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Review article

Interaction of arsenic with biochar in soil and water: A critical review

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ABSTRACT

Biochar exhibits a great potential to act as a universally applicable material for water and soil remediation due to extensive availability of feedstocks and favorable physio-chemical surface characteristics; nevertheless, studies related to its application on the remediation of toxic metalloids are relatively rare. Hence, this review highlights biochar production technologies, biochar properties, and recent advances in the removal and immobilization of a major metalloid contaminant, As in water and soil. It also covers surface modification of biochars to enhance As removal and microbial properties in biochar amended soil. Experimental studies related to the adsorption behaviors of biochar and the underlying mechanisms proposed to explain them have been comprehensively reviewed. Compared to the number of research publications in SCOPUS database on "Biochar+Water" (≈1290 – Scopus), the attention drawn to examine the behavior of biochar on the remediation of As is limited (≈85 - Scopus). Because of the toxicity of As, the subject urgently needs more consideration. In addition to covering the topics listed above, this review identifies research gaps in the use of biochar as an adsorbent for As, and proposes potential areas for future application of biochars.

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1. Introduction

Arsenic (As) is the 20th most abundant element in the geosphere, and the 14th in seawater. However it has been recognized as an extremely toxic metalloid for humans as well as for fauna and flora [1–3]. The mean amount of As in the earth's crust is known to be approximately 1.8 mg/kg [4], but this number is increased due to anthropogenic pollution. Inorganic anionic As species, arsenite [As(III)] and arsenate [As(V)], as well as organic species, particularly mono-, di- and, tri-methyl arsenates, have been recognized as major toxic species of As in natural water systems. Furthermore, more noxious organic and inorganic thio-As species can be found widely in geothermal and marine environments [5,6]. Elevated concentrations of As in groundwater have been reported in many parts of the world [7]. Interestingly every year, some new locations are found with high background arsenic concentrations. As noted, As can be found in soils due to both geogenic and anthropogenic activities, and it may occur at a wide range of concentrations, ranging from μg/kg levels to extremely high concentrations such as 250,000 mg/kg [8,9]. The levels of As is extremely minute to be a causative factor for health issues and hence, the safe permissible value has kept very low compared to other toxic metals (10 μg/L) by the World Health Organization (WHO).

A variety of technologies such as chemical oxidation, precipitation, adsorption, ion exchange, reverse osmosis, and membrane separation has been adopted for the removal of As in water and wastewater. Adsorption is considered as an effective remediation strategy due to its low cost and relatively simple design [10–12]. However, the removal of As from aqueous solutions is a serious challenge for researchers, engineers, and technologists due to varying As speciation depending on pH of the media. Few studies have confirmed the application of some materials that are efficient in remediating both As(III) and As(V) species irrespective of the pH [13,14]. Interactions of microorganisms with different As species also are important in remediating As contaminated environmental systems [15]. Up to date, many materials, such as titanium carbonitride-derived adsorbents, agricultural wastes (rice husks), and iron oxide granules, which have been tested for As remediation, are either speciation specific or pollutant-specific, and, hence, they are not applicable for the simultaneous removal from a mixture of contaminants in aqueous solutions. Therefore, explore materials that can be used for the simultaneous remediation of many different pollutants and their species may receive strong attention. Activated carbon covers a wide spectrum of applications in drinking water treatment due to its high performance, high surface area, mechanically strong properties and avoids chemical waste products that need to be added in other applications. However; it is hardly applicable for soil remediation due to the cost involved in the production [16]. Hence, current focus has been drawn to biochar, because it is a cost effective and environmentally feasible carbonaceous product derived by the pyrolysis of certain feedstocks that has applications in a variety of contaminated environments [17,18]. However, yet biochar has not achieved high surface area as in the case of Activated carbon and poor in mechanical properties hence, it limits the application into water treatment.

In the past decade, biochar has been experimented extensively in various agricultural and environmental problems, due to its strong influence on immobilization of contaminants, improvement in soil health, and carbon sequestration in relation to climate change [19,20]. In addition, research has revealed that biochar also has an affinity for, and can retain, both heavy metals and organic compounds that contaminate wastewaters [17,21]. Moreover, biochar can be produced from residues that are often burnt in fields or buried in landfill, thus having a triple line benefit namely economic, reduction in polluted soil and water and production of renewable energy [22]. Many studies have reported an excellent ability of biochars to remove heavy metals, organic pollutants, and other pollutants from aqueous solutions [17,18,21–23]. Due to the above-revealed factors, research on biochar have been increasing at an exponential rate over the past few years.

1.1. Research on arsenic and biochar

The use of charcoal in agriculture or, biochar, as it is now referred to is a millennium old practice in all continents but specifically in Japan and China, Brazil, India, Australia and parts of Africa [24,25] [30]. Studies of its use has shown that soils where charcoal has been incorporated for centuries have resulted much more fertile than the surrounding soils. Publications related to As adsorptive remediation both in soil and water environment during the years from 1980 to 2014 (according to ISI Web of Science™) have been growing steadily [Fig. 1]. The figure shows the growing interest of the scientific community on As remediation research, and the trend on the As remediation in soil and water has extended from the phase of scientific research to engineering applications. There has been a significant increase of field scale and pot experiments during the last decade that have been conducted to investigate the effectiveness of biochar as a soil amendment to immobilize As [26,27]. However, there is still a gap between research focused on soil remediation and research on As remediation in aqueous media [Fig. 1(a)]. Only a few studies are focused on As immobilization in soil than the water research. At the same time, there has not been a centre of attention to understand the As mobilization/release mechanisms due to the application of different biochar produced from various production technologies.

Existing publications on biochar mainly deal with its application in technical, economical, climate-related aspects; soil quality and remediation; and remediation of water and wastewater [17,20,21,28–31]. With the increasing interest in scientific research on biochar and its surface modifications, an integrated understanding of the mechanisms of biochar to remediate As in

