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Review article

Biochar versus bone char for a sustainable inorganic arsenic mitigation in water: What needs to be done in future research?

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ABSTRACT

Arsenic (As) is an emerging contaminant on a global scale posing threat to environmental and human health. The relatively brief history of the applications of biochar and bone char has mapped the endeavors to remove As from water to a considerable extent. This critical review attempts to provide a comprehensive overview for the first time on the potential of bio- and bone-char in the immobilization of inorganic As in water. It seeks to offer a rational assessment of what is existing and what needs to be done in future research as an implication for As toxicity of human health risks through acute and chronic exposure to As contaminated water. Bio- and bone-char are recognized as promising alternatives to activated carbon due to their lower production and activation cost. The surface modification via chemical methods has been adopted to improve the adsorption capacity for anionic As species. Surface complexation, ion exchange, precipitation and electrostatic interactions are the main mechanisms involved in the adsorption of As onto the char surface. However, arsenic-bio-bone char interactions along with their chemical bonding for the removal of As in aqueous solution is still a subject of debate. Hence, the proposed mechanisms need to be scrutinized further using advanced analytical techniques such as synchrotron-based X-ray. Moving this technology from laboratory phase to field scale applications is an urgent necessity in order to establish a sustainable As mitigation in drinking water on a global scale.

1. Introduction

Arsenic (As) is a carcinogenic metalloid that exists in the environment due to geogenic sources as well as anthropogenic activities. It has been found that there are > 250 types of As bearing minerals in the environment (Rahaman et al., 2008). Arsenopyrite (FeAsS) is the most abundant As bearing mineral and other As bearing minerals such as niccolite (NiAs), enargite (Cu_3AsS_4), sperrylite ($PtAs_2$), cobaltite (CoAsS), loellingite ($FeAs_2$), realgar (AsS) and orpiment (As_2S_3) can be widely found in the natural environment (Herath et al., 2016b). Naturally occurring geochemical and biological processes tend to enhance the release of more mobile species of As from the aforementioned mineral phases into the environment. Moreover, anthropogenic activities including mining of As bearing mineral ores, coal and oil exploitation, use of As containing pesticides, herbicides and pharmaceuticals may directly contributed to the release of a variety of As species into the environment. Because of both naturally occurring sources and man-made activities, As is accumulated in environmental, geological, and biological systems at elevated concentrations.

The mobility of As and its immobilization properties in water are highly sensitive to changes in redox potential and pH (Darling, 2016). Generally, As exists in the forms of organic (methylated arsenic compounds, arsenocholine, arsenobetaine, etc.) and inorganic (mono-di-tri-tetra-arsenites and -arsenates) in the environment. However, inorganic

forms of As in water is of particular concern in terms of its mobility, transformation and toxicity. In aqueous phase, As occurs in two principal inorganic forms, including arsenate [As(V)] and arsenite [[As(III)] depending on solution pH (Duker et al., 2005; Sorg et al., 2014). Under oxidizing conditions (250–750 mV), As(V) exits in four different species, including H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Bissen and Frimmel, 2003). In aerobic water (500–750 mV), arsenic acid (H_3AsO_4) becomes the prevalent form of As(V) at extremely acidic pHs (pH < 2), whereas As(V) occurs in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$ in a wide range of pH (pH 2–11). In mildly reducing environments (−250–+250 mV), arsenious acid (H_3AsO_3) appears at a wide range of pHs (1–9), but it tends to convert to $H_2AsO_3^-$ with the increase of solution pH up to 12 at redox potential ranging from −250 to −500 mV (Panagiotaras and Nikolopoulos, 2015). When the pH value exceeds 12, it occurs in the form of $HAsO_3^{2-}$ in extremely high reducing environments (Bissen and Frimmel, 2003). In natural systems, inorganic As(III) species are of particular interest in terms of their high toxicity, mobility and redox transformation (Mandal and Suzuki, 2002). The concentrations of As in groundwater typically are in the range of 1–2000 μg/L (Figoli et al., 2016). The World Health Organization (WHO) has revised the recommended permissible limit (guideline value) of As in drinking water from 50 μg/L, which was set by the EPA in 1975 (Yamamura et al., 2003), to 10 μg/L (WHO, 2011). However, As contaminated groundwater has been used for drinking and irrigation in many parts of the world, particularly in developing countries where treatment/mitigation options are limited due to political/regulatory lack of awareness as well as poor economic situations (Herath et al., 2016b).

Different technologies have been used for the removal of As from water. Table 1 summarizes the technologies which have been used to remove As from water including some of the advantages and disadvantages of each process. Adsorption has been extensively used for the removal of contaminants from water at different scales, ranging from single household to industrial scale. However, the suitability (including economic and environmental sustainability) depends on removal effectiveness and the possibility of regenerating the sorbent and recycling the contaminants. Different types of feedstock have been used as sorption media, including natural materials, such as zeolites (Xu et al., 2000) and red mud (Genç-Fuhrman et al., 2005; Zhang et al., 2008); industrial by-products such as hydrous titanium (Pirilä et al., 2011); biological and agricultural wastes including rice husk (Pehlivan et al., 2013), laboratory woodchip bioreactors (Hua et al., 2016), sludge

waste (Tavares et al., 2012), hydrogels (Sanyang et al., 2014) and biopolymers represented by chitosan (Boddu et al., 2008; Yamani et al., 2016). In order to increase the selectivity of the removal process, recent studies have adopted thermal, chemical and physical modifications to produce composite materials that are efficient for the removal of As in water (Trakal et al., 2018; Wang et al., 2017; Zhang et al., 2016).

Biochar is a heterogeneous carbon material comprising a variety of surface functional groups produced by the thermal alteration of a variety of waste materials. A typical biochar is a carbon-rich product obtained when biomasses, such as wood, leaves, manure, municipal waste sludge, etc. is heated in a closed system with little or absence of air (Lehmann and Joseph, 2015). Biochar derived from different waste feedstocks is widely applied for the removal of organic and inorganic pollutants such as heavy metals (Xu et al., 2019), metalloids (Trakal et al., 2018), pesticides (Herath et al., 2016a) and pharmaceuticals (Zeng et al., 2019) that are present in contaminated-water. On the other hand, animal bone char is another form of biochar that can be produced under similar controlled thermal conditions to produce a phosphorus (P) rich product (Zwetsloot et al., 2016). Bone char produced from animal bones which is the result of partial calcination or the pyrolysis of meat industry waste, is mainly composed of hydroxyapatite (HAP) [$Ca_{10}(PO_4)_6(OH)_2$] and carbon (Sternitzke et al., 2012). It has been reported as a promising adsorbent for fluoride ions in water (Kaseva, 2006; Leyva-Ramos et al., 2010; Medellin-Castillo et al., 2007). However, there is a limited number of studies on the effectiveness of bone char applied in water treatment processes for the removal of metal(loid) (Chen et al., 2008), organic pollutants (Egbuchunam et al., 2016) and dyes (Sun and Yang, 2003). More than 60% of heavy metal(loid)s removal process is attributed to the interaction with the inorganic part (calcium carbonate) of the bone char (Mendoza-Castillo et al., 2015) due to three immobilization mechanisms: ion exchange, dissolution-precipitation reactions, and complexation (Sternitzke et al., 2012). In recent years, there has been increased attention on the modification of the biochar surface as an effective approach to alter the surface properties, pore volume, pore size and surface charge for the selective removal of targeted contaminants from water systems. However, there are limited studies adopting the modification of bone char for water treatment purpose, especially for As removal from water. Thus, engineered biochar and bone char, are a result of either physical or chemical modification using potential natural or synthetic materials (alkaline or acid solutions, zeolite, chitosan, polymers, etc.).

Table 1
Some advantages and disadvantages of different technologies used for arsenic removal in water.

Removal technology	Advantages	Disadvantages	Reference
Coagulation	• Applicable over a neutral pH levels • Chemicals are available commercially	• The need for post-treatment units (sedimentation and filtration) • Highly contaminated solid waste disposal/management issues	Franco and Carro (2014) Mohan and Pittman (2007) Nicomel et al. (2016)
Adsorption and ion exchange	• Commercially available chemicals (such as activated alumina and resins) • Suitable for removing both As(V) and As(III) • Easy operation • No sludge produced • Cost-effective	• The need for further remediation (disposal/management issues) • Regeneration issues represented by concentrated liquid waste	Chiavola et al. (2015) Mohan and Pittman (2007) Singh et al. (2015)
Chemical oxidation precipitation	• Break through monitoring is not required • Cost effective method	• Concentrated sludge disposal issues • Not suitable for large scale water treatment • Efficient pH control is required	Anjum et al. (2009) Arar et al. (2014) Bora et al. (2016)
Membrane process	• Efficiently remove both inorganic arsenic forms from water	• High energy demand and cost of reverse osmosis • Liquid waste management in membrane technologies • Fouling issues • Sensitive to pH levels • Time consuming process • Using reagents	Greenlee et al. (2009) Nicomel et al. (2016) Perez-Gonzalez et al. (2012) Shokri et al. (2016)
(Micro)biological remediation	• Economic and promising technology	• Needs more in-depth studies and skilled operators • Have some limitation related to the climate conditions	Hayat et al. (2017) Li et al. (2016)

This review provides a critical overview of the production, characterization and modification of different types of biochar and bone char along with a comprehensive evaluation of their application in the immobilization of various As species in water. Overall, the present review critically analyses and discusses the current knowledge on the As sorption capacity of different types of unmodified and engineered biochar as well as the sorption mechanisms which trigger the immobilization of As species on the biochar surface. The understanding of existing research gaps on arsenic-biochar and arsenic-bone char interactions in different water systems is of utmost importance in order to develop more innovative remediation strategies in future research which would pave the way to establish sustainable As mitigation on a global scale.

2. Methodology

The present review provides a critical assessment of existing research on the application of biochar and bone char for the removal of soluble inorganic As on laboratory and small scale experiments. The review is a collection of appropriate resources extracted from credible sources such as reputable international journals, google scholar books, governmental reports, standards and library catalogue. Fig. 1 depicts the outline of process that was followed for constructing the review. The key words "bone char", "biochar", "arsenic removal", "arsenic immobilization" and "water treatment" were used to collect the relevant literature (regardless to the publication date). Firstly, the documents were collected and organized based on the source of the adsorbent (i.e. bone char or biochar). Secondly, careful screening was followed based on the modification method and the removal of As from water. In some cases, electronic mails were sent to the corresponding authors to clarify some controversial points in their research work. Google scholar alerts were also used for an update to the latest publications related to the topic of the manuscript. For the sake of effective presentation of literature results, quantitative data were compiled and summarized in tables. In some occasions, calculations were made to unify the units or to compare the percentages of As removal on bone char/biochar. Graphical representations of adsorption mechanisms were constructed based on the reported reactions in the literature. As per the knowledge of the authors, reports with controversial results and/or those that lack scientific justifications were avoided. The authors attempted to critically analyze and provide justifications for the results reported in previous studies based on their own knowledge and available information in this field.

