# **Chapter 13 Biochar-Based Remediation of Heavy Metal Polluted Land**



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**Abstract** The excessive use of heavy metals has led to the problem of pollution of land by heavy metals. The non-degradability, persistence, bioavailability and high mobility of heavy metals make them dangerous to human health and environment. In the previous decades, biochar has been suggested to remove the heavy metals from the soil effectively. Biochar is a carbonized material prepared by thermal treatment of a biomass feedstock. The variation in feedstock and thermal treatment affects the properties of the char produced. The properties of high sorption capacity, large surface area, high porosity, alkaline pH and remarkable oxygen-containing surface functional groups enable Biochar to minimize the mobility and bioavailability of the heavy metals. The high stability of biochar aids in removing the heavy metals for a long period of time. Mechanisms such as ion exchange, precipitation, diffusion, complex formation, electrostatic interaction and sorption, help in removal of heavy metals from the soil. Additionally, biochar could help in waste management, bioenergy production, crop production enhancement and climate change mitigation, which are indicative of the wide-ranging advantages associated with biochar production and its application. Keeping these things in mind, the chapter was conceptualized to review the developments in the field of biochar application for remediation of heavy metal polluted sites. The chapter has focussed upon its production, modification methods, physicochemical properties, and heavy metal removal mechanisms utilized by biochar. Additionally, the impact of biochar on mobility and bioavailability of heavy metals and case studies across the various parts of the world have been explored. Lastly, applications other than heavy metal removal, advantages and risks associated with biochar application and future scope for biochar production and application have been discussed.

**Keywords** Heavy metals · Biochar · Pyrolysis · Remediation · Sorption · Climate change

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<sup>©</sup> The Author(s), under exclusive license to Springer Nature Switzerland AG 2023 V. C. Pandey (ed.), *Bio-Inspired Land Remediation*, Environmental Contamination Remediation and Management, [https://doi.org/10.1007/978-3-031-04931-6\\_13](https://doi.org/10.1007/978-3-031-04931-6_13) 

#### **13.1 Introduction**

Our planet has seen emergence of numerous disasters inclusive of climate change, depletion of natural resour[c](#page-27-1)es and pollution (Kumar et al.  $2021b$ , c). Each of the issues is threatening for the survival of the planet and sustenance of the organisms thriving on it. Heavy metal pollution is one such significant issue that is undesirable for the twenty-first century and affects the socio-economic lives of people (Bhattacharya et al. [2021;](#page-23-0) Kumar et al. [2021a\)](#page-27-2). The persistence and bioavailability of heavy metals make them toxic for the living organisms (Zhang et al. [2013](#page-34-0)). A number of remediation methods have been developed to remove the heavy metals from the environment (Pandey and Singh [2019\)](#page-29-0). These methods could be physical, chemical or biological (Khalid et al. [2017](#page-26-0); Pandey and Singh [2019](#page-29-0)). The physical methods include vitrification, isolation, soil replacement and electro-kinetic remediation. The chemical methods are inclusive of encapsulation, soil washing and chemical immobilization. The biological methods include phytoremediation (Pathak et al. [2020](#page-29-1); Pandey and Bajpai [2019\)](#page-29-2), bioremediation and biochar-based remediation (Dwibedi et al. [2022](#page-25-0)). Biochar is very optimistic technique for removing the heavy metals from soil and water (Dwibedi et al. [2022\)](#page-25-0).

