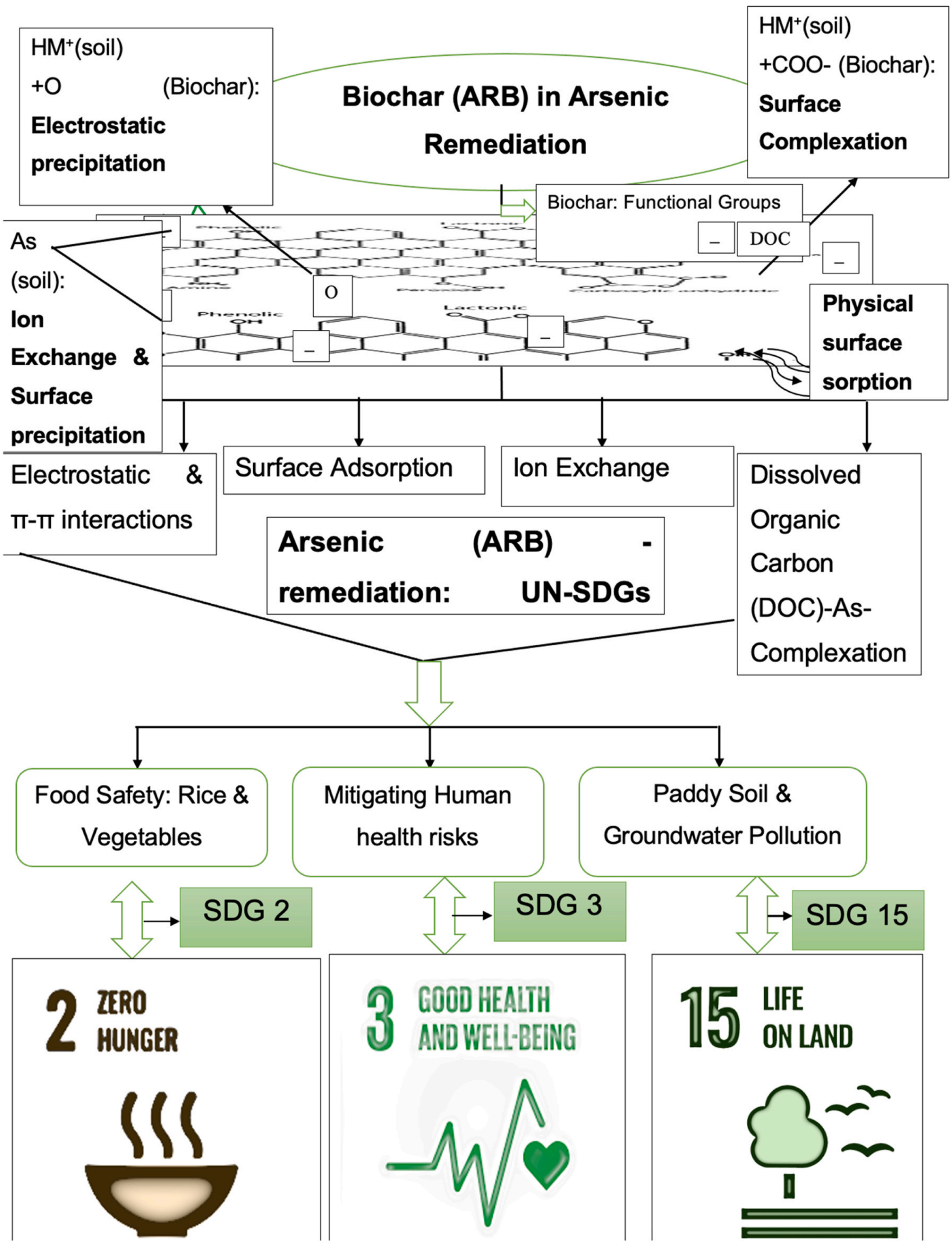

Fig. 5. The multiple mechanisms and ARB-physico-chemical attributes to augment food safety and United Nation's (UN)-Sustainable Development Goals (SDGs) mediated by As remediation from drinking water, soil and food crops.

beneficial policy incentives such as subsidies and carbon-credits are offered to farmers [42]. However, excluding the efforts of some European countries and China, it is rather unfortunate that strategic regulatory or participatory measures are lacking in inorganic-As and organic-As pollution-prone or vulnerable countries across the global agricultural landscapes [6; 153]. Henceforth, more policy measures are warranted from global regulatory institutions like UN and FAO to mitigate As pollution, as exemplified by the mission for mitigating land pollution and encouraging soil restoration under the 'United Nations Environment Programme' (UNEP) and the FAO [4,14,153]. However, the stakeholders associated with multifaceted science and technology disciplines must ensure inclusion of 'citizen science' including the farmer's participation, before coming-up with the concrete policy formulations on ARB-mediated As remediation for facilitating sustainable agriculture. This may be useful for various stakeholders, global regulatory institutions, and policy makers, including agronomists, environmentalists, earth scientists, and bio-engineers for devising concrete As mitigation measures for planetary health stewardship.

9. Conclusions

The environmental challenges of agro-industrial-wastes management and As pollution in groundwater-soil-food crop interface can be sustainably addressed with biochar deployments in vulnerable agro-ecosystems. Nonetheless, pristine biochar have physico-biochemical limitations, which can be potentially addressed with designer or nano-biochar, that can remarkably alleviate the As pollution in agriculture systems. The nano-biochar driven As remediation is attributed to multitude of enzymatic and non-enzymatic oxidative stress tolerance pathways. Furthermore, the role of phytohormones, organic acids, signal molecules, and nano-scale particles can also be vital in biochar-based As removal from soil and food crops. The As remediation from soil and food crops of vulnerable global agricultural landscapes is inextricably linked with sustenance of arable-fertile agroecosystems for food security/-safety. Increased soil fertility maintains the food safety of staple crops like rice and leafy vegetables to safeguard the public health. The pragmatic future studies on As remediation-linked physico-biochemical or oxidative stress tolerance pathways, redox homeostasis, and interaction with phytohormones can further leverage the As remediation in sensitive landscapes. The elucidation of biochemical antioxidant responses under As stress in concert with molecular addressal mechanisms from the environmental matrices are tightly aligned with the attainment of multiple UN-SDGs. Nano-biochar driven As decontamination in groundwater-soil-food crops interface can help achieve the environmental sustainability, climate-resilient-smart sustainable agriculture, and human well-being. However, the scalable deployments of nano-biochar warrant participatory approaches among scientists, agronomists, engineers, farmers, consumers, and policy makers for sustainable As remediation.

CRediT authorship contribution statement

Prabhat Kumar Rai: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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Declaration of Competing Interest

There is no competing interests.

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