3. Arsenic from health perspective

The toxicity of As usually depends on its change in oxidation state (Jain and Ali, 2000). The As(III) is highly cellular toxic due to its ability to hinder the metabolism of glucose, thereby interrupting the energy production through replacing phosphate (PO_4^{3-}) group in adenosine triphosphate ($C_{10}H_{16}N_5O_{13}P_3$) (Singh et al., 2011). As(III) is more toxic than As(V) as it deteriorates the function of many proteins due to binding to sulfhydryl groups (Oremland and Stolz, 2003), and has high affinity to interact with the vicinal thiols in pyruvate dehydogenase and 2-oxoglutarate dehydrogenase (National Research Council, 1999) and with the glucocorticoid receptor (Singh et al., 2011). However, As(V) can effect on metabolism in human body is due to the interaction with PO_4^{3-} receptors and it is less toxic as it needs to be reduced to As(III) to be more reactive with the cells (Molin et al., 2015). Toxicological effects of As exposure are highly associated with aberrations of skin, kidney and liver cells of numerous animal species and humans. The consumption of As contaminated water for a long time may result in various chronical health effects including cardiovascular diseases, neurological disorders, gastrointestinal disturbances, liver disease and renal disease, reproductive health effects, dermal disease and cancers (Bundschuh et al., 2017; Jomova et al., 2011). It has been reported that long-term ingestion of As at 500 μg As/L via drinking groundwater can cause one death per 10 people due to lung, bladder, and skin cancers (Smith et al., 2000). Inorganic As is extremely toxic to living organisms due to high binding ability with protein-sulphydryl (SH) groups and the overproduction of cellular reactive oxygen species (ROS) (Elia et al., 2018). Subacute concentrations of As(III) and dimethylarsinic acid (DMA(V)) are highly sensitive to the cell lines such as human hepatocellular carcinoma and epithelioma papulosum cyprinid generating excessive levels of ROS which may damage of the antioxidant defense system. In addition, the As(III) is in-vitro cytotoxic and genotoxic on human keratinocytes and in-vivo DNA damage in leukocytes and lymphocytes (Sadaf et al., 2018). Because of such critical health consequences of chronic and acute exposure to As, the remediation of As contaminated ground-surface-, drinking- and irrigated- water as well as As contaminated-wastewater through environmental friendly and cost effective strategies is an urgent necessity.

4. Biochar and bone char production and characterization

The pyrolysis temperature and type of feedstock are considered to be key factors in controlling the physio-chemical characteristics of biochar such as surface area, pore size/pore distribution, pH and surface functional groups (Vithanage et al., 2017). Many studies have been well established on the production of various types of biochar, factors affecting their properties, and their application in the remediation of contaminated soil and water systems (Cao and Harris, 2010; Meng et al., 2013; Sun et al., 2014; Vithanage et al., 2017). Biochar and bone char can be produced by using different processes, including low temperature processes, pyrolysis and gasification (Fig. 2) (Mohan et al., 2014; Novotny et al., 2015). At low temperatures (50–300 °C), hydrothermal carbonization, torrefaction and ratification processes take place. These processes produce about 80% of solids with high O/C ratio (Novotny et al., 2015). At higher temperatures (300–700 °C), pyrolysis processes take place. Fast pyrolysis involves a rapid heating of the feedstock in the absence of oxygen followed by a rapid cooling and quenching (Brewer et al., 2009). Fast pyrolysis with short residence time (< 2 s) (Mohan et al., 2006) results in about 40% bio-oil and only 12% solid fraction. The char produced from this process possesses high surface area and porosity and low O/C and H/C ratio compared to those produced via slow pyrolysis. Slow pyrolysis (conventional pyrolysis) is performed in the absence of oxygen using slow heating methods and long residence time, which ranges from hours to days (Dutta et al., 2012). The amount of char produced from this process is about 35% of the final product (Mohan et al., 2014), however the surface characteristic depends particularly on the type of feedstock and pyrolysis temperature (Ahmad et al., 2014). In gasification methods, the biomass is partially combusted in an oxidizing atmosphere producing a relatively small amount of char (about 10%) (Libra et al., 2011). The solid fraction produced via gasification is a porous media with high surface area and low O/C and H/C ratio (Novotny et al., 2015).

In general, increasing the pyrolysis temperature will result in decreasing biochar yield, while increasing ash content, cation exchange capacity (CEC) and surface area (Brewer et al., 2009; Cao and Harris, 2010; Meng et al., 2013; Sun et al., 2014). The existence of different types of functional groups on the biochar surface is related to the pyrolysis temperature and the pH of the solution. Moreover, the CEC of a biochar depends on the charring temperature. Tan et al. (2015) reported that up to a certain temperature (based on the source of the feedstock), the CEC of biochar will increase due to the change in the levels of free OH groups available on the char surface. Then the CEC tends to be decreased as the aromatic crystallites get evolved at higher charring temperature (Harvey et al., 2011). It is prudent to remark that applying pressure during the pyrolysis process may also alter the quality of the char. Cetin et al. (2004) reported that increasing pyrolysis pressure can result in decreasing the surface area of the biochar from 296 m^2/g at 0.1 MPa (1 bar) to 236 m^2/g at 2.0 MPa (20 bar) (using N_2
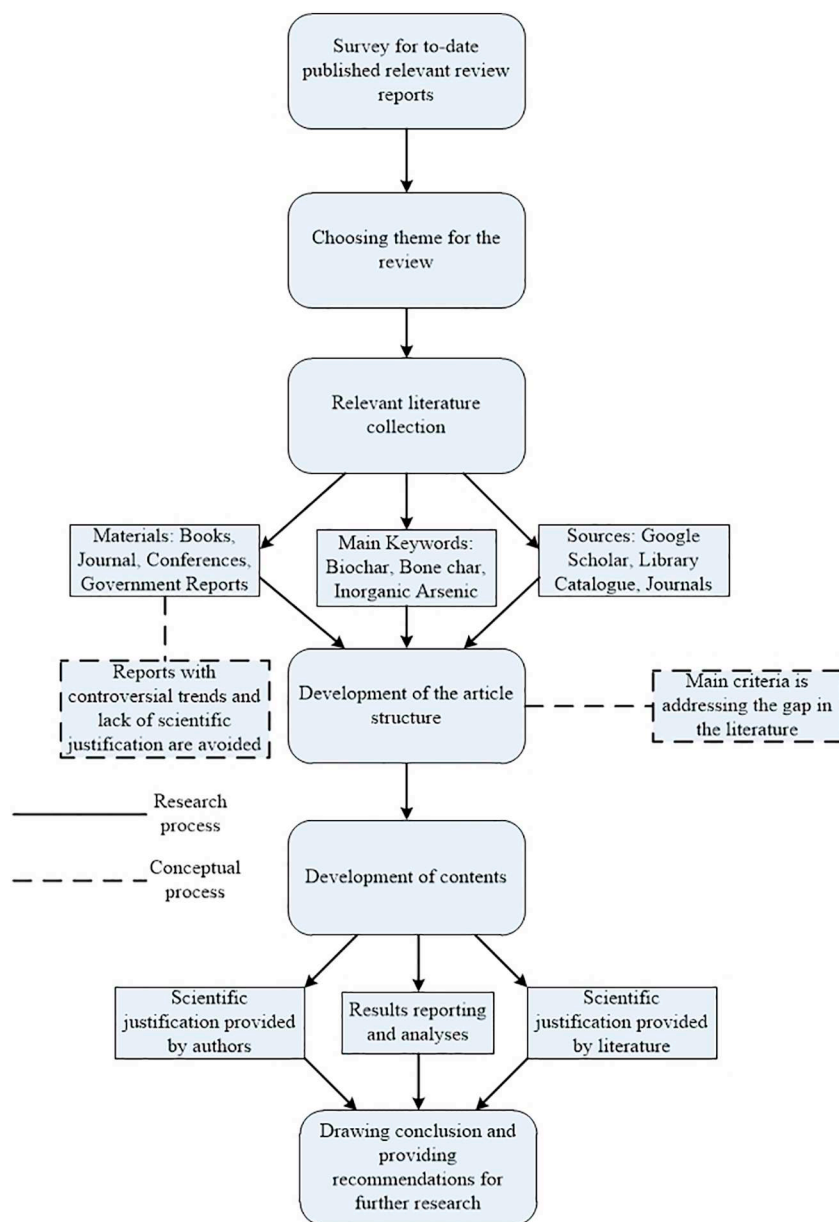
Fig. 1. Schematic diagram of the methodology of the review.

surface area measurements).

The particle size of the feedstock used for char production is also of a particular concern in order to improve the reactivity of biochar through its effect on the intraparticle heat transfer (Lei et al., 2009). It is a fact that the higher intraparticle contact area achieved with smaller particle size can enhance heat transfer inside the grain particles. However, the effect of particle size of the biochar depends on pyrolysis process and feedstock type. Up to now, there is no satisfactory data regarding the relationship between grain size and the adsorption capacity for biochar produced by slow pyrolysis. Nevertheless, it is evident that increasing residence time (Downie et al., 2009) is capable of providing sufficient heat to overcome heat transfer resistance for large particles of feedstock (Demirbas, 2004; Rapagna and Latif, 1997).

Several studies have been published with the primary goal of investigating the effect of particle size during fast pyrolysis and gasification on gas, bio-oil quality and char reactivity (Beaumont and Schwob, 1984; Huang et al., 2008; Lin et al., 2017; Septien et al., 2012). Biochar produced via fast pyrolysis is found to be more reactive and porous than those from slow pyrolysis (Zanzi et al., 1996). Generally,

the particle size of biochar from organic sources is significantly lower than those of the feedstock due to the shrinkage and attrition during the pyrolysis. Nevertheless, in some other cases, there will be an increase in the particle size of the biochar due to the particles' agglomeration (Cetin et al., 2004).

The adsorption capacity of biochar for the removal of contaminants is attributed to the existence of functional groups on the biochar surface. The surface charge of the particles can be controlled through the protonation and deprotonation of the existing functional groups (Yuan et al., 2011). At pH levels less than the point of zero charge (pH_{PZC}) of the biochar surface, protonation of some surface functional groups such as carboxyl, ammine, hydroxyl etc. will take place, resulting in an overall positive surface charge on the biochar surface (Waghmare et al., 2015). Thus, the biochar having acidic pHs would favor the adsorption of negatively charged pollutants such as arsenates/arsenites, antimonates/antimonites, etc. Biochar produced at low temperatures (200–400 °C) is preferred for the removal of inorganic and polar organic contaminants due to their binding with O– containing functional groups of the biochar (Ahmad et al., 2014) and the higher O/C molar ratio for
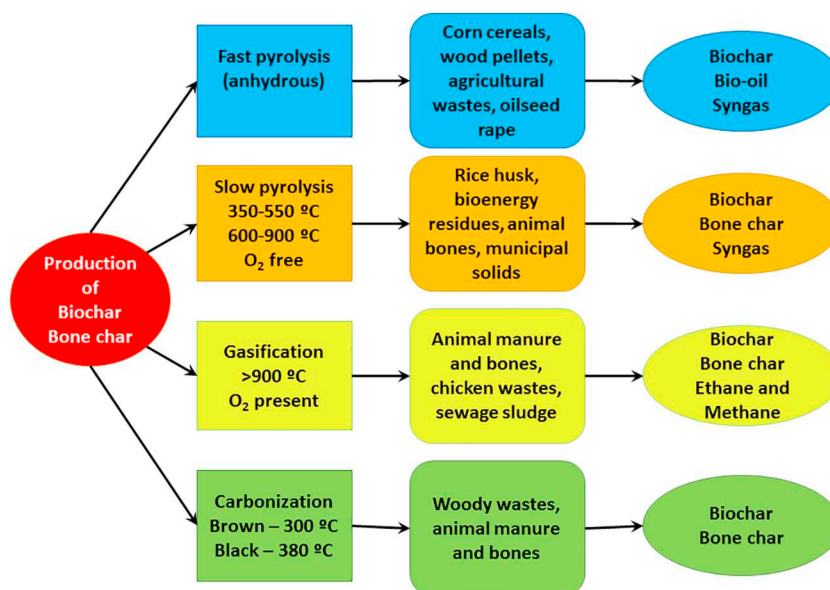
Fig. 2. Schematic diagram of biochar and bone char production methods from different feedstock types. [Adapted from (Vithanage et al., 2017)].

the biochar produced at low temperature (Uchimiya et al., 2011). Therefore it is clear that the availability of functional groups, O/C ratio, polarity indices (O + N)/C and zeta potential are crucial factors in determining the potential of biochar to remove contaminants from aqueous solutions (Samsuri et al., 2013).