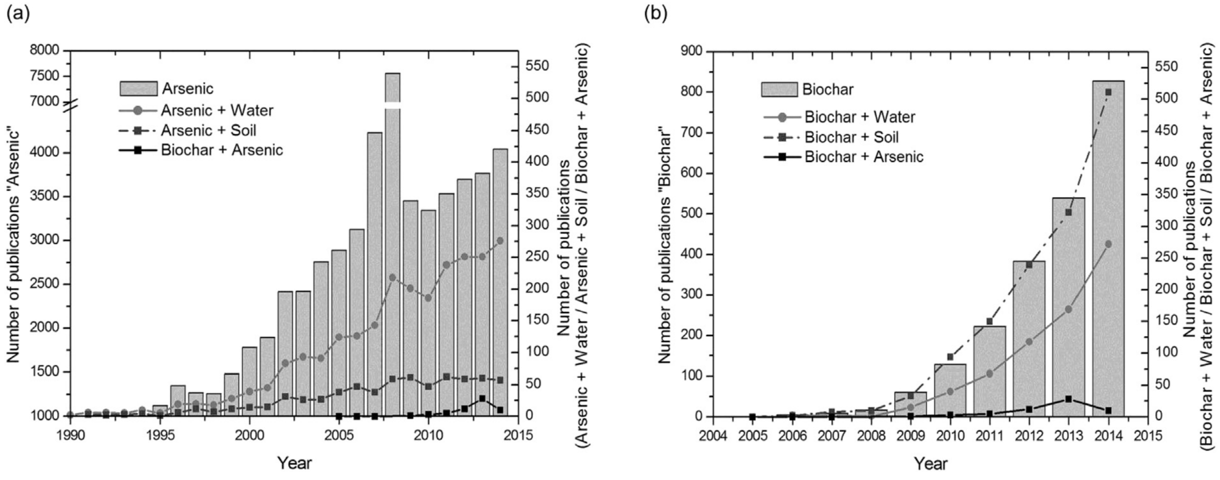

Fig. 1. Science Citation Indexed publications on As (a) and biochar (b) in SCOPUS.

contaminated water and soils via enhancing functional aspects of biochar for future engineering scale applications. Hence, the aim of this review is to analyze recent literature related to the application of biochar for the immobilization and/or removal of As in soil and water environments. This review further summarizes the recent developments in the preparation and properties of pristine (non-activated) and engineered biochar, as well as the mechanisms involved in the adsorption of As with regard to water and soil aspects.

2. Production and properties of biochar

Biochar production technologies and their properties have been well reviewed [17,21]. Tan et al. [21] have demonstrated that slow pyrolysis is the most commonly used technology for the production of biochar that can be used widely in water and wastewater treatment. Biochar can be produced from invasive plants, crop residues, woody biomass, animal litter, bones, and municipal solid wastes by using various thermochemical processes (e.g., slow pyrolysis, fast pyrolysis, hydrothermal carbonization, flash carbonization, torrefaction, and gasification) (Fig. 2) [32,33].

The yield of biochar and its characteristic features depend on the thermochemical processes, operating conditions, and feedstock. It has been well established that the low temperature derived biochars from slow pyrolysis result in low hydrophobicity and aromaticity but in high surface acidity and polarity. Major biomass decomposition tends to occur between 200 and 500 °C via several steps including, partial hemicellulose decomposition, complete hemicellulose decomposition, and full cellulose and partial lignin decomposition [35]. The content of ash in biochar can have an impact on the immobilization of contaminants, and it tends to increase gradually with rising pyrolysis temperatures. The ash content of pine needle biochar produced at 700 °C was nearly 10-fold higher than that of its biomass, which was likely due to the accumulation of alkaline minerals and organic matter with the increase of the pyrolytic temperature [36]. The elemental composition of biochar changes with the pyrolytic temperature and depends on the type of feedstock. Carbon content tends to increase with increasing production temperature, while nitrogen, sulfur, hydrogen, and oxygen, which form gaseous products during pyrolysis, decrease [17,37]. Biochars produced from biosolids and animal manures typically contain high amounts of N, P, K and S [17,23,37,38]. Biochars derived from plant biomass, manure, and biosolids generally are characterized by having high N, P, K, and S compared to biochars produced from woody feedstocks. Liard et al. [38] showed that nearly half of the N and S can be lost during pyrolysis when temperature increases from 350 to 600 °C. The same authors found that the residual N in biochar is not bioavailable, whereas the bioavailability of phosphorus depends on soil pH. Hence P shows a low bioavailability in calcareous soils and a high bioavailability in acidic soils.

Physical characteristics, including pore structure, surface area, and adsorption properties, are related to the pyrolytic temperature and feedstock composition [39,40]. Volatile compounds that are present in the feedstock tend to be removed from the matrix with increasing pyrolytic temperature. This enhances the surface area and ash content while decreasing the surface functional groups along with exchange sites. With increasing pyrolytic temperature, aliphatic carbon species are converted into aromatic rings forming a graphene like structure that improves the pore distribution, pore volume, and surface area of the biochar [17]. Biochars containing large amounts of C in condensed aromatic rings tend to possess few functional groups. Surface functional groups play a crucial role in the adsorption capacity of biochar, and the content and type of functional groups are dependent on the feedstock and the pyrolytic temperature [41,42]. Low-temperature chars with low aromaticity contain more C=O and C–H functional groups that promote adsorption for contaminants [43]. The molar oxygen to carbon (O/C) ratio is an indication of the surface hydrophilicity and can be used to estimate the polar functional groups present on the biochar surface [44]. At higher temperatures, the O/C ratio is low indicating more aromatic and fewer hydrophilic surfaces due to high carbonization and loss of polar functional groups [44]. The (O + N)/C ratio serves as an indicator of polarity. It decreases with increasing pyrolytic temperature [44].

In addition to slow pyrolysis, hydrothermal carbonization is another, efficient thermochemical technology to produce biochar. It results high carbon yield. Compared to slow pyrolysis, hydrothermal carbonization is high in energy consumption. Although hydrothermal carbonization uses unconventional wet biomass sources the thermal energy depends on the moisture content and the water to solid ratio that is needed [45]. Biochars produced by hydrothermal carbonization are high in oxygen functional groups and cation exchange capacity (CEC). They are more acidic than biochars produced under slow pyrolysis [46,47]. However, hydrothermal carbonization biochars are readily biodegradable and, hence, the slow pyrolysis biochar is more stable and has a higher potential for carbon sequestration [17]. Nevertheless, pot trials have