Biochar is a carbon–neutral recalcitrant substance obtained from the thermal treatment of a carbonaceous biomass (Manyà [2012](#page-28-0); IBI [2015\)](#page-26-1). Depending upon the type of biomass and thermal treatment technique used, properties of biochar vary (Tang et al. [2013](#page-32-0)). Biochar helps in reducing heavy metal pollution by decreasing their mobility and bioavailability (Kumar and Bhattacharya [2021](#page-27-3)[,2022](#page-27-4)). Further, biochar improves the quality of soil, which helps in improving the soil and plant productivity (Lehmann et al. [2006](#page-27-5)). Additionally, biochar could help in waste management by consuming the waste materials for production of biochar; climate change mitigation by carbon sequestration and greenhouse gas emission reduction; fossil fuel management by biofuel production; and food security management by enhanced crop production (Lehmann et al. [2011;](#page-27-6) Titirici et al. [2012](#page-32-1); Zhang et al. [2013](#page-34-0); Mohan et al. [2014;](#page-29-3) Windeatt et al. [2014;](#page-33-0) Hossain [2016](#page-26-2); Lee et al. [2018](#page-27-7); Manyà et al. [2018](#page-28-1)). Therefore, production and application of biochar could be a sustainable solution for a number of threatening issues in addition to remediating heavy metal polluted soils.

#### **13.2 Biochar and Its Production**

Biochar is a stable carbonaceous residue (IBI [2015](#page-26-1)), obtained after thermal treatment of carbon-containing feedstock (Kumar et al[.2022a,](#page-27-8) [b](#page-27-9); Shaikh et al. [2022b,](#page-31-0) [a\)](#page-31-1). Biochar is different from 'Amazonian dark earth', i.e. Terra preta, in structure and composition. Terra preta is produced by mixing low-temperature char with plant residues, bones, faeces and compost (Balée et al. [2016a,](#page-23-1) [b](#page-23-2)). Identification of Terra preta's nutritional significance, promoted the production and use of biochar for various applications (Glaser et al. [2002](#page-25-1)).

A number of thermal treatment techniques have been used for biochar production (Kumar et al. [2020\)](#page-27-10). These techniques include pyrolysis, combustion, torrefaction, gasification and carbonization (Meyer et al. [2011](#page-29-4)). Pyrolysis has been the most widely used method for producing biochar. It involves oxygen-deficient conditions and could be carried out in a kiln or furnace. The wide utilization of pyrolysis for biochar production is due to its efficiency and simplicity (Cha et al. [2016\)](#page-24-0).

The properties of biochar vary depending upon the treatment method, conditions and the type of feedstock used (Sahota et al. [2018](#page-30-0); Zhang et al. [2018a\)](#page-34-1). Some of the properties significant for heavy metal removal are inclusive of large surface area, high porosity, high cation exchange capacity, a non-carbonized fraction and oxygencontaining surface functional groups (Mukherjee et al. [2011;](#page-29-5) Ahmad et al. [2014](#page-22-0)). Application of biochar for removing heavy metals from polluted lands has emerged in the recent times (Mohan et al. [2014](#page-29-3)).

#### *13.2.1 Feedstock Variation*

Theoretically, biochar could be produced by any type of biomass, but the costs of production and the applicability of biomass for compost and biofuel production, restrict the range of feedstock for biochar production (Kuppusamy et al. [2016](#page-27-11); Tripathi et al. [2016\)](#page-32-2). Additionally, feedstock composition and its calorific value are determined for biochar production. Some of the feedstock biomasses used for the production of biochar are crop residues, kitchen waste, animal litter, poultry litter, sewage sludge, rubber tyres and algae (Beesley and Marmiroli [2011;](#page-23-3) Cantrell et al. [2012;](#page-24-1) Lu et al. [2012](#page-28-2); Ghani et al. [2013](#page-25-2); Xu et al. [2013a;](#page-34-2) Zhao et al. [2013;](#page-35-0) Mazac [2016\)](#page-28-3). Importantly, utilization of waste material for production of biochar would assist in waste management by decreasing generation of waste, which could decrease the pollution of soil and groundwater, increase the levels of sanitation and reduce the number of landfill sites.