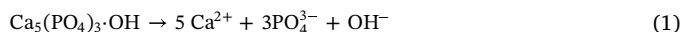## 5. Biochar and bone char for arsenic removal from water

Biochar produced from different types of feedstock such as pine wood and bark, oak wood and bark, solid waste, rice husks, biosolids, and animal products, has been used to test their effectiveness for As removal from water. However, unmodified biochar has been found to be possessing limited sorption ability of As in aqueous media. This is because the potential of biochar for As removal is predominantly dependent on the surface charge (Hu et al., 2015). 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_{PZC}, while it is net positive below the pH_{PZC} (Vithanage et al., 2016). Hence, the pH_{PZC} is an influential parameter to determine the net charge of the char surface for the adsorption of As in aqueous media. The sorption capacity of both biochar and bone char can be improved by changing the surface charge through physical and/or chemical modification methods (Liu et al., 2014). Interestingly, bone char derived from cattle bones can be applied for the removal of As from water to a significant extent without any surface modification. Therefore, this review comparatively discusses the effects of modified and unmodified biochar and bone char for the removal of As from water in order to understand the gaps in existing research which need to be addressed by future research.

5.1. Bone char for arsenic removal from water

Several studies investigated the sorption mechanisms and factors affecting sorption efficiency for enhancing the removal of As(V) using bone char produced from waste animal bones such as cattle and fish bone. Czerniczyniec et al. (2007) reported that the high salinity (0.05–0.5 mol/L) and hardness levels of water can enhance the adsorption of As(V) on cow bone char in drinking water. The increment in salinity levels may result in increasing Ca^{2+} concentration in the solution due to the increase in the solubility of biogenic hydroxyapatite (HAP). High hardness levels were capable of increasing the positive surface charge on bone char, thereby increasing the interaction

between negatively charged As(V) and char surface. The maximum removal (75%) was achieved onto the bone char produced at 900 °C at an initial As(V) concentration of 1 mg/L (up to 0.142 mg As/g sorbent). On the other hand, decreasing the charring temperature to 500 °C resulted in an increase of the sorption capacity by more than two-fold due to the increase in surface area (from 2.6 to 376.4 m^2/g). Bone char effectively removed As(V) from drinking water (up to 95.2%) at pH 10 and an initial As(V) concentration of 0.5 mg/L (Chen and Chai, 2008).

The effect of pH, contact time, adsorbent dosage and initial As concentration on As(V) sorption onto commercial bone char (supplied by Biochemistry Ltd., Sichuang, China) were investigated by Chen et al. (2008). This study demonstrated that As(V) sorption is rapid in the first 30 min and that the initial concentrations (0.5, 1.0 and 1.5 mg/L) did not affect the equilibrium time. The pH range of 2 to 13 and the adsorbent dose of 0.1 to 0.8 g/L significantly influenced the removal efficiency. The maximum As(V) removal was 99.18% (0.827 mg/g) at pH 10 and an initial As(V) concentration of 0.5 mg/L. This study further suggested that the maximum removal achieved at high pH levels may be attributed to co-precipitation between $HAsO_4^{2-}$ and HAP in the presence of Ca^{2+} and ion exchange between hydroxyl and As(V) ions (Fig. 3). Similarly, Begum et al. (2016) investigated As(V) removal using commercial bone char (produced at 450 °C and purchased from Anthracite Filter Media Company) in the pH range of 1–11, initial As(V) concentrations of 0.1–1 mg/L and adsorbate dose of 1–5 g/L. A maximum adsorption capacity of bone char of 0.134 mg/g was achieved at pH 4, As(V) concentration of 1 mg/L and adsorbate dose of 3 g/L which agreed with the predicted value by Langmuir isotherm model. This indicates that As(V)adsorption was a monolayer one with the homogenous bone char surface. Liu et al. (2014) studied the adsorption of As (V) from wastewater onto a commercially produced cow bone char at 500 °C having a surface area of 1.51 m^2/g, via batch and column experiments. Using the Langmuir isotherm model to fit the experimental results, the maximum sorption capacity for As(V) was 0.335 mg/g at pH 4 and an initial As(V) concentration of 10 mg/L. The mechanisms that trigger the removal of As(V) were found to be dissolution, ligand exchange and electrostatic attraction as expressed by Eqs. (1)–(3) (Liu et al., 2014).
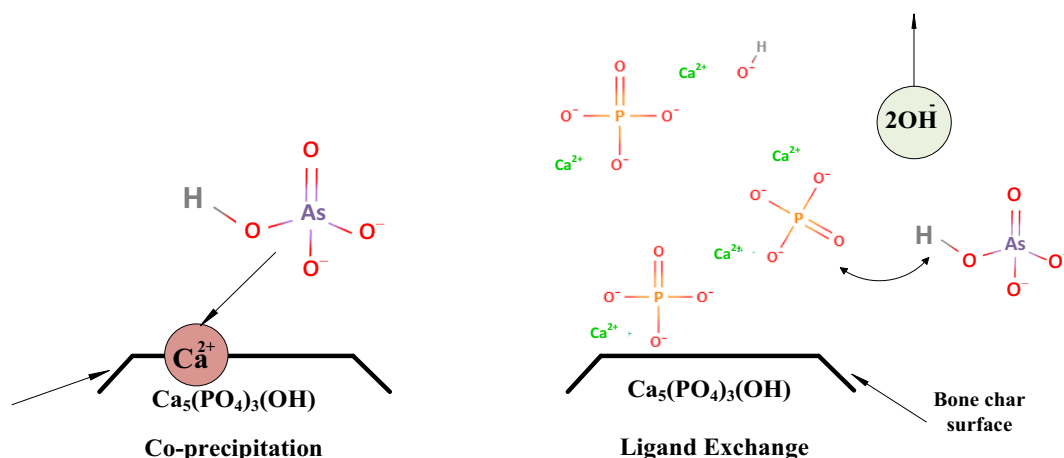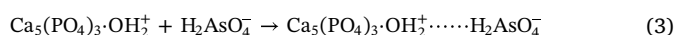
$$Ca_5(PO_4)_3 \cdot OH \rightarrow 5\,Ca^{2+} + 3PO_4^{3-} + OH^- \qquad (1)$$

$$Ca_5(PO_4)_3 \cdot OH + H_2AsO_4^- \rightarrow Ca_5(PO_4)_3 \cdot H_2AsO_4 + OH^- \qquad (2)$$

Fig. 3. As adsorption through co-precipitation and ligand exchange mechanisms on the unmodified bone char surface.

$$Ca_5(PO_4)_3 \cdot OH_2^+ + H_2AsO_4^- \rightarrow Ca_5(PO_4)_3 \cdot OH_2^+ \cdots \cdots H_2AsO_4^- \qquad (3)$$

Synthetic HAP, which is an emerging bioceramic used in biomedical applications possesses many similarities to the naturally occurring HAP in animal bone and teeth (Nayak, 2010). Hence, it is acceptable to utilize this structural similarity to predict the efficiency and gain understanding of As removal mechanisms with bone char (Fig. 3). Sneddon et al. (2005) compared the performance of synthesized HAP with barite (HAP + B) (produced from commercially available bone-meal, from Vitax Ltd) and granular activated carbon (GAC) for the removal As(V) from aqueous solution. A maximum removal of As(V) by HAP + B was observed to be 0.32 mg/g at 4 mg/L initial As concentration, 10 g/L bone char dose and initial pH of 5.0. Because unmodified bone chars are less effective for the removal of As from water, some recent studies have used modified bone char to increase the removal efficiency of As from aqueous solutions. It is noteworthy to remark that up to date, only single study is available on the investigation of As(III) removal by bone char possessing a maximum removal capacity of 0.22 mg/g (Mlilo et al., 2009). Thus, further study is recommended to investigate this aspect, as it would be more cost-effective to eliminate the pre-oxidation of As(III) to As(V).

5.2. Modified bone char for arsenic removal

To our knowledge, the effect of coating bone char with Fe oxide nanoparticles on the removal of As(V) has been studied for the first time by Soltani et al. (2017). In this study, composites of cattle bone char, Fe_3O_4 nanoparticles (with diameter < 50 nm) and chitosan biopolymer were applied for the immobilization of As(V) in an aqueous solution at a range of pH 2-11. The removal capacity of As(V) decreased under both extreme acidic and basic conditions due to the formation of H_3AsO_4 at pH < 2.0, and the increase in OH^- competing ions at high pH levels, respectively. The maximum As(V) removal capacity estimated by the Langmuir isotherm model was found to be 112 µg/L. This composite has been recognized as a spontaneous adsorbent for As(V) removal from aqueous solution. The removal mechanism proposed by this study is electrostatic interaction force between negatively charged As(V) species and the positively charged $Fe_3O_4^-$ nanocomposite surface at neutral pH range. However, it is noteworthy to mention that the adsorption mechanism of As(III) on such iron oxide coated char surfaces is strongly affected by a surface complexation mechanism. Fig. 4 depicts the proposed mechanisms for the adsorption of As(V) and As(III) in iron oxide modified bone char surface. As(III) and As(V) are capable of adsorbing onto the iron oxide coated bone char surface by an inner-sphere ligand-exchange mechanism. In this ligand exchange, As oxyanion gets exchanged with surface $-OH$ or $-OH_2$ groups which are directly co-ordinated on Fe^{3+} at the iron oxide surface. For the adsorption of As

(V), the absorbed As(V) is usually coordinated to two adjacent structural Fe^{3+} cations by iron oxide (Fig. 4(a)) which is a bidentate binuclear-bridging complex. In contrast, in the adsorption of As(III), both bidentate binuclear-bridging complexes and monodentate complexes can exist (Fig. 4(b)). A monodentate complex is formed when a single oxygen atom of the As(III) oxyanion coordinates with a single structural Fe^{3+} at the iron oxide surface. It has been confirmed that the bonding of As(III) on iron oxide surface predominantly takes place through either a monodentate bond or the formation of an outer-sphere complex (Yoon et al., 2016). In an outer sphere complex, the ligand is not co-ordinated directly to the structural Fe^{3+}, instead it is bound to the surface $-OH$ or $-OH_2$ groups through hydrogen bonds (Fig. 4(c)). Therefore, it is predicted to be a strong and easy adsorption of As(III) onto adsorbents modified with Fe_3O_4 than As(V) in the adsorption process.

A commercial bone char (from Sichuan Biochemistry Co. Ltd. in China) was effectively modified by using nano-sized manganese (using $MnSO_4$ solution) for As removal in water (Liu et al., 2016). The modification of bone char surface with manganese resulted in increasing the specific surface area of uncoated bone char from 1.51 m^2/g to a maximum of 4.6 m^2/g for the modified bone char at 15 g/L initial Mn^{2+} concentration. The results of this study revealed that the adsorption capacity of modified bone char for As(V) is 78 times higher than the uncoated bone char, and the removal efficiency linearly increases with increasing the manganese concentration (0.025–14.5 mg/g). The maximum As(V) removal was 9.46 mg/g at 30 g/L of manganese coated bone char, which was much higher than that of the uncoated bone char (0.12 mg/g). Such a modification of char surface for As(V) removal was presumably attributed to the enhancement of electrostatic interactions between As(V) and the bone char surface.

Liu et al. (2010) proposed a chemical modification method to remove As(V) from simulated groundwater (with initial concentration of 0.195–0.959 mg/L) by doping Cu onto synthesized HAP. Copper doping onto the HAP (CuHAP) significantly increased the surface area from 6.63 m^2/g of unmodified bone char to 77.5 m^2/g of modified bone char. As a result, the maximum As(V) uptake by CuHAP was 0.048–1.091 mg/g at pH 7.7–8.0 which was 1.6–9.1 times higher than that of untreated HAP (0.03–0.1199 mg/g). The adsorption mechanism of As(V) by CuHAP may be a complex process due to the formation of different Ca-HAP complexes with other metal impurities in bone char such a $Ca_{(10-3 \times /2)} Al_x(PO_4)_6(OH)_2$, $Ca_{(10-x)} Mg_x(PO_4)_6(OH)_2$, and $Ca_{(10-3 \times /2)} La_x(PO_4)_6(OH)_2$ (Chen et al., 2018). Therefore, chemical characterization of bone char would be a critical step before the surface modification via metal doping.