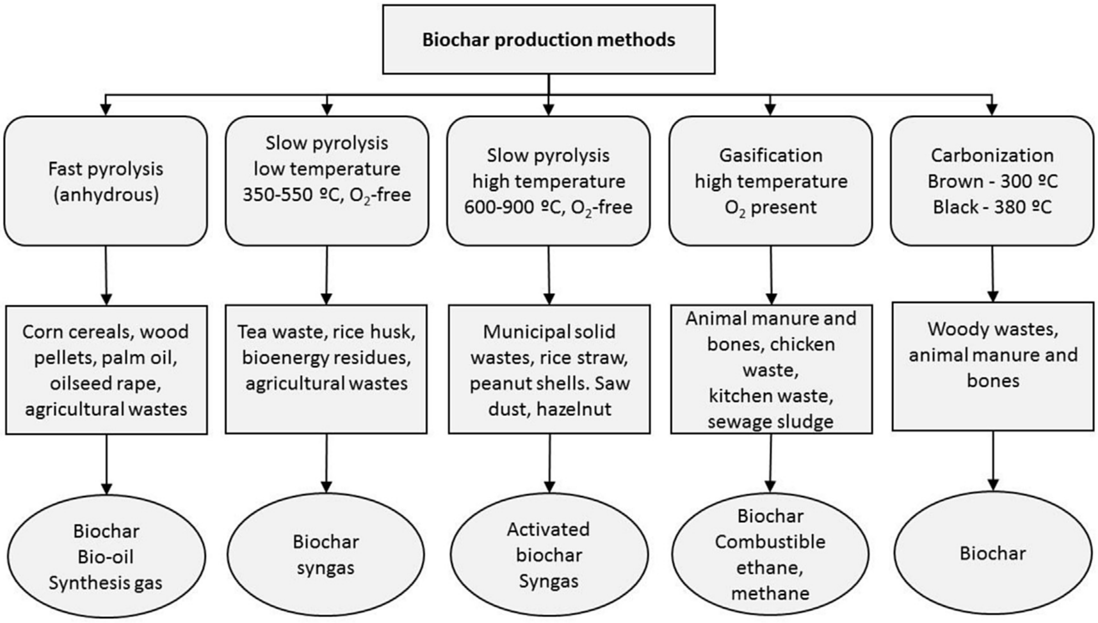

Fig. 2. Schematic representation of biochar production methods with regard to their common feedstock types (adapted from Ref. [34]).

shown low yields in hydrochars compared to chars from slow pyrolysis [48].

Little information has been reported regarding the application of biochars produced from flash carbonization, torrefaction, and gasification technologies in the remediation of pollutants in wastewaters, because these technologies focus on the production of bio-oil, solid fuel, or synthetic gas. Flash carbonization is used to produce biochar through the detonation of a flash fire at high pressure (at about 1–2 MPa) in a packed bed of biomass. Fast pyrolysis rapidly can heat biomass to produce predominately bio-oil, and, subsequently, gas and biochar [21]. Gasification is applied widely in the production of gases such as CO, CO_2, H_2, and N_2 at the expense of oils and biochar. Torrefaction is a thermal pretreatment technology performed at low temperatures typically of 225–300 °C which produces biochar as a byproduct, when the biomass is pyrolysed over a long residence time (~60 min) [49,50]. The first torrefaction reaction step decomposes hemicellulose of the biomass into an unsaturated solid product (70–88 wt%) that is likely to be characteristic with typical biochar properties [32,50]. Hence, it is clear that in flash carbonization, torrefaction, fast pyrolysis, and gasification, the biochar can be obtained as a by-product. However, the use of such biochars in wastewater treatment is perhaps not feasible due to their unfavorable properties depending on the type of pollutants [16,51].

3. Application of biochar for As remediation in water

The capacities of biochar for As removal appear to be dependent upon the feedstocks and production technology. Biochars derived from various types of feedstocks, such as pine wood and bark, oak wood and bark, solid waste, rice husks, biosolids, and animal products, have been used to test their effectiveness on As removal from water (Table 1). However, testing of more feedstocks, such as those that are highly available as waste materials including byproducts of the bio-energy industries and municipal and domestic waste materials, is crucial to optimize the remediation of As contaminated waters. The remediation of both species of As, As(III) and As(V), in aqueous solution using biochar has been successful [13,54]. Raw pine cone derived biochar and its Zn-loaded version have been used to remove As(III) from aqueous solution, with removal efficiencies of 66 and 88%, respectively [59]. Moreover, biochar produced from sewage sludge (biosolids) was highly effective (89%) in the removal of As(V) from water [10]. However, many researchers have focused only on the removal efficiency of As species in single ion systems. A limited number of studies have been conducted to understand the effect of activated and non-activated biochars on the adsorption of inorganic forms of As (III) and As(V) present in binary systems [13]. Moreover, to our knowledge, no study has been conducted to investigate the interaction of biochar with different organic species of As such as methylated and thio-arsenate compounds. This will be a challenging task in future research. Nevertheless, none of the studies paid attention on real environmental water rich in As and co-occurring ions.

3.1. As remediation by non-activated biochar

Many biochars tested for As removal are low temperature derived biochars (300–500 °C), as the presence of more functional groups encourages a better the adsorption of heavy metal(loid)s compared to those derived at higher temperature (Table 1).

3.1.1. Effect of pH

The pH of the medium can have an impact on charge properties of the surface of biochar as well as speciation of As. For instance, various functional groups such as amine, alcohols, carboxylic, etc. that might be present on the surface of biochar tend to be protonated depending on solution pH, thereby changing the surface charge of biochar. On the other hand, solution pH influences the speciation of As into its different neutral and anionic forms including, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} etc. The $H_2AsO_4^-$ species can be dominated at pH 3–6, whereas $HAsO_4^{2-}$, and AsO_4^{3-} become main species of As at 8 > pH [60]. Moreover, trivalent forms of As are stable at pH 0–9 as neutral H_3AsO_3, while $H_2AsO^-{}_3$, AsO_3^{3-}, and AsO_3^{-3} become stable in the pH ranges 9–12, 12–13, and 13–14, respectively [61]. Therefore the adsorption mechanisms of different forms of As on certain type of adsorbents would be more complex due to different

Table 1
Physio-chemical analysis of biochars used in As remediation literature.

Biochar	Temperature °C	As(III)/As(V)	pH	EC dS/m	Proximate analysis %				Elemental analysis %				Reference
					Moisture	Ash	Volatile C	Fixed C	C	H	N	O	
Rice husk	300	As(V)	NA	NA	10.1	17.4	81.6	1.0*	NA	NA	NA	NA	[52]
Sewage Sludge	300	As(V)	NA	NA	84.5	25.9	73.7	0.4*	NA	NA	NA	NA	[52]
Solid Waste	300	As(V)	NA	NA	58.3	32.0	65.8	2.2*	NA	NA	NA	NA	[52]
MSW	400	As(V)	8.0	NA	NA	6.1	22.3	65.2	48.6	12.2	1.3	31.7	[37]
	500	As(V)	8.5	NA	NA	9.2	26.4	63.8	59.5	9.1	1.4	20.8	[37]
	600	As(V)	9.0	NA	NA	6.2	15.1	78.2	70.1	8.4	1.3	13.7	[37]
Empty fruit bunch	700	As(III)	9.4	NA	2.0	13.9	NA	NA	48.0	3.8	1.3	30.0	[13]
Rice husk	700	As(III)	8.5	NA	3.7	27.2	NA	NA	45.0	2.3	0.17	17.0	[13]
Oak wood char	400–450	As(III)	NA	NA	3.17	2.92	15.6	78.3	82.8	2.7	0.3	8.0	[11]
Pine wood char	400	As(III)	NA	NA	2.69	2.30	16.9	78.1	83.5	3.0	0.3	8.2	[53]
Oak bark char	400	As(III)	NA	NA	1.56	11.1	22.8	68.5	71.2	2.6	0.5	13.0	[16]
Sewage Sludge	550	As(III)	NA	NA	2.3	70.2	8.1	8.0	88.0	1.8	8.0	0.4	[54]
Pine cone biochar	500	As(III)	NA	NA	3.12	2.13	27.2	67.5	67.9	3.9	0.6	22.0	[55]
Pine wood biochar	600	As(V)	NA	NA	NA	4.02	NA	NA	85.7	2.1	0.3	11.2	[56]
Rice husk biochar	300–350	As(V)	10.2	2.9	NA	NA	NA	NA	7.78	NA	0.2	NA	[57]
Empty fruit bunch biochar	500	As(V)	9.5	5.3	NA	NA	NA	NA	58.1	NA	1.6	NA	[57,58]