Decreasing the moisture content in feedstock is necessary to increase the feasibility of the thermal treatment of biochar (Bryden and Hagge [2003;](#page-23-4) Lv et al. [2010](#page-28-4)). Moisture content in the feedstock above 30% depletes the rate of heating, thereby increases the time needed to achieve the conditions necessary for thermal treatment. Therefore, it is vital to decrease the moisture content in feedstock by drying it through natural or human-assisted means. Naturally, it could be dried under the sun or by the influence of wind. Feedstock drying through human assistance incorporates use of microwave ovens or instruments that generate heat. However, natural ways must be preferred to decrease the energy consumption burden, which could help in tackling energy security partially.

Thermal treatment of feedstock decomposes hemicellulose and cellulose at 200– 315 °C and 315–400 °C, respectively (Sadaka et al. [2014\)](#page-30-1). Lignin decomposition occurs beyond 400 °C. Therefore, feedstock rich in hemicellulose and cellulose could produce biochar at low-temperature thermal treatment. However, low-temperature chars are considered to be less efficient for heavy metal removal because of the low

surface area, low porosity, less cation exchange capacity and less oxygen-containing surface functional groups obtained at lower temperatures (Igalavithana et al. [2017](#page-26-3); Weber and Quicker [2018](#page-33-1); Zhang et al. [2018b](#page-35-1)). Therefore, high-temperature chars are preferred for heavy metal removal purposes due to their high efficiency and efficacy. High lignin content in feedstock is necessary to increase the yield of biochar production at high-temperature thermal treatments (Angin [2013](#page-22-1); Shivaram et al. [2013\)](#page-31-2). Therefore, feedstocks with less moisture content and high lignin content are preferred for the production of biochar for remediating heavy metal-polluted soils.

#### *13.2.2 Thermal Treatment*

The thermal treatment processes involve thermal conservation of biomass feedstock. The different thermal treatment techniques are torrefaction, combustion, gasification, carbonization and pyrolysis (Meyer et al. [2011](#page-29-4); Zhang et al. [2013](#page-34-0)). The various treatment methods have been summarized in Table [13.1.](#page-4-0) Low-temperature thermal treatment of feedstock in oxygen-depleted conditions is referred to as torrefaction. The temperatures are in the range of 200–300 °C. Torrefaction could be used for feedstock pre-treatment in gasification to enhance the quality of biochar produced.

Combustion involves direct burning of the feedstock to convert the stored chemical energy into thermal energy. However, combustion needs pre-treatment due to the low yield of biochar production (McKendry [2002](#page-28-5)). Gasification involves thermal treatment of feedstock at very high temperatures ranging from 700 to 900 °C. The feedstock is partially oxidized in gasification and the carbon content is transformed into a gaseous product apart from generation of soils and liquid products. Gasification results in 85% syngas, 10% biochar and 5% bio-oil as products (Neves et al. [2011](#page-29-6); Asensio et al. [2013\)](#page-23-5).

Carbonization is majorly of two types—flash carbonization and hydrothermal carbonization. In flash carbonization, feedstock is heated at 350–650 °C and elevated pressure for time less than 30 min. Flash carbonization yields syngas and biochar in equal amounts (Antal et al. [2003;](#page-23-6) Asensio et al. [2013\)](#page-23-5). On the other hand, in hydrothermal carbonization, the wet biomass is thermally treated at elevated pressure and temperature. It results in conversion of wet biomass into hydrothermal carbon, i.e. hydrochar, along with the release of energy (Wang et al. [2018b\)](#page-33-2).

Pyrolysis is the most widely used method for thermal treatment of feedstock. Pyrolysis involves thermal treatment of feedstock in oxygen-depleted conditions at 300–900 °C. Oxygen-deficit conditions allow feedstock to be heated above the thermal stability limits, resulting in formation of biochar with high stability. Additionally, bio-oil and syngas is also obtained in pyrolysis. As pyrolysis proceeds, the heat decomposes and devolatilizes the feedstock constituents. Oxygen-rich functional groups such as hydroxyl and carboxyl are formed on the surface after pyrolysis (Ekström et al. [1985](#page-25-3)). Pyrolysis