Moreover, Passman et al. (2014) added a layer of commercial bone char to a clay filter in a prototype model to investigate the removal of
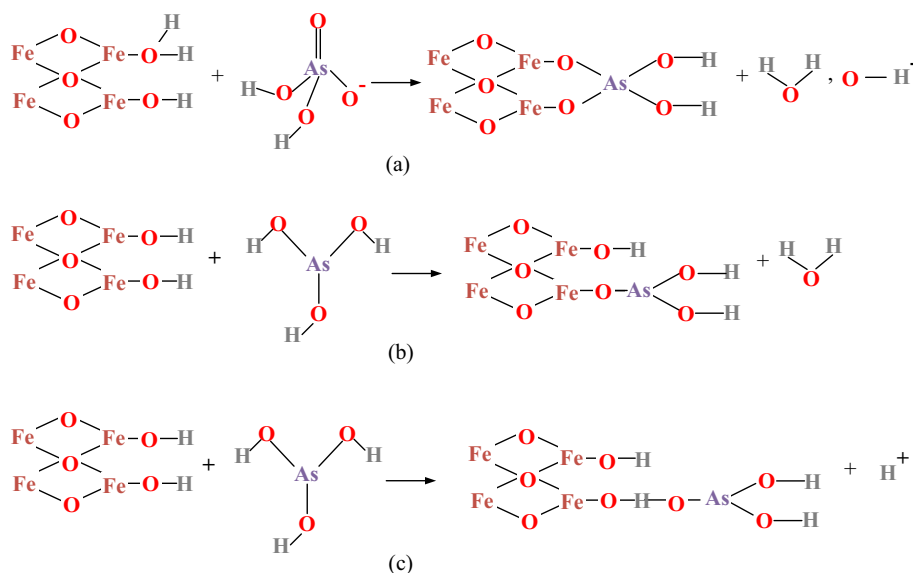
Fig. 4. The proposed mechanism for the surface complexation of As(V) on iron oxide coated bone char surface (Yoon et al., 2016).

As as well as the removal of microorganisms in drinking water. In this method, two types of filters including clay and bone char were attached to each other and the water was passed through the filters to remove coliform bacteria on the clay filter and subsequently As species on the bone char layer. This modified system interestingly decreased the As concentration from 0.5 mg/L to < 0.01 mg/L in the effluent (below WHO and United States Environmental Protection Agency (US EPA) standard limits). Hence, the application of this type of materials in large scale would be a promising strategy for lowering the concentration of As below 10 μg/L in drinking water.

5.3. Biochar for arsenic removal

Recent studies have recognized different types of feedstock including agricultural, solid and sludge wastes and industrial by-products as promising sources for the production of biochar which will also be an alternative waste management option in the environment. Biochar derived from waste materials and agricultural residues has been widely investigated for the immobilization of As species in water (Vithanage et al., 2017). For instance, Agrafioti et al. (2014a) studied the adsorption and desorption at different initial As(V) concentrations (90–850 μg/L) in aqueous solutions using three types of biochar produced from rice husk (BC–RH), solid wastes (BC–SW), and sewage sludge (BC–SS). For an initial As(V) concentration of 90 μg/L, the maximum As(V) removal by BC–RH (8 g/L adsorbent dose and surface area of 155 m^2/g) was only 2.813 μg/g. On the other hand, the maximum As(V) removal was 2.98 and 3.094 μg/g on the BC–SS and BC–SW, respectively. The BC–SW biochar, having a high ash content of 32% w/w with 49.38% of CaO, is likely to be efficient in As(V) removal at pH 9.5 due to its strong interactions with the biochar surface. On the other hand, in an alkaline solution with high Ca content, As(V) removal takes place through the precipitation. The removal of As(V) by BC–SS was increased at low pH due to the presence of the ferrous oxide on the biochar surface in which the sorption mechanism is governed by a redox reaction between As(V) and Fe(II).

Mohan et al. (2007) investigated the adsorption of As(III) onto biochar produced by fast pyrolysis from barks and woods of oak and pine at 450 °C. At pH levels < 2, oak-bark biochar removed a maximum of 70% of As(III) from the solution. The removal of As(III) by oak and pine wood biochar increased from 0 to 20% at pH 2–4. The optimal As (III) removal was 12.15 mg/g at pH 3.5 on pine bark char as predicted by the Langmuir isotherm model. The higher removal capacity of pine bark biochar was due to its higher surface area and pore volume compared to the other biochar samples.

Industrial activities distributed throughout the world tend to generate solid wastes at excessive quantities. The use of industrial by-products as a low-cost sorbent will contribute to improve waste disposal management in developed as well as developing countries due to improper waste handling and disposal practices. Examining the possibility of reusing the by-product of these processes for environmental remediation may justify their validity as an alternative for fossil fuels. For instance, Yadav et al. (2014) used sponge iron char (SIC) having a surface area of 78.63 m^2/g for As(III) and As(V) removal from wastewater. The maximum As removal was found to be at pH 12, adsorbent dosage of 6 g/L, initial As concentration of 150 μg/L and equilibrium contact time of 3 h. The maximum adsorption capacity predicted by the Langmuir isotherm model was 28.58 and 27.85 μg/g for As(V) and As (III), respectively.

Up to date, limited studies exist on biochar produced from the by-products of biological processes for As removal from water. For instance, the high surface area and positively charged surface functional groups have been observed in anaerobically digested sugar beet tailing based biochar. Such biochar types are supposed to be more suitable for anionic contaminant reclamation (Yao et al., 2011). Moreover, the existence of large amount of nano-sized MgO on the biochar surface provides a strong binding ability to remove negatively charged contaminants in an aqueous solution (Yao et al., 2011). The mechanism of As(V) and As(III) immobilization on biochar are not fully understood due to heterogeneous nature of biochar surface with various types of functional groups; however, a small number of studies have proposed some mechanisms including ion exchange (Begum et al., 2016) and co-precipitation (Liu et al., 2014). Therefore, the immobilization mechanisms of different As species on the biochar surface need to be addressed by future research.

5.4. Enhancing arsenic removal by engineered biochar

Engineered biochar has been recognized as a viable option to enhance the effectiveness of As removal from water and soil systems (Rajapaksha et al., 2016). Modification of biochar via chemical and physical methods has endeavored to improve the surface area and surface functional groups of biochar, thereby enhancing its sorption capacity (Zhou et al., 2013). Physical modification of biochar, conducted through purging steam, N$_2$, CO$_2$, or Ar, provides a smooth

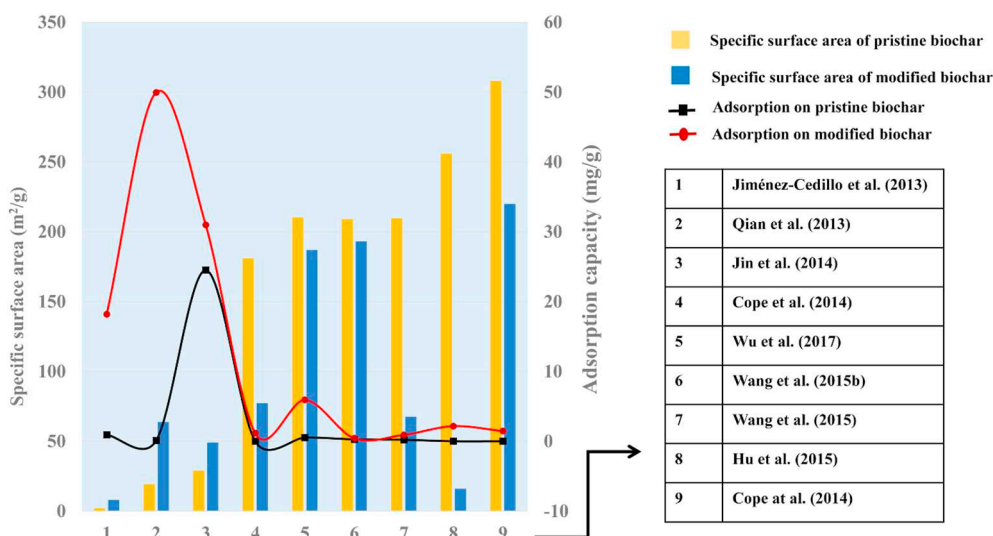|	
1	Jiménez-Cedillo et al. (2013)
2	Qian et al. (2013)
3	Jin et al. (2014)
4	Cope et al. (2014)
5	Wu et al. (2017)
6	Wang et al. (2015b)
7	Wang et al. (2015)
8	Hu et al. (2015)
9	Cope at al. (2014)

Fig. 5. The effect of biochar modification on its specific surface area and As(V) sorption capacity.

biochar surface along with high surface area and uniform pore distribution (Mohan et al., 2014). Chemical activation is performed either prior to or during combustion through the addition of some chemicals such as mild acids, alkaline solutions, organic solvents, and other chemicals such as NaOH, Ca(OH)$_2$, Fe salts, or Fe oxide minerals depending on the type of contaminant and its application (Niazi et al., 2016). Activation of the biochar surface by acidic solutions plays an important role in removing metallic residues and impurities from the biochar surface, while alkaline solutions remove ashes from the surface leading to higher surface area and pore volume (Liou and Wu, 2009; Rajapaksha et al., 2016). Chemical and physical methods can be used either separately or combined together to improve the capability of biochar to remove contaminants from water. Fig. 5 shows the effect of biochar modification on the specific surface area and the sorption capacity of the biochar before and after modification. Cho et al. (2013) reported that the surface area of marine macro-algae-derived biochar can be increased up to 57.9 and 1287 m^2/g after physical (steam activation) and chemical activation (with KOH solution), respectively. Several studies reported that chemical modification of biochar, specifically impregnation with chemical elements results in a decrease in the surface area due to clogging the pores of the biochar surface. However, such alteration can increase the adsorption capacity due to surface chemistry alteration (Cope et al., 2014; Hu et al., 2015; Wang et al., 2015a).

For As removal from water, the activation of municipal waste sludge biochar using 2 M of KOH solution increased the adsorption capacity for As(V) nearly 1.3-fold higher than that of unmodified biochar (Jin et al., 2014). Such an efficient removal of As(V) is attributed to the enhancement of surface area and porous texture of the biochar after the modification with KOH. The modification resulted in a replacement in the functional groups and an increase in the positive surface charge of the biochar, which resulted in a higher affinity of As(V) species to the biochar surface (Jin et al., 2014). Compared to acid-wash, alkali-modification increases surface aromaticity increasing C/H ratio while decreasing O/C ratio (Ahmed et al., 2016b). Thus, the higher aromaticity of the base-leaching derived biochar and its high carbon content prompt the alkaline agent crosslinking to the biochar surface (Ma et al., 2014).

Chemical modification of biochar surface is an effective strategy for enhancing the sorption capacity. Chemical substances that are newly introduced to the biochar surface provide a great affinity for contaminants to form surface complexes through strong inter-molecular interactions (Rajapaksha et al., 2016). However, the disadvantages of some chemical activation methods include the use of corrosive

activating agents, such as strong acids and bases, and the need for washing after the chemical treatment (Rashidi and Yusup, 2016). In order to treat As contaminated water, chemically engineered biochar can effectively be used for such purposes. However, compared to the chemical modification methods adopted for the removal of inorganic contaminants in recent studies, application of biochar for the removal of As(III) (Jiménez-Cedillo et al., 2013; Lin et al., 2017; Van Vinh et al., 2015) and As(V) (Cho et al., 2017; Hu et al., 2015; Qian et al., 2013; Wang et al., 2015a; Zhang and Gao, 2013) species is very limited and mostly focuses on the removal of As(V) rather than As(III).