distribution capabilities of As(III) and As(V) species in aqueous solution as a function of pH. The dissociation of As species at different pHs may be expressed as following reactions [61]. Hence, different forms of As can be adsorbed on the surface of adsorbent at different pH values, so that it is quite problematic to distinguish whether the main form of As at particular pH value could be the dominated As species on the surface as well as how the As- surface complex can vary with changing solution pH. Therefore, more innovative future researches are essential in order to understand the adsorption mechanisms of different species of As on biochar type carbon materials at different pHs.

$$H_3AsO_{3(aq0)} \Leftrightarrow H^+_{(aq)} + H_2AsO^-_{3(aq)} pK_1 = 9.23 \tag{1}$$

$$H_2AsO^-_{3(aq)} \Leftrightarrow H^+_{(aq)} + HAsO^{2-}_{3(aq)} pK_2 = 12.10 \tag{2}$$

$$HAsO^{2-}_{3(aq0} \Leftrightarrow H^+_{(aq)} + AsO^{3-}_{3(aq)} pK_3 = 13.41 \tag{3}$$

$$H_3AsO_{4(aq)} \Leftrightarrow H^+_{(aq)} + H_2AsO^-_{4(aq)} pK_1 = 2.3 \tag{4}$$

$$H_2AsO^-_{4(aq)} \Leftrightarrow H^+_{(aq)} + HAsO^{2-}_{4(aq)} pK_2 = 6.8 \tag{5}$$

$$HAsO^{2-}_{4(aq)} \Leftrightarrow H^+_{(aq)} + AsO^{3-}_{4(aq)} pK_3 = 11.6 \tag{6}$$

A study conducted on pyrolysed sewage sludge used for As(III) removal showed that the adsorption capacity at two acidic pHs, which were pH 3–3.5 and pH 6–6.5, was about the same for As(III) removal [54]. However, the pH affected the equilibrium time for adsorption onto sludge biochar. There was slightly higher and faster removal at pH 6–6.5 than the lower pH [54]. In another study, the percentage As(III) removal was a 20–40% at pH 3–4 for oak wood and bark and pine bark biochars [53]. In each case, As(III) sorption decreased above pH 4.0 and the adsorption was virtually insignificant at pH 5.0 and higher [53]. Similar results have been observed for the removal of As(III) by pine cone biochar (PC) [55]. The point of zero charge (pH_{zpc}) for PC was found at pH 4.66; therefore, the biochar surface was positively charged at pH < 4.66; thus, the adsorption of As was higher at pH < 4.66. Furthermore, As(III) adsorption decreased with the increase of pH up to 7.0, which was likely due to the van der Waals interaction between the elemental As and biochar surface. Thereafter, above 7.0 pH, there was a decrease in adsorption, because of the electrostatic repulsive forces between the negatively charged surface of PC with negatively charged As(III) species [55]. The surface of biochar can itself carry both positive and negative charges at a range of pHs; however, the surface becomes net negative above its pH_{zpc}, while it is net positive below the pH_{zpc} [13,62]. Hence, the pH_{zpc} is an influential parameter, because it determines the net charge of the biochar surface for the adsorption of As.

3.1.2. *Effect of redox conditions*

In the soil-water-interface of many hydromorphic or wetland soils such as rice paddies, floodplains, riverine soils, marshes, bogs, and fens, redox conditions can vary [63,64]. The redox potential is one of key factors that can have an impact on the interactions between As and biochar surface [65]. Biochar can act as an electron pump donating electrons to more oxidized species [66]. Nevertheless, the oxidation rate of biochar surface is quite a slow process and hence the biochars possess a high tendency to accept electrons from other reducing agents as well [67]. In a recent study, biochars produced from wood and grass at temperature 200–700 °C were capable of reversibly accepting and donating up to 2 mmol of electrons per gram of biochar and grass biochars having high mineral ash contents showed an increased electron exchange capacities than wood derived biochars [68].

Redox active species such, FeO(OH), MnOOH (E^0 - 1.5 V), MnO_2 (E^0 - 1.2 V), NO_3^- (E^0 - 0.88 V), etc. which are attached with the biochar surface can transform more mobile As(III) to less mobile As(V) species, thereby controlling the mobility of more mobile and toxic As species present in such biochar treated soil and water systems [65,67]. It has been found that depending on the feedstock types, some biochars consist of redox active mineral phases of Fe and Mn and many of these species may exist as nanoparticles [69]. These redox active mineral phases could catalyze the redox reactions associated with different As species as tubular pores of biochar along with mineral phases have different electrochemical potentials [70]. For instance, the oxidation of As(III) to As(V) by MnO_2 is particular of concern to sequestrate mobile As species in soil, sediments and water systems. In this oxidation process, firstly Mn(IV) gets oxidized to Mn(III) producing an intermediate product MnOOH* (reaction 7) [7].

$$2MnO_{2(s)} + H_3AsO_{3(aq)} \Rightarrow 2MnOOH^{(*)}_{*} + H_3AsO_{4(aq)} \tag{7}$$

Secondly, the MnOOH* oxidizes H_3AsO_3 to H_3AsO_4 followed by the adsorption of reaction product of As(V) on the surface of MnO_2 (reaction 2).

$$2MnOOH_{*}^{(*)} + H_3AsO_{3(aq)} \Rightarrow 2MnO_{(s)} + H_3AsO_{4(aq)} + H_2O_{(l)} \tag{8}$$

Rinklebe et al. [65] observed a similar occurrence in the Eh/pH and the As immobilization mechanisms in As contaminated floodplain soil as well as in the same soil amended with biochar.