5.4.1. Biochar coating with metals and/nano-sized metals

Biochar coating with metal oxides, carbon nanotubes or graphene was recently adopted to improve biochar properties for selective removal of contaminants such as pharmaceuticals and heavy metals (Rajapaksha et al., 2016). However, the only coating method found in the literature for improving As removal is the coating of metal oxides with different particle sizes (ranging from micro to nano scale). Modification of biochar using nanoparticles has been reported as a promising method for improving sorption capacity of biochar for water and soil remediation due to the special physical and chemical properties of added nanomaterials including their particle size, surface area, chemical properties, photo-electronic and photocatalytic properties (Liu et al., 2011). Metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers are able to enhance sorption capacities for water treatment purposes (Savage and Diallo, 2005). Zhang and Gao (2013) stated that modification of biochar with nanoparticles increases the sorption capacity for different contaminants such as heavy metals, metalloids, PO$_4^{3-}$, NO$_3^-$ and organic compounds.

Impregnation of Zn(NO$_3$)$_2$ on pine cone biochar increased the surface charge thereby improving As(III) removal through electrostatic interactions (Van Vinh et al., 2015). This Zn-loaded biochar showed a higher removal capacity for As(III) at pH 2–4, at which As(III) is dominant as neutral H$_3$AsO$_3$ and H$_2$AsO$_3^-$. Similarly, rice, soybean, and peanut straw biochar coated with Al(III) showed an increased sorption capacity for the removal of As(V) due to shifting zeta potential-pH curves to a positive direction under acidic conditions (Qian et al., 2013). The Al(III) modification on aforementioned biochar significantly increased the sorption of As(V) compared to the unmodified biochar (Table 2). Zhang and Gao (2013) developed a composite material from biochar and AlOOH nanoparticles to improve the As(V) sorption capacity in aqueous media. This study reported that the biochar-AlOOH composite can be used as an effective material for As(V) removal from polluted water although it takes quite a long time (12h) to reach the

Table 2
The effect of surface modification of biochar to remove arsenic from water.

Biochar	As(III) removal mg/g	As(V) removal mg/g	pH	Initial concentration mg/L	Charring temperature °C	Surface area m²/g	Pore volume cm³/g	Author
Soybean straw (SSB)	-	Negligible	5	22.5–89.9	350	1 ± 0.2	-	Qian et al. (2013)
Peanut straw (PSB)						2.1 ± 0.5		
Rice straw (RSB)						19.3 ± 1.1		
0.3M-Al/SSB		33.32				72.7 ± 2.7		
0.6M-Al/SSB		48.37				89 ± 3.5		
0.6M-Al/PSB		48.37				39.9 ± 1.5		
0.6M-Al/RSB		49.95				63.9 ± 2.7		
Biochar/AlOOH nanocomposite	-	17.41	-	50	600	-	-	Zhang and Gao (2013)
Pine cone biochar (PC)	0.0057	-	4	-	500	6.598	0.016	Van Vinh et al. (2015)
Zn-loaded PC	0.007		4			11.543	0.028	
Mn oxide/Pine biochar	-	0.59	7	1.0–20	600	463.1	0.022	Wang et al. (2015a)
Birnessite/Pine biochar		0.91				67.7	0.066	
Unmodified pine biochar		0.2				209.6	0.003	
Amorphous Mn/Grape stalk biochar	-	34.1[a]	7.0	74.922	600	44	-	Trakal et al. (2018)
Corn stem biochar	2.89		3	0.2–50	620	60.9		Lin et al. (2017)
Fe-Mn/Corn biochar	8.25					208.8		
Pinewood biochar with Ni/Mn oxides	-	0.549	-	0–20	600	125		Wang et al. (2016)
Ni/Mn-layered double Hydroxides/Pinewood biochar	-	6.25	-	0–40		282.8		
Wheat straw biochar	Negligible	-	9.3	5–200	500	124.44		Zhu et al. (2016)
Bismuth/wheat straw	16.2					190.4		
Empty fruit bunch biochar (EFBB)	18.9	5.5	For As(III) at pH 8–9,	3–300	-	1.89	-	Samsuri et al. (2013)
Rice husk biochar (RH)	19.3	7.1	For As(V) at			25.161		
Fe/EFBB	31.4	15.2	pH 6					
Fe/RH	30.7	16.9						
Oedogonium/Fe biochar	-	80.7	-	0.0075–749.22	300	-	-	Johansson et al. (2016)
Gracilaria/Fe biochar	-	62.5						
Petroselinum crispum/Fe³⁺	0.06	0.19	6.5	0.05–2	500	1.13	0.006	Jiménez-Cedillo et al. (2013)
Petroselinum crispum biochar/Fe³⁺	0.31	18.17				8.05	0.008	
Rise husk (RHC)	-	Negligible	4	0–2.5	550	181	-	Cope et al. (2014)
Fe/RHC		1.15 ± 0.1				77.3		
RHC		Negligible			950	308		
Fe/RHC		1.46 ± 0.11				220		
11.4% Rice husk-Ca²⁺	-	> 0.095	10.8	8	300	-	-	Agrafioti et al. (2014b)
11.41% Rice husk-Fe⁰		0.029	7.4					
11.4% Rice husk-Fe³⁺		> 0.76	2.4					
11.4% Solid waste-Fe⁰		> 0.063	10.9					
11.4% Solid waste-Fe³⁺		> 0.38	2.8					
2.3% Rice husk-Fe⁰		0.025	7					
2.3% Rice husk-Fe³⁺		0.036	6.8					
2.3% Solid waste-Fe⁰		> 0.063	10.4					
2.3% Solid waste-Fe³⁺		> 0.063	9					
Hickory chips biochar	-	Negligible			600	256	-	Hu et al. (2015)
Fe-impregnated biochar		2.16	5.8	0–55		16		
Pinewood biochar	-	0.265	7	1–50	600	209.6	-	Wang et al. (2015b)
Hematite biochar (HPB)		0.429				193.1		
Rice straw biochar	0.448	0.522	As(V) at pH 6 As(III) at pH 10	1–50	600	210.29	-	Wu et al. (2017)
Rice straw/Red mud	0.52	5.923				186.95		
Water hyacinth biochar-Fe²⁺/Fe³⁺		7.41	5.3	2–105	250	69		Zhang et al. (2016)
Magnetic biochar with colloidal γ-Fe₂O₃	-	3.147	-	0–200	700	-	-	Zhang et al. (2013)
Kans grass straw biochar-Fe³⁺/Fe²⁺	2	3.1	13.5	0.4–0.8	500	31.45	0.177	Baig et al. (2014)
Rice straw biochar	-	3.681	4	0.2–50	450	-	-	Liu et al. (2017)
Magnetic biochar		10.6	3			-	-	
Chitosan magnetic biochar		17.88	5			-	-	
Chestnut shell biochar	-	17.5	4	0.2–50	500	-	-	Zhou et al. (2017)
Magnetic gelatin/Chestnut shell biochar	-	45.5				-	-	
Municipal waste sludge biochar	-	24.49		5–400	500	29.1	0.039	Jin et al. (2014)
KOH/Municipal waste sludge	-	30.98				49.1	0.357	
Hydrogel/Rice husk biochar	-	28.32	6	1–150	-	-	-	Sanyang et al. (2016)
Rice husk biochar		-						
FeCl₃/Coffee ground under CO₂	-	8.9	4.5	12.4–95	700	512	0.249	Cho et al. (2017)
FeCl₃/Coffee ground under N₂		13.1				8.3	0.018	

Table 2 (*continued*)

Biochar	As(III) removal mg/g	As(V) removal mg/g	pH	Initial concentration mg/L	Charring temperature °C	Surface area m²/g	Pore volume cm³/g	Author
Granular and activated sludge biochar	Negligible	Negligible	–	50	300	–	–	Zwetsloot et al. (2016)
FeCl₃/Granular sludge biochar	6.1	11.5			500			
ZVI/Red oak biochar	15.58 (Total As)		7–7.5	0–25	900	–	–	Bakshi et al. (2018)
ZVI/Switchgrass biochar	7.92 (Total As)							

[a] Data calculated from the information reported in the article.

equilibrium adsorption.

Table 2 summarizes the efficiency of engineered biochar over un-modified biochar for the removal of As from aqueous solutions. Hydrous manganese oxides and birnessite have the ability to immobilize soluble As(V) due to different mechanisms including adsorption, surface complexion or precipitation (Trakal et al., 2018). Wang et al. (2015a) studied the kinetics and sorption capacity of As(V) sorption onto unmodified pine wood biochar (PB) and modified PB with MnCl₂.4H₂O (MPB) and birnessite (BPB). The sorption capacity of BPB for As(V) was 0.59 mg/g, which is significantly higher than that of PB (0.20 mg/g), and the highest sorption capacity of BPB is due to strong redox interaction with birnessite particles. The surface structure of the biochar used for As removal is of a great deal in the effectiveness of the composite in removing the targeted contaminants. Following the same procedure to produce a biochar birnessite composite, Trakal et al. (2018) reported a higher removal capacity (3.42 mg/g) for As(V) using grape stalks as a feedstock. Modifying the same biochar using amorphous manganese (AMO) had resulted in a greater removal of As(V) from solution. Compared to the limited ability of the unmodified biochar, the removal capacity was increased from 64 to 91% (about 34.1 mg/g) after increasing the AMO ratio coated on the char. This was explained by the higher CEC of the composite compared to the unmodified biochar (Trakal et al., 2018). A higher adsorption capacity (8.25 mg/g) for As(III) resulted from the impregnation of Mn and Fe oxides onto corn stem biochar (Lin et al., 2017). Higher removal capacity of the ferromanganese oxide is due to enhanced specific surface area (208 m²/g) compared to that of unmodified biochar (61 m²/g), thereby providing a large surface area to promote the oxidation of As(III) to As(V). In the removal mechanism, Mn(III) oxides promote mainly the oxidation of As(III) to As(V), while Fe oxides act as sorption sites for As(V) to be adsorbed onto the biochar surface (Fig. 6).

Therefore, it is clear that the Fe-Mn oxides incorporated with biochar play an important role in strengthening the adsorption capacity of corn steam biochar.

Moreover, Wang et al. (2016) synthesized two biochar composites through pyrolysis of pinewood biochar with Ni/Mn oxides (NMMF) as well as precipitation of Ni/Mn-layered double hydroxides (LDHs) onto the pinewood biochar (NMMB) using MnCl₂.4H₂O and Ni(NO₃)₂.6H₂O. The removal efficiency of NMMB and NMMF at 12 mg/L of As(V) solution was 98 and 10.6%, respectively and hence, the maximum As(V) sorption capacity of NMMF and NMMB (0.549 g/kg and 6.520 g/kg, respectively) was improved compared to the unmodified biochar. The most significant mechanisms which govern the removal of As(V) by both modified adsorbents were found to be electrostatic interactions and surface complexation with hydroxyl (-OH) at pH 8 (Wang et al., 2016). Fig. 7 illustrates the potential mechanisms which trigger the immobilization of As on a modified biochar surface. Since the pH_{PZC} for both NMMB and NMMF was higher than solution pH 8, the surface of biochar becomes positively charged which facilitates strong electrostatic forces between As(V) and the surface (Fig. 7). On the other hand, $HAsO_4^{2-}$ is capable of complexing with −OH groups that are present on the LDHs and thereby exchanging other negatively charged ions such as Cl^- and NO_3^-, which provides a greater stability for As(V) removal from water.

The As(III) was effectively removed from water using wheat straw biochar impregnated with bismuth (by sonication) at pyrolytic temperatures of 400, 500 and 600 °C (Zhu et al., 2016). The highest As(III) removal capacity of bismuth activated biochar produced at 500 °C was achieved at pH 9.3. At this level, the surface of modified biochar gets protonated while promoting a Lewis acid-base reaction between the active adsorption site and the neutral H_3AsO_3. Similarly, a column packed with a composite of wheat straw biochar and periphyton was able to remove a maximum of 95.4% of As(III) at initial concentration
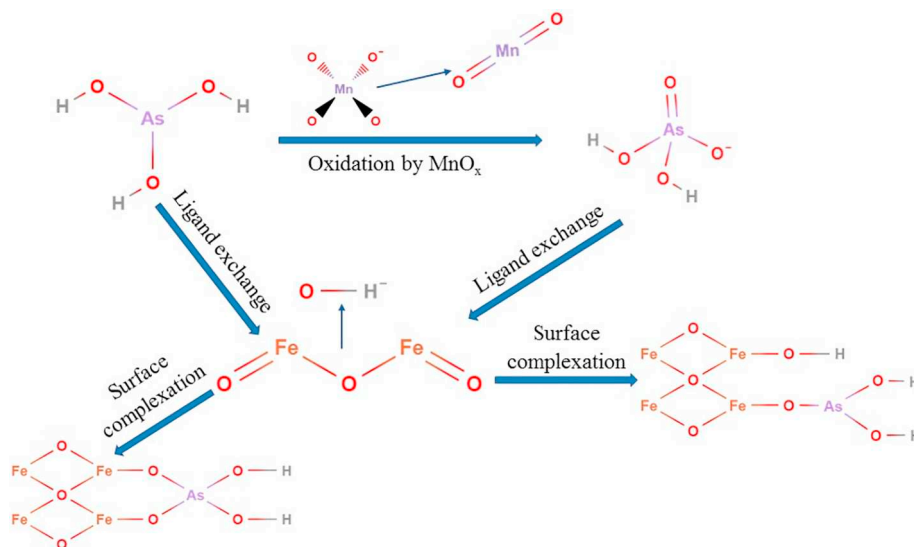

Fig. 6. The Mechanism of As removal in the presence of Fe and Mn oxides.
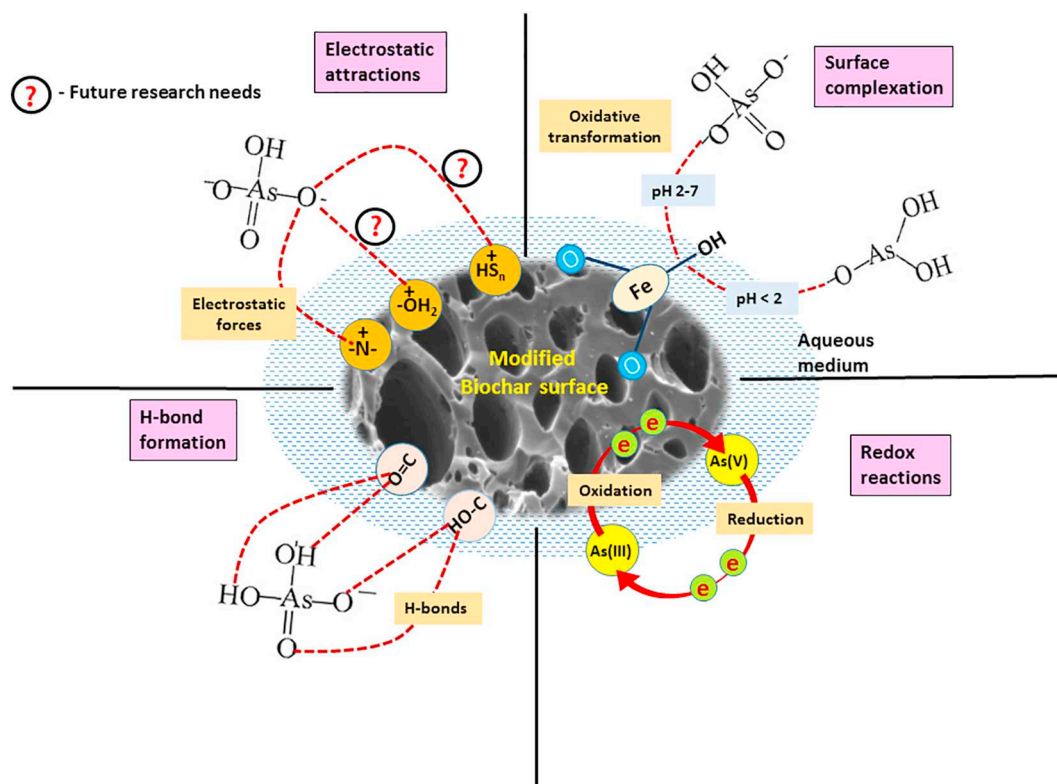
Fig. 7. Graphical representation of potential mechanisms for the immobilization of As on modified biochar surface.

of 2 mg/L and flow rate of 1 mL/min (Zhu et al., 2017). The mechanisms which trigger the immobilization of geogenic As species in the presence of Fe oxides under natural conditions have also been recently discussed (Herath et al., 2016b). Naturally occurring Fe oxides, particularly ferrihydrite ($Fe_2O_3\cdot2H_2O$) tend to immobilize the mobile species of As through a ligand exchange mechanism with HO_2^- and OH^- in the coordination spheres of the surface structural Fe atoms (Fig. 4). The existing knowledge regarding these mechanisms has been recently applied in producing modified biochar materials for the remediation of water. For example, nano-zero valent iron [(Fe(0)] incorporated into biochar can enhance the immobilization of As(V) species in water through strong chemisorption interactions produced from an oxidation and reduction reaction on the biochar surface (Fig. 7). During the oxidation of Fe(0), As(V) gets partially reduced to As(III) which possesses a high affinity to be adsorbed on the hydrous ferric oxides (HFO) formed on the biochar surface during the oxidation of Fe(0). Moreover, magnetic biochar has been investigated as a promising adsorbent for As removal, since the presence of Fe oxides as magnetite on the biochar surface provides more favorable adsorptive sites increasing the removal efficiency (Rajapaksha et al., 2016; Zhang et al., 2013; Zhu et al., 2016). Similarly, Samsuri et al. (2013) investigated the effect of Fe coating on the removal of As(III) and As(V) using empty fruit bunch biochar (EFBB) and a rice husk biochar (RHB). Regardless of the higher surface area of the RHB, both EFBB and RHB showed almost similar adsorption efficiencies for As(III) from water. Thus, the total amount of oxygen-containing functional groups, the lower zeta potentials (-24 mV for EFBB at pH 4; and -14.3 mV for RHB at pH 6), O/C ratio (0.61 and 0.37 for EFBB and RHB, respectively), and polarity indices (O + N)/C (0.64 and 0.38 for EFBB and RHB, respectively) were considered as important factors in determining the removal efficiency of As (III) on biochar.

Studies have been carried out on the effects of biochar produced from macroalgae wastes such as *Gracilaria* and *Oedogonium* that were treated with Fe as a mean of removing As from mining effluents (Johansson et al., 2016). A higher removal capacity was observed after

pre-treating the *Gracilaria* waste and *Oedogonium* algae with Fe^{3+} during fast pyrolysis. The Fe-biochar derived from *Oedogonium* had a higher adsorption capacity (80.7 mg/g) than that of biochar produced from *Gracilaria* waste (62.5 mg/g) for As removal from mining effluents. Jiménez-Cedillo et al. (2013) applied biochar produced from *Petroselinum crispum* which was modified with iron particles in removing As(III) and As(V) from an aqueous solution. The biomass (non-pyrolyzed) modified with Fe^{3+} was ineffective (0.007%) in removing both As species in the solution, whereas the maximum adsorption capacity of modified biochar for As(III) and As(V) was a 5- and 95-fold increase, respectively compared to that of Fe^{3+} modified non-pyrolyzed biomass at pH 6.5. With regard to the immobilization of As(III), at pH 6.5, As(III) is dominantly present in the form of H_3AsO_3, which is more reactive with the $FeOH_2^+$ on the Fe^{3+} modified biochar than the FeO- group available on the surface of Fe^{3+} modified non-pyrolyzed biomass due to their respective pH_{PZC} values of 9.73 and 4.43. Similarly, high removal efficiency of As(V) by Fe^{3+} modified biochar at pH 6.5 is attributed to strong electrostatic forces between positively charged $FeOH_2^+$ present on the modified biochar surface ($pH_{PZC} = 9.73$) and anionic As species including $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Jiménez-Cedillo et al., 2013). In addition, the surface area of Fe^{3+} modified biochar was nearly 4-fold higher than that of unmodified biochar (2.02 m^2/g) which further facilitated the removal of As species from the aqueous solution. Investigations have shown that a combined modification of rice husk and municipal solid wastes biochar impregnated with CaO, Fe^0 and Fe^{3+} can improve the removal of As(V) from water (Agrafioti et al., 2014b). Modification of biochar with Ca^{2+} and Fe^{3+} removed 95% of As(V), whereas the rice husk biochar impregnated with zero valent iron (ZVI) was able to remove only 58% of As(V) from aqueous solutions. Precipitation and electrostatic interactions are likely to be the mechanisms which trigger the removal of As(V) from aqueous solutions. However, the modification of biochar can cause a reduction of the surface area, while increasing the sorption capacity of As because of an increased O/C ratio after the modification (Hu et al., 2015). The pyrolysis of pine wood biochar in the presence of natural hematite mineral

and the formation of magnetic hematite-biochar have a great effect on the biochar ability to remove As(V) from an aqueous solution due to the presence of γ-Fe_2O_3 particles on the biochar surface, which provides sorption sites for As to be adsorbed on the surface (Wang et al., 2015b). The mechanisms of As adsorption by this type of modified biochar can be explained by the same reaction pathway shown in Fig. 4. Magnetic biochar derived from invasive water hyacinth biomass chemically modified through co-precipitation of Fe^{2+}/Fe^{3+} followed by pyrolysis at 250 °C demonstrated high potential to remove aqueous As(V) (Zhang et al., 2016). This modified biochar resulted in a 90% removal of As(V) at a wide range of pH ($3-10$) along with a sorption capacity of 7.41 mg/g which is higher than the results previously reported by Zhang et al. (2013). Ligand exchange and hydrogen bond formation were recognized as the mechanisms which are responsible for the adsorption of As(V) on magnetic biochar (Fig. 7).

5.4.2. Biochar modification using polymers/biopolymers

Crosslinked polymeric and biopolymeric materials including, poly (acrylamide) and *N,N′*-methylenebisacrylamide have been successfully used to boost the As sorption ability of biochar (Barakat and Sahiner, 2008; Sanyang et al., 2016). Hydrogels possess a high affinity to interact with negatively charged As species due to the protonation ability of hydrophilic surface functional groups such as $-OH$, $-COOH$, $-NH_2$, $-CONH_2$, and $-SO_3H$ that are present in the hydrogel molecules (Ozay et al., 2009; Sanyang et al., 2014). Hydrogel prepared from poly(3-acrylamidopropyl) trimethylammonium chloride was capable of removing 99.7% of As(V) at 1.5 g/L of hydrogel and pH 9 for 50 mg/L of As(V) aqueous solution (Barakat and Sahiner, 2008). In a similar study, a hydrogel-biochar composite prepared by embedding rice husk biochar into poly(acrylamide) hydrogel with *N,N′*-methylenebisacrylamide was able to remove a maximum of 94.85% of As(V) with a sorption capacity of 28.32 mg/g (Sanyang et al., 2016).