Iron can be present in biochars in the forms of iron oxide (Fe_2O_3, Fe_3O_4, FeOOH) depending on the pyrolysis conditions, since iron in the oxidation states of both Fe^{2+} and Fe^{+3} may be an essential element in many types of feedstocks [71]. For example, the amount of iron in a biochar derived from bio-solid feedstock has been reported to be 2.3% of the total weight of the biochar [72]. It has been found that iron oxide may be present in biochars as magnetite or hematite. The redox transformation of As(III) to less toxic As(V) and its adsorption on iron oxide has also been examined in several studies [73–75]. Moreover, the combined effects of both oxidation of As(III) and reduction of As (V) and their sorption properties on iron oxide, goethite, and magnetite have been studied under laboratory conditions [76]. The findings of this study revealed that, at pH 6–9, the As(III) is adsorbed to a similar or greater extent (reactions 9 and 10) than As(V) on iron oxide and goethite and the sorption of As(V) on both materials (reactions 11, 12, and 13) is more favorable than that of As(III) below pH 5–6 [13,74,76].

$$Biochar\equiv FeOH_{(s)} + AsO_{3(aq)}^{3-} + 3H_{(aq)}^{+} \leftrightarrow \equiv FeH_2AsO_{3(s)} + H_2O_{(l)} \tag{9}$$

$$Biochar\equiv FeOH_{(s)} + AsO_{3(aq)}^{3-} + 2H_{(aq)}^{+} \leftrightarrow \equiv FeHAsO_{3(aq)}^{-} + H_2O_{(l)} \tag{10}$$

$$Biochar\equiv FeOH_{(s)} + AsO_{4(aq)}^{3-} + 3H_{(aq)}^{+} \leftrightarrow \equiv FeH_2AsO_{4(s)} + H_2O_{(l)} \tag{11}$$

$$Biochar\equiv FeOH_{(s)} + AsO_{4(aq)}^{3-} + 2H_{(aq)}^{+} \leftrightarrow \equiv FeHAsO_{4(s)}^{-} + H_2O_{(l)} \tag{12}$$

$$Biochar\equiv FeOH_{(s)} + AsO_{4(aq)}^{3-} + H_{(aq)}^{+} \leftrightarrow \equiv FeAsO_{4(s)}^{2-} + H_2O_{(l)} \tag{13}$$

Understanding and application of such biochar-As-redox complexes would be a crucial alternative option in order to establish sustainable environmental management strategies for the remediation of wastewater and multi-metal polluted soil systems s. However, the elucidation of the underlying mechanisms of biochar-As interactions in different soil systems still remains poorly understood and, hence, key aspects related to this topic need to be addressed by future research.

3.1.3. *Kinetics and isotherm aspects for biochar-As interactions*

Understanding of kinetics and isotherm aspects related to the adsorption of As on biochar surface is beneficial to examine reaction rates, effect of some variables including initial concentration of As, and re-arrangement patterns of As atoms on the surface. Adsorption of As(III) and As(V) by pristine biochars has been reported to be a function of time [10,37,53–55]. In studies with biochars derived from rice husk, organic fraction of municipal solid wastes and sewage sludge, the sorption of As was well described by the pseudo-second-order kinetic model.

Fitting experimental data to a pseudo-second-order model suggests the dependency of reaction rate on available binding sites in the surface of the adsorbent. The rate-limiting step may be a chemical adsorption between the biochar surface and the contaminant [37,54,55].

Table 2 shows maximum adsorption capacities of different biochars. Highest sorption capacities were reported by Jin et al., 2014 for As(V) sorption, whereas for As(III) the maximum sorption was reported by Samsuri et al. [13] for empty fruit bunch and rice husk biochars produced at 700 °C. Many studies have reported that the Langmuir model widely fits the adsorption isotherms of both As(III) and As(V) onto biochars [10,13,37,53–55,57]. Reports on thermodynamics are limited; however, only one study was found to evaluate the thermodynamic parameters necessary to predict the feasibility of adsorption under natural conditions [55]. Interestingly, some studies have used highly unrealistic initial concentrations for their studies ranging from 50 to 400 mg/L [13,57] and this could lead to bring in wrong conclusions since very high concentrations can lead into surface precipitation on solids.

This study revealed that the adsorption of As(III) on pine cone biochar in aqueous solution is energetically favorable ($\Delta G°$, −4.42 kJ mol^{-1}; $\Delta S°$, 0.058 kJ mol^{-1} K^{-1}) and exothermic ($\Delta H°$, 13.25 kJ mol) [55]. The adsorption of As on biochar is a function of several factors, including the concentration and type of

Table 2
Arsenic adsorption capacities of biochars produced from different feedstocks.

Biochar	Temperature °C	As(III)/As(V)	pH	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Initial Metal Concentration (mg/L)	Optimum Adsorbent dose (g/L)	Maximum Removal	Reference
Rice husk	300	As(V)	6.7–7	155	0.153	0.90	8	2.59 μg/g	[52]
Sewage Sludge	300	As(V)	6.7–7	51	0.058	0.90	16	4.25 μg/g	[52]
Solid Waste	300	As(V)	6.7–7	5	0.029	0.90	16	3.54 μg/g	[52]
MSW	400	As(V)	6.0	21	0.027	5–400	2	24 mg/g	[37]
	500	As(V)	6.0	29	0.039	5–400	2	25 mg/g	[37]
	600	As(V)	6.0	30	0.038	5–400	2	28 mg/g	[37]
Empty fruit bunch	700	As(III)	8.0	1.89	0.011	50	5	18.9 mg/g	[13]
		As(V)	6.0	–	–	50	5	5.1 mg/g	[13]
Rice husk	700	As(III)	8.0	25.1	0.018	50	5	19.3 mg/g	[13]
		As(V)	6.0	–	–	50	5	7.1 mg/g	[13]
Oak wood char	400–450	As(III)	5.0	2.04	0.73	0.01–0.1	10	4.13 mg/g	[53]
Pine wood char	400	As(III)	5.0	2.73	0.41	0.01–0.1	10	2.62 mg/g	[53]
Oak bark char	400	As(III)	5.0	25.4	0.86	0.01–0.1	10	3.00 mg/g	[53]
Pine bark char	400	As(III)	5.0	1.88	1.06	0.01–0.1	10	13.1 mg/g	[53]
Sewage Sludge	550	As(III)	3–3.5	70	NA	1	10	0.07 mg/g	[54]
Pine cone biochar	500	As(III)	4.0	6.6	0.016	0.10	10	0.006 mg/g	[56]
Rice husk biochar	500	As(V)	9.5	23.2	0.009	0–200	2	0.35	[57]
Empty fruit bunch biochar	300–350	As(V)	10.2	46.3	0.008	0–200	2	0.42	[57]

oxygen functional groups, zeta potential, O/C ratios, (O + N)/C ratios and polarity indices [(O + N)/C] [13,23,55,57,77].

3.2. *Use of modified biochar for As treatment*

Many different surface modifications have been examined for As sorption onto biochars. Among those, a zero valent Fe coating is the most prominent, because Fe is one of the most effective materials for As removal from water [12,56,78–81]. However, the materials and methods used for Fe coating vary. In one study, a hematite suspension was mixed with a feedstock and pyrolysed together to induce thermal activation of hematite and maghemite formation [56]. Evaporative methods and direct hydrolysis are common procedures used to produce iron-oxide amended biochars [12,78,79]. Other than iron, AlOOH, manganese salts, or minerals have been used for surface activation of biochars to remove As [80,82]. KOH has been used to activate the surface of municipal solid waste biochars by mixing them with 2 M KOH for 1 h [37]. Activation of biochar by producing nano-composites may lead to an increase in the adsorption capacity due to a high surface area of the nano material [81,82].

Activation of biochar as an amendment has enhanced As sorption as shown in Table 3.

Chemical activation of biochar is so far the sole method that has been used to improve the adsorption capacity via increasing surface area, pore volume, pore size distribution, and partially by changing functional groups on the surface of biochars [18]. The electrostatic interactions are suggested to be the main mechanism that triggers the immobilization of various heavy metal(-loid)s on either positively or negatively charged biochar surfaces [77]. Enhanced surface area and pore volume may enable the diffusion of As into the biochar pores, thereby providing more metal (loid)active sites to bind metal ions on the biochar surface [84]. Thus, the adsorption of As on biochar can be optimized by expanding the surface area and pore size distribution (micro-, meso- and macro-). However, poor adsorption of As was shown in some materials that are characterized with high surface area and pore volume, suggesting that pore size distribution is an additional parameter that influences sorption capacity [17,77]. This implies that many factors can govern the adsorption mechanisms resulting in great variation in the sorption capacities of the adsorbent. Surface complexation with functional groups of biochar is possibly responsible for the adsorption of As ions [12,82]. Biochars produced at low temperatures are rich in oxygenated functional groups, such as carboxylic and phenolic groups [17,21].

The ionizable functional groups of biochar surface may acquire charge through protonation and deprotonation with solutes [85]. Amine groups are one of such surface functional groups which may present on biochar surfaces, can protonate at acidic pHs and result electrostatic attractions with negatively charged arsenate species (reactions 14) [86]. However, further studies are extremely necessary in revealing the actual mechanism in molecular level. Hence, the elucidation of molecular-level interactions controlling the sorption of As on biochar would be of major theoretical and practical interest in future research.

$$Biochar - NH_2 + H^+ \xrightarrow{\text{Protonation}} Biochar - N^{\oplus}H_3 \xrightarrow{H_2AsO_4^-} Biochar - NH - AsO_4 \qquad (14)$$

Assuming the presence of different types of acidic surface sites in hydrated biochar as C_iOH surface reactions for As complexation may written as follows;

Table 3
Arsenic adsorption capacities of modified biochars.

Biochar	Type of Biochar	Temp. °C	As(III)/As(V)	pH	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Initial Metal Concentration (mg/L)	Optimum Adsorbent dose (g/L)	Maximum Removal mg/g	Reference
Mn Oxide modified biochar	Pine wood	600	As(V)	NA	463	0.022 cc/g	10	2.5	0.59	[56]
Birnessite modified biochar	Pine wood	600	As(V)	NA	67.4	0.066 cc/g	10	2.5	0.91	[56]
Hydrogel biochar	Rice husk	300	As(V)	6.7–7	51	0.058	1–150	0.167–16.7	28	[83]
Magnetic biochar	Pine wood	600	As(V)	NA	193.1	NA	20	2.5	0.43	[80]
NZVI-biochar	Bamboo	400	As(V)	NA	NA	NA	5–400	2	24	[81]
KOH activated biochar	Municipal solid waste		As(III)	8.3	49.1	0.357	50	5	31	[37]
Fe-biochar	Hickory chips	550	As(V)	NA	NA	NA	55	1	2.16	[79]
Empty fruit bunch-Fe biochar	Fruit bunch	700	As(III)	NA	NA	NA	50	5	31.4	[13]
			As(V)	NA	NA	NA	50	5	15.2	
Rice husk-Fe biochar	Rice husk	700	As(III)	NA	NA	NA	50	5	30.7	
			As(V)	NA	NA	NA	50	5	16.9	
AlOOH-biochar	Cotton wood	600	As(V)	NA	NA	NA	50	2	17	[82]
Magnetic biochar	Cotton wood	600	As(V)	NA	NA	NA	50	2	3.1	[82]
Fe coated Rice Husk biochar	Rice husk	550	As(V)		77.3	NA	2	0.5	6.0	[78]

$$\equiv C_iOH + H_3AsO_3 \Leftrightarrow \ \equiv C_iHAsO_3^{2-} + H_2O \tag{15}$$

$$\equiv 2C_iOH + 2H_2AsO_4^{-} \Leftrightarrow \ \equiv 2C_iHAsO_4^{2-} + 2H_2O \tag{16}$$

Where C is any of the surface active sites that were taken for the adsorption, here it may be carbon functional group. In some cased biochar is supported with titanium dioxide as a photocatalyst [87]. If TiO_2 is impregnated to biochar, the most common hydrated Ti(IV) may react with As(III) and As(V) and the postulated mechanisms are as equations (17) and (20) [88].

$$Ti^{(IV)} - OH_2^{+} + H_3AsO_4 \Leftrightarrow Ti^{(IV)} - OH_2^{+} \bullet \bullet AsO(OH)_3 \tag{17}$$

$$Ti^{(IV)} - OH_2^{+} + AsO_2(OH)^{2-} \Leftrightarrow Ti^{(IV)} - OH_2^{+} \bullet \bullet AsO_2(OH)_2^{-} \tag{18}$$

$$Ti^{(IV)} - OH_2^{+} + AsO_3(OH)^{2-} \Leftrightarrow Ti^{(IV)} - OH_2^{+} \bullet \bullet AsO_3(OH)^{2-} \tag{19}$$

$$Ti^{(IV)} - OH_2^{+} + AsO_4^{3-} \Leftrightarrow Ti^{(IV)} - OH_2^{+} \bullet \bullet AsO_4^{3-} \tag{20}$$

4. Application of biochar in As contaminated soil

Pot experiments with different plants such as ryegrass (*Lolium perenne* L.), tomato (*Solanum lycopersicum* L.), *Miscanthus giganteus*, and maize (*Zea mays* L.) have been conducted with As-contaminated soils using biochars produced at various temperatures. Soils that have been used were contaminated by geogenic As, including mine soil [89,90], as well as industrially contaminated soil [91], and As containing pesticides applied soils [92,93].