Biochar-chitosan composites are also utilized as a natural, low-cost, abundantly-available, non-toxic pre-cursor material (chitin) for the removal of heavy metals and metalloids from aqueous solutions (Gerente et al., 2007; Zhou et al., 2013). Such modified biochar composites take advantage of its surface modification via amine (-NH_2) functional groups and well-developed porous structure. In a recent study, a magnetic chitosan-biochar composite (Fe^{2+}/Fe^{3+} molar ratio of 2:3) was able to remove 90% of As(V) from aqueous solution at pH 5 resulting in a sorption capacity of 11.96 mg/g which was nearly 4-fold higher than that of its unmodified biochar (3.68 mg/g) (Liu et al., 2017). At pH 5, the $-NH_2$ group present on chitosan tends to be protonated into H_2N^+ as the solution pH is lower than the pH_{PZC} (5.25) and hence the positively charged biochar surface gets strongly attracted by negatively charged $H_2AsO_4^-$ or $HAsO_4^{2-}$ through electrostatic forces. This composite has been recognized as a superior adsorbent for As(V) removal from water due to its higher removal capacity compared to all other magnetic biochar types tested in previous studies (Baig et al., 2014; Zhang et al., 2016; Zhang et al., 2013). Furthermore, the As(III) adsorption mechanism on biochar modified with $-NH_2$ groups can be explained by a type of Bechamp reaction due to the presence of aromatic $-NH_2$ (similar to aniline) in the biochar composite structure (Fig. 8). In this reaction pathway, aromatic rings bearing with -NH_2 groups can react with arsenic acids (As(III)) followed by an electrophilic aromatic substitution to produce arsanilic acid which is a strong chemisorption interaction.

5.5. Summary of arsenic removal mechanisms on modified biochar

It is obvious that the capacity of unmodified biochar to remove oxyanion pollutants including As is relatively low due to their negative surface charge and poor anion exchange capacity. Therefore, the surface of biochar needs to be transformed to gain a high adsorption capacity for the removal of negatively charged As species. In order to achieve this, the reactivity of As with ions or oxides of metals such as

Al, Mn, Ca, Fe, Mg, etc. are widely used to increase the positive charge and ligand-binding density of biochar, thereby enhancing its removal capacity. Surface modification by hydrous iron oxide (Fe—O) and manganese oxide (Mn—O), Mg—Al and Fe—Al type layered double hydroxides and activated magnesium oxide (Mg—O) attributed to increase the adsorption capacity for the removal of As from water as discussed in the previous section. Surface complexation, electrostatic interactions, ion exchange, chemical reduction and oxidation (redox reactions), and precipitation are the principal mechanisms which trigger the removal of As by modified biochar from aqueous solutions (Fig. 7) (Tan et al., 2016).

Carbothermal alteration of biomass into metal-biochar composites results in a change in surface zeta potential as well as promotes a porous carbon structure, thereby improving the chemical composition for more active sorption sites of biochar surface (Li et al., 2018). Inorganic As species, including AsO_3^{3-} and AsO_4^{3-} can undergo redox reactions in the presence of strong oxidizing (O_2, H_2O_2, MnO_4^-, CrO_3, etc.) and reducing agents (Fe, Al, Zn, Mn, Mg, etc.) on the biochar surface resulting in strong chemisorption interactions between As and biochar surface. For example, the removal of As(V) species is predominantly governed by chemical reduction on the biochar surface modified with zero valent iron (Fe^0) (Wang et al., 2017) and FeOOH (Hu et al., 2015). In the natural environment, microbes play a vital role in the control of oxidation and reduction reactions of As and hence, the inoculation of bacteria into such modified biochar would be highly efficient in the remediation of As contaminated water. Apart from redox reactions, the adsorption of As(III) by a ZnO loaded biochar is likely to be due to ligand exchange at Zn-OH producing a new As-O-Zn complex on the biochar surface (Van Vinh et al., 2015). Furthermore, in MnO_x-biochar composites, the adsorption of As(V) is mainly through surface complexation and ligand exchange with Mn—O and Mn—OH (Liu et al., 2016). Depending on the pH of the medium, some functional groups present on biochar surface, particularly ammine ($-NH$), alcoholic ($-OH$) and carboxyl ($-COOH$) groups, become protonated making the biochar surface more positively charged which promotes strong electrostatic interactions with negatively charged As species (Fig. 7). On the other hand, sulfur is a strong electrophile and thus the modification of biochar surface via thiol groups to produce sulfur-biochar composites will be of particular interest in future research for the removal of As from contaminated water. However, molecular level studies based on X-ray absorption synchrotron techniques such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) are an urgent necessity to confirm the formation, and stability such chemical bonds between the As and biochar surface.

6. Influence of co-existing solutes on arsenic removal by biochar and bone char

Natural water resources contain various inorganic and mineral ions such as F^-, Cl^-, PO_4^{3-}, NO_3, HCO_3^- and SbO_4^{3-} due to naturally occurring geochemical processes as well as anthropogenic sources (Guo et al., 2018; Herath et al., 2017). Therefore, the knowledge on the existing competing anions present in natural water systems such as mining water, geothermal fluids and surface/groundwater is very important in order to design water treatment schemes for the removal of As species from such water bodies. Table 4 summarizes the effect of the existence of some oxyanions on bone char and biochar efficiency to remove As species. The complication in water treatment methods is mainly associated with the existence of other competing metal/metalloid species and inorganic ions, since such competing ions tend to impede the removal efficiency of As species on the adsorbent surface by competitively binding on the active sites (Mack et al., 2007). The effect of F^- on simultaneous removal of As(III) and As(V) by cattle bone char (with specific surface area of 99.2 m^2/g) was investigated (Mlilo et al., 2009). This study showed that the maximum sorption capacity of As(III) and As(V) was 0.022 and 0.065 mg/g, respectively in the absence of F^-,
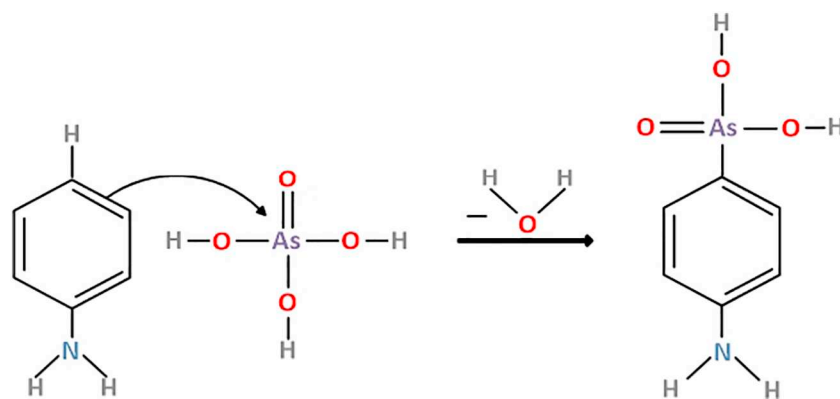
Fig. 8. The potential As adsorption mechanism by $-NH_2$ modified biochar composites (adapted from Gibaud and Jaouen, 2010).

whereas in the presence of F^-, the sorption capacity decreased up to 0.015 and 0.024 mg/g, respectively. In a similar study, the presence of 10 mg/L of F^- affected the removal of As(V) on fish bone char which was about 0.06 mg/g, as predicted by the Langmuir isotherm. In contrast to these findings, a previous study reported that fish bone char is capable of removing F^- and As(V) simultaneously with minimal competition in the water sample (Brunson and Sabatini, 2009).

Coexisting ions, including Al^{3+} and Mn^{2+} were found to enhance the sorption capacity of bone char surface due to the formation of amorphous Al and Mn coating on the bone char surface, while the presence of SO_4^{2-}, PO_4^{3-}, and SiO_3^{2-} oxyanions showed negative impacts on the immobilization of As(V) sorption on bone char because of strong competition with AsO_4^{3-} for the available sorption sites on bone char surface (Liu et al., 2014). These findings are corroborated by a previous study which showed that the negative effect of coexisting oxyanions (concentration range of 0.5–20 mg/L) in the removal of As(V) by cellulose-carbonated HAP nanocomposites decreases in the order of $SiO_3^{2-} > PO_4^{3-} > NO_3^- > SO_4^{2-}$ (Islam et al., 2011). The presence of 1 mg/L of PO_4^{3-} has a similar competition effect as 10 mg/L of $SSiO_3^{2-}$ in reducing the adsorption of As(V) onto rice husk biochar (Cope et al., 2014). It has been reported that the PO_4^{3-} has a great effect on the reduction of As adsorption on magnetic Kans grass biochar where the removal efficiency of this biochar for As(III) and As(V) was decreased by 20 and 80%, respectively at 1.0 mmol/L of PO_4^{3-} concentration (Baig et al., 2014). Similarly, the increase in the ionic strength of PO_4^{3-} from 1 mmol/L to 100 mmol/L resulted in decreasing the removal efficiency of As(III) onto Fe–Mn oxide impregnated with corn stem biochar by 22% (Lin et al., 2017). Therefore, it is clear that the PO_4^{3-} is the most competitive oxyanion to As(V) ions followed by SiO_3^{2-} and SO_4^{2-}, since the HPO_4^{2-} species can form almost similar surface complexes to the $HAsO_4^{2-}$ ion (Hu et al., 2015). The higher reduction capacity for the As(V) removal in the presence of SiO_3^{2-} and PO_4^{3-} may be attributed to their relatively large ionic radii as well as the degree of the anionic charge which are considered to be main factors for determining the effect of coexisting anions in adsorption processes. Moreover, the pH of solution plays a vital role and the immobilization of As species on bone char would be preferable at neutral or alkaline pH levels since there will be a higher release of PO_4^{3-} anions in acidic conditions.

Furthermore, Soltani et al. (2017) examined the effect of some inorganic and organic compounds present in aqueous solutions on the removal As(V) by Fe_3O_4-bone char nanocomposite. This nanocomposite removed 96% of As(V) from the solution compared to the control, whereas the removal efficiency of As(V) decreased up to 25, 34, 38 and 23% in the presence of PO_4^{3-}, SO_4^{2-}, NO_3^- and humic acid, respectively. Natural water systems such as ground-surface-water, geothermal water, and mining water may be contaminated with oxyanions of antimony (Sb) particularly antimonates $[Sb(OH)_5, SbO_3^-]$ which are likely to coexist with As in the natural environment (Herath et al., 2017). On the other hand, these species possess similar toxicological effects as As in environmental and biological compartments. To our knowledge, there

is no information available on the application of biochar and bone char in simultaneous removal of As in the presence of such chemically and structurally equivalent oxyanions. Therefore, future research should be more inclined towards expanding the use of adsorption technology using biochar and bone char in order to develop water treatment facilities to remediate such multi-metal contaminated water systems which would pave the way for a sustainable As mitigation on a global scale.

7. Regeneration of biochar and bone char

Biochar regeneration is an important aspect that determines the economic benefits and environmental sustainability of biochar as a sorbent for the removal of As from water (Inyang and Dickenson, 2015). Several techniques such as the use of chemicals at different concentrations to displace adsorbed metals, controlling the pH of the solution, purging gas or fluid and changing the partial pressure are used for releasing the adsorbed contaminants from modified biochar (Ahmed et al., 2016b). Zhang et al. (2016) examined the reusability of a magnetic biochar for As(V) removal from water by using a 0.1 M HCl solution in which the removal capacity decreased from 100% to 80, 65.5 and 50.8% after four regeneration cycles, respectively. Similarly, a regeneration study of bone char-Fe_3O_4 nanocomposite using 0.1 M HCl solution revealed a reduction of < 20% within three repeated runs over 60 min at 1 g/L of adsorbent dosage, 100 μg/L of initial As(V) concentration (Soltani et al., 2017). Table 3 summarizes the results obtained from previous As desorption experiments for a better understanding of the extent of regeneration capability of biochar and bone char. It is convenient to remark that among all the solutions used for As(V) desorption experiments, regeneration of biochar samples is not applicable with acidic solutions or water. The higher desorption rate (up to 98%) was through using NaOH solution with different concentration. Using 0.5M NaOH solution resulted in flushing out 68% of As(III) from magnetic Kans grass biochar but at very high pH level (13.5) (Baig et al., 2014). The high pH levels where the maximum desorption was achieved are not applicable for water treatment facilities. In addition, using 0.05 mol/L NaHCO_3 resulted in 85% As(V) removal from water at pH 8.5. With regards to As(III) desorption, further investigations need to be conducted as the only examination for As(III) desorption was reached at a very high pH value (Baig et al., 2014). The application of regenerated char as a sustainable waste management strategy in the remediation of water is an urgent necessity. The potential options for disposing the As loaded adsorbents are dumping in landfills, mixing with livestock waste and mixing with building construction materials (Sullivan et al., 2010). On the other hand, the disposal of the concentrated As solution after regeneration of the adsorbent can be overcome by reusing the solution in green industry. For instance, (Riveros et al., 2001) reported the suitability of using As waste after precipitating them with Fe(III) (to form insoluble ferric arsenate

Table 3

Desorption capability of regenerated biochar and bone char in aqueous media.