4.1. Response of soil physio-chemical properties of As-contaminated soils to biochar

High extractable dissolved organic carbon (DOC), Ca, Mg, K, SO_4^{2-} contents were observed in soils amended with wood and bioenergy derived biochars [92,94,95]. A rapid reduction of As(V) to As(III) in biochar amended soils has been observed, because organic matter and various functional groups such as phenolic, alcoholic and carboxylic associated with the biochar can act as electron donors to govern the reduction reactions (reactions 21, 22, 23) [96]. Because of such naturally occurring redox reactions in biochar incorporated soils, the mobility of As(III) species is increased, while As(V) is strongly retained, thereby reducing the leachate concentrations of As(V) and increasing the bioavailability of As(III) in such biochar-soil systems [96,97].

$$AsO_{4(aq)}^{3-} + 2H_{(aq)}^{+} + 2e \rightarrow AsO_{3(aq)}^{3-} + H_2O_{(l)} \tag{21}$$

$$Biochar{\equiv}C_6H_5OH_{(s)} \rightarrow C_6H_5O_{(s)} + e + H_{(aq)}^{+} \tag{22}$$

$$Biochar{\equiv}R(OH)_{(s)} \rightarrow \equiv R = O_{(s)} + e + H_{(aq)}^{+} \tag{23}$$

Cation exchange capacity (CEC) and pH of soils demonstrate a considerable increase with increasing application rates of biochar which may contribute to controversial interpretations. High pH may lower the positive charge on soil-BC system which could reduce the anionic As sorption whereas high EC may induce more cations to be present and that may induce As sorption or precipitation [98]. However, none of the studies have focused their attention on the influence of the increase in pH and CEC by the addition of BC on As sorption. In some previous studies the addition of biochar as a soil amendment decreased the DOC in pore water collected from field and pot trials, since soil carbon pool is relatively stable and insoluble [94,99,100]. However, it was shown that Orchard Prune residue biochar increased the organic matter content by approximately >50%, which might increase the mobilization of As(V) and move it into soil solution [94]. The interactions of As with phosphate ions, which are associated with biochar, are also of concern, because phosphate ions are linked with the mobility and bioavailability of As species [101,102]. In a solution culture, the presence of high contents of P reduced the mobility and bioavailability of As(V) due to their competitive effects that allowed As(V) to be more retained and, and, consequently, it was less available for uptake by plants. However, application of P in soil systems increased the dissolution of As(V), thereby enhancing its bioavailability [101]. Hence, it is clear that the interactions of As–P are dependent on the environmental system as well as the existing concentrations of As and P [102].

Studies on biochar ageing in As contaminated soils are scarce. However, the age of the biochar likely determines its surface charge, which is an essential parameter to describe to understand the adsorption behavior of various ionic forms of contaminants [103]. When biochars are placed in soil, porous organomineral layers form on the surface (Joseph et al., 2013). These have a high concentration of function groups that can bind with heavy metals [104]. However, studies have revealed contradictory data, some of which indicate that ageing of biochar does not increase in surface charge [103], whereas other studies have demonstrated an increase in surface charge with ageing biochar [105,106]. Additional experiments on soil ageing with biochar may develop a better mechanistic understanding of the interactions of biochar and soil.

4.2. Role of biochar on As in soil

The application of biochar in many As contaminated systems results in an increase in its mobility and bioavailability [93,94,107,108]. Hence, this suggests that future researchers should not apply some biochar types in the field for remediation of As contaminated soils [89]. To solve this conflicting behavior of biochar-As systems, recent studies have suggested the use of biochars along with phytoremediation for decontamination of soils with As [94,96]. Although similar As concentrations can be found in soils, inherent differences can be observed in soil systems, which are likely due to differences in soil properties such as texture, P, pH, Fe, OM, and DOC before and after biochar additions, and they may influence As mobility and bioavailability [91]. At the same time, As mobility/sink in soil depends strictly on the co-existence of organic/inorganic sulfur and iron [109–111]. Understanding molecular level characteristics may provide information concerning the mechanisms involved, but studies are limited at this level [109].

Biochar ageing studies have confirmed that high CEC in soil leads to the formation of stable biochar-metal complexes. Reduction in As concentration in the shoots of maize (*Zea mays* L.) plants grown in biochar amended sandy soil was observed, which was mainly attributed to the adsorption of As onto the biochar surfaces [107]. The results showed a decrease in As uptake by the maize depending on the application rate. In a soil rich in As due to the long-term application of pesticides, bioavailability of As for phytoextraction by *Lolium perenne* L. was studied [92]. The authors showed that the bioavailability of As with low-temperature (350 °C) derived biochars was less than that from biochars derived from high-temperatures (650 °C) (Reduction in bioavailability were 100% and 70% respectively compared to the control) [92]. The amount of water-extractable As can be reduced temporarily because of the precipitation of As with metal cations, such as Ca^{2+}. However, they may readily re-dissolve, releasing As again to the aqueous solutions [92,112]. In the ryegrass study [76], when the application rate of biochar was increased from 30 to 60%, the concentrations of As in shoot tissues of ryegrass were increased indicating that higher application rates would be suitable for increasing As phytoextraction in soils.

Application of biochar produced from orchard prune residue as a soil amendment in an As contaminated mine soil increased the concentrations of As in pore water (500–2000 μg L^{-1}) and decreased the accumulation of As in roots and shoots of tomato plants (*Solanum lycopersicum* L.) grown in the mining soil. This interesting observation was explained by the formation of soluble As-DOC complexes, which are mobile but may not be able to diffuse through the tissues of tomato plants (Fig. 3). Accumulation of As in tomato fruits was low due to reduction of the phyto-availability of As in the biochar treated mine soil [89]. Contents of P and Fe in soils can be increased by over 20-fold by the addition of biochar [89,113]. Macro-, micro- and nano-porous structure of biochar surfaces can facilitate the reduction of Fe [114] and Mn species found in soils [66], which results in a negative Eh value. Negative Eh conditions promote the reduction of As(V) to As(III) species which is not readily adsorbed in soils and hence under negative redox potentials, As species are more mobile in soils [115].

However, some studies have demonstrated insignificant effects of fresh biochar on As adsorption compared to soils without biochar [91,103]. This suggests a possibility of As complexation with DOC from biochar, which can be prominent in soils with high organic C. Slight changes in soil pH may not influence the sorption of As in biochar amended soils [103]. Competition of DOC, P, and As for the vacant sorption sites on soil surfaces can lead to an increase of the solubility of As in soil [91,94]. In some cases, biochar application may induce solubilization of As in the pore water (>2500 mg/L), which may be attributed to high pH. However, in a study where a compost amendment was used, As toxicity was reduced due to a reduction in extractable metals and an increases in soluble P [91,94]. More detailed molecular level studies are needed to provide insights into the influence of ageing, DOC, P interactions, and microorganisms on the soil-As interactions.

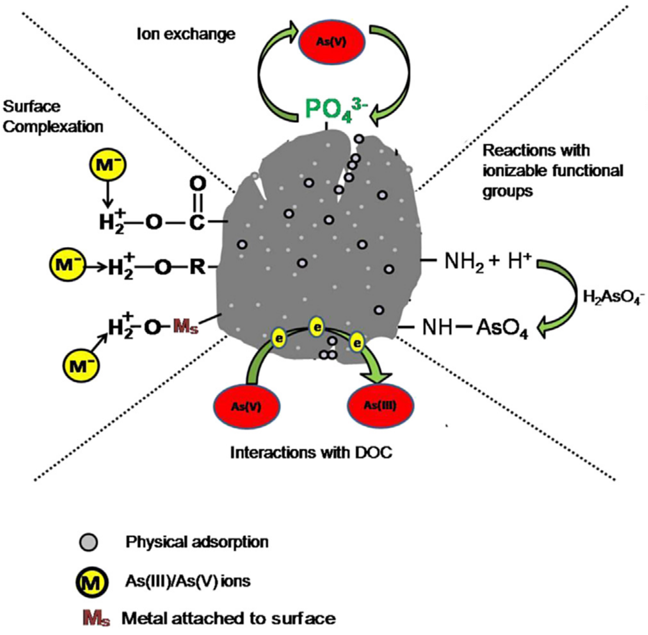

Fig. 3. Graphical illustration of postulated mechanisms for As adsorption on biochar surface. (A colour version of this figure can be viewed online.)

4.3. Response of microbiological properties in biochar amended As contaminated soils

Biochar amendments have been found to have less of an effect on microbial biomass nitrogen (MBN) than microbial biomass carbon (MBC) [116]. A long-term field study showed that the MBC:MBN was increased by biochar, thereby reducing the temporal variability of microbial growth in the environment [116].

Only a few studies have been carried out on the responses of microbes in biochar amended As contaminated soils [92,93,117,118]. Biochar amendments in soils can increase microbial activity [116]. The improvement of both plant growth and soil microbial activity may be due to nutrient supply by biochar (K^+, Ca^{2+}, Mg^{2+}) and the labile C fraction of biochar that is considered as a food source of microbes [92]. Microbial activity in soils can also affect the redox conditions of the soil as well as speciation of As. Hence, microbial activity can lead to reduction of As(V) to As(III), thereby impacting the mobility and bioavailability of As. Dehydrogenase (DHA) activity is considered to serve as an indicator of total microbial activity. In one study [76], addition of biochar produced under both low and high pyrolytic temperatures resulted in an increase in DHA compared to the control. However, no significant difference was observed with the application rate [92]. The labile fraction of carbon (C), which is higher in low temperature derived biochar than in high temperature biochar, can act as an energy source for soil microorganisms [119]. Such a readily available energy source can enhance microbial activity resulting in a higher soil DHA, which may contribute to the short-term reduction in the water-extractable concentration of As [92]. In a study regarding the speciation and reduction of As(V) in As contaminated mine tailing sediments amended with biochar, the populations of As(V) reducing bacteria, *Geobacter, Anaeromyxobacter, Desulfosporosinus, and Pedobacter*, were increased after the addition of biochar and this biochar-bacterial consortium stimulated the reduction of As(V) to As(III) and increased the concentrations of dissolved organic matter in the biochar amended mine sediments [117]. More research is necessary to understand mechanistically the soil-microbial activities that are associated with biochar amended soils with As.

4.4. Summary and future research

Many papers have been published on the applications of biochar to remediate soil and water systems that are polluted by toxic organic and inorganic contaminants. However, few laboratory or field studies have been done regarding the interactions of biochar and metalloids. More research is needed to study biochar-As interactions. The present review focuses on recent developments related to the interactions of biochar and As species found in water and soil systems.

Arsenic adsorption properties are influenced by pyrolytic temperature, residence time, feedstock, and pyrolysis technology. Depending on the pyrolytic temperature, biochar can be used as an adsorbent for arsenic. Low-temperature biochars are more effective in As sorption than high-temperature biochars. Adsorption of As is affected by the solution pH, adsorbate and adsorbent dose, and equilibration time. Much attention has been given to enhancing As sorption by modifying the biochar surface. Modifications have been performed using different coatings of iron, including nano zero valent iron and other materials such as Al and Mn. The most predominant adsorption mechanisms for As by biochar include electrostatic attraction, ion-exchange, physical adsorption, and chemical bonding (complexation and/or precipitation). However, due to the low surface area and weak mechanical properties, biochar has not been considered as promising as activated carbon in the water treatment. Modifications to biochar which increase the surface area and mechanical properties, may allow it to be used in water treatment suitable for oxy-anions and metalloids hence, the research towards such would be in high interest in terms of material science point of view. The studies in the literature for biochar-As interaction in water consist of rather different parameters and methods from study to study and hence, comparison is impossible. Also, no studies have focused the attention on organic arsenic removal using biochar and that would be promising for future research. Enhanced biotranformation of methylated arsenic by bacteria incorporated biochar may be a potential future study since biochar provides residency for microbes. Molecular level interactions of biochar-functional groups need to be studied more, which may provide clear information on the mechanisms involved.

Biochar-induced changes in soil physio-chemical properties may influence the bioavailability and phytotoxicity of As. Contrasting results have been reported in terms of As mobility in soil due to changes in other solutes in the soil solution, DOC, pH, CEC, and Phosphate. Even though the use of biochar as an adsorbent is increasing, number of research gaps exist. More research is essential to confirm the use of nano-biochar composites in the environment. Low-cost modifications such as using steam-activation, acid-activation, or other activations may facilitate As remediation. Activation by nitrogen may provide amide functional groups which could be useful in increasing arsenic sorption, however, no research has been focused. Hence, more attention need to be driven towards assessing interaction of different arsenic species on nitrogen activated biochars. Interactions with rhizosphere microbes, iron plaques interactions with biochar in soil needs fundamental molecular level attention may be using advanced techniques like Nanoscale secondary ion mass spectrometry etc. Speciation and fractionation of different arsenic species in soil may influence the mobility, bioavailability, fate and transport with the presence of biochar due to the changes in soil chemistry, which have no attention paid yet. The interaction of biochar and soil microbes in relation to the immobilization of toxic As species, including the use of methylated and thio-arsenates, need to be studied. None of the studies have performed any cost-benefit analysis for biochar and other materials which can be considered as a gap in the research related to As-biochar interaction.

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