Biochar	Targeted As species	Used agent	pH	Desorption rate of adsorbed As (%)	Reference
Fe impregnated hickory biochar	As(V)	0.05 mol/L NaHCO₃	5.8	85	Hu et al. (2015)
Solid waste biochar	As(V)	Deionized water	–	4	Agrafioti et al. (2014a)
Sewage sludge biochar				10	
Rice husk biochar				0	
Magnetic chitosan/Biochar (after 5 cycles)	As(V)	1.0 mol/L NaOH	–	68	Liu et al. (2017)
NMMB	As(V)	0.1 M NaOH	–	81.7	Wang et al. (2016)
NMMF				75.0	
Fe coated rice husk biochar	As(V)	30% HCl	1.5	12.3	Pehlivan et al. (2013)
		1 M NaOH	14	90.6	
Bone char	As	Ultra-pure water	4	30	Liu et al. (2016)
Mn coated bone char				0.2–0.6	
ZVI/Pine biochar composite	As(V)	0.1 M NaOH	–	98.2	Wang et al. (2017)
Bone char	As(V)	Distilled water and 0.1 M NaOH	–	50–70	Liu et al. (2014)
Magnetic kans grass biochar	As(III)	0.5 M NaOH	13.5	68	Baig et al. (2014)
	As(V)			89	

Table 4

The effect of co-existing anions on the removal of As by biochar and bone char.

Anions	Concentration	Reduction in As(V) removal (%)	Reduction in As(III) removal (%)	Adsorbent	Reference
NO_3^-	0.5 mg/L	9	–	HAP (synthesized)	Islam et al. (2011)
	> 2 mg/L	The effect levelled off			
SiO_3^{2-}	0.5–10 mg/L	30	–		
	> 10 mg/L	40			
PO_3^{4-}	< 2 mg/L	12	–		
	0.5–20 mg/L	32			
SO_4^{2-}	At any concentration	No significant effect	–		
PO_4^{3-}	1.0 mM	20	70	Kans grass straw biochar-Fe^{3+}/Fe^{2+}	Baig et al. (2014)
Cl^-	1.0 mM	5	12		
HCO_3^-	1.0 mM	5	10		
PO_4^{3-}	1.0 mM	44	–	Fe_3O_4/Bone char in chitosan biopolymer	Soltani et al. (2017)
SO_4^{2-}	1.0 mM	35	–		
NO_3^-	1.0 mM	31	–		
Humic acid	1.0 mM	46			
PO_4^{3-}	1.0 M	23[a]	–	Chitosan magnetic biochar	Liu et al. (2017)
SO_4^{2-}	1.0 M	10[a]	–		
CO_3^{2-}	1.0 M	10[a]	–		
NO_3^-	1.0 M	8.2[a]	–		
Cl^-	1.0 M	8.2[a]	–		
PO_4^{2-}	5 mg/L	24		hickory chips biochar	Hu et al. (2015)
	50 mg/L	58			
SO_4^{2-}	5 mg/L	4			
PO_4^{3-}	1 mg/L	17.18[a]	–	Fe/RHC	Cope et al. (2014)
	10 mg/L	34.93[a]	–		
SiO_3^{2-}	10 mg/L	15.76[a]	–		
SO_4^{2-}	10 mg/L	4.79[a]	–		
F-	10 mg/L	63.1[a]	31.8	Bone char	Mlilo et al. (2009)

[a] Reduction in As removal due to competition of co-existing ions was calculated based on the following formula:

$$Reduction\ (\%) = \frac{Removal\ without\ competing\ ions - Reduction\ with\ competing\ ions}{Removal\ without\ competing\ ions}.$$

compounds) which can be used in metallurgical industry.

8. Cost effectiveness

The amount of the timber and agricultural organic wastes produced in Australia in the financial year 2016–2017 was about 2.1 Mt and 16.1 Mt, respectively (Bagasse, cotton gin trash and manures) (Pickin et al., 2018). In 2018 (until September 2018), the red meat production in Australia was 2,608,866 metric tons (Australian Bureau of Statistics, 2018), generating over 313,064 t of bones as a waste by-products to be disposed in the landfills. Only 1.97 Mt (million tons) out of 67 Mt total waste produced has been used as an energy source (90% were by capturing methane from landfills). The high cost spent for the treatment of waste can be avoided by developing suitable thermal treatment plants for biofuel production and

char produced as a waste product can be used for environmental remediation processes. For instance, the Australian government invests about US$ 60.000 per year on handling cotton industry residues which can be used as a source of energy and biochar for environmental remediation via thermal treatment (Hamawand et al., 2016). Extensive studies inspected the energy balance and the annual revenue of biochar production confirming a positive energy balance for the biochar production using cotton gin trash (Coates, 2000), oil palm empty fruit bunches (Harsono et al., 2013), late stover, early stover, switch grass and yard waste (Zhang et al., 2019).

The cost of biochar/bone char production may vary depending on the production conditions such as energy consumption during the charring process, the cost of transportation, feedstock treatment and drying the precursor, equipment, maintenance and labor cost (Ahmed et al., 2016a). For instance, the net energy consumed in the production

of biochar using electricity is higher than those produced using diesel fuel (Harsono et al., 2013). Moreover the cost of biochar production through slow pyrolysis is lower than those produced via fast pyrolysis (Kung et al., 2014). Generally, in the case of feedstock from forests residues and food industry (such as nut shells, grains and fruits bunches), biochar has been reported as a source of positive energy (Zhang et al., 2019). In addition, the amount of the net energy production and GHG emission is related to the production process and the type of equipment used.

The literature available for the cost benefits and revenue from biochar market is mainly concentrated on the application of biochar as a soil amendment, whereas there is a lack of relevant information available for bone char market and production cost. In water treatment applications, biochar takes much attention as an alternative to activated carbon (AC) due to its environmental benefits in terms of waste management, mitigation of climate change, soil improvement, and energy co-generation (Lehmann and Joseph, 2015). The cost of biochar production was estimated to be US$ 246/ton versus US$ 1500/ton for AC (Inyang and Dickenson, 2015), while the cost of biochar production can vary from US$ 0.09/kg in Philippines to US$ 8.85/kg in United Kingdom (Tan et al., 2017). The cost of bone char production for As removal needs to be investigated as it is only reported for water de-fluoridation. The economic benefits represented by the use of low cost waste materials as a precursor, bioenergy production, and non-activation requirements during the production process (Ahmad et al., 2013; Zhang et al., 2015) justify the use of biochar as a promising alternative for AC. With regards to the economical validity of biochar, it has been reported that the estimated break-even price of biochar is 1/6 of commercially available AC (Zhang et al., 2015). Moreover, the regeneration of AC may be costly compared to that of biochar when it is used as a sorbent in wastewater treatment processes at a commercial scale (Ahmad et al., 2014; Gupta and Ali, 2012; Mohan et al., 2014).

9. Limitations of current research and what needs to be done in future

Environmental consequences of toxic As species present in water have been significant over the past decades. The relatively brief history of the application of adsorption technology using biochar and bone char has endeavored to implement the removal or immobilization of As from aqueous solutions to a considerable extent.

The high pH_{PZC} values of most of biochar types makes their surface more negatively charged, which promotes repulsive forces between the biochar surface and negatively charged As species. Because of that, selecting a suitable type of unmodified biochar for the removal of As from aqueous solutions is indeed a challenging task; this is the major problem to be overcome by future research for the remediation of As contaminated water. Although the engineered char performs well over unmodified char in the removal of As from water, drawbacks associated with the modification methods such as high cost, less regeneration capacity, and use of toxic chemicals are of particular concern. Furthermore, the stability of the modified char is of great concern to maintain the reagents used in the modification method and thereby minimizing environmental contamination (Trakal et al., 2018).

The utilization of different types of organic and biological waste materials which are available at large quantities in the environment for the production of biochar and bone char, will be a promising waste management strategy in the environment. Additionally, using these materials will facilitate the reduction of global warming and greenhouse gas emission from landfills. As the present review demonstrated, the existing research related to regeneration of used bone char and biochar are insufficient and therefore, the disposal of the As adsorbed chars is essentially taken into consideration in future research. Mechanistic understanding of biochar-As and bone char-As interactions has so far attached little research concern and hence there is a significant research gap in the interpretation and confirmation of potential mechanisms and types of chemical bonds which trigger the adsorption of As species onto the adsorbent surface. Synchrotron-based X-ray techniques, particularly EXAFS and XANES are essential in future research to understand the change in oxidation state of As species and certain types of chemical bonding between As and bio-bone-char surface. The removal efficiency of As by particular types of biochar or bone char is greatly decreased in the presence of chemically or structurally equivalent oxyanions, so that the application of this technology for the remediation of wastewater is still subject to debate. Moreover, research of the use of biochar and bone char is limited to laboratory scale experiments and hence, moving this technology from laboratory phase to field scale applications, needs to be undertaken by future research in order to establish a sustainable mitigation of toxic As species in drinking-surface-ground-and irrigated water systems. However, the application of these adsorbents on a commercial or industrial scale is limited due to several restriction issues raised in some countries. The main limitation for the use of bone char as an adsorbent for water treatment purpose is related to some cultural and religious beliefs. For instance, the use of bone char for fluoride removal from water were rejected in Ethiopia based on cultural and religious reasons (Osterwalder et al., 2014; Saxena and Patel, 2018). The effect of the charring temperature on the biochar production is a crucial factor in terms of environmental pollution due to the emission of other toxic particulate matter. Hamawand et al. (2016) reported that biochar produced at temperatures below 600 °C has the potential of releasing toxic elements and heavy metals to the environment (formaldehyde, arsenic and cadmium), and raising charring temperature to > 800 °C may lead to releasing more N_2 gas and providing more GHG to the environment (Hamawand et al., 2016).

10. Conclusions

Inorganic As is extremely toxic to living organisms due to high binding ability with protein-sulfydryl (SH) groups and the over-production of cellular reactive oxygen species. Hence, the application of bio- and bone-char for As removal from water has been thoroughly scrutinized in this review with the aim of shedding light on recent achievements and pinpointing the gaps in this research area. The higher point of zero charge of most of the char types makes its surface more negatively charged, promoting repulsive forces between the surface and negatively charged As species. Hence, selecting a suitable char type for the removal of As has become a challenging task. The surface modification via chemical methods has been adopted to alter the surface charge and surface area to improve the adsorption capacity for anionic As species. Nano-sized manganese coated bone char increases the removal of As(V) by 78-fold compared to the non-modified bone char. The removal of As(V) by bone char produced at 500 °C was 2-fold higher than that which is produced at 900 °C. A magnetic chitosan-biochar composite removes 90% of As(V) from aqueous solution at pH 5 resulting in a sorption capacity of 11.96 mg/g which was 4-fold higher than that of its unmodified biochar. The main proposed mechanisms of As removal using bio- or bone- char are surface complexation, ion exchange, electrostatic interaction and co-precipitation. These mechanisms are governed by surface area, ion exchange capacity, surface functional groups and pH_{PZC}. In addition to the advantage of the char being a product of recycled waste, it has another attractive trait of being regenerative using acidic or alkaline wash. Overall the present review concludes that the engineered biochar can effectively remove As while unmodified bone derived char itself possessing a great adsorption capacity for As removal from aqueous solution. However, more research is essential in the future to fully understand the As-char interactions along with their bonding nature under various environmental conditions to develop more reliable and sustainable char types for water treatment applications on an industrial scale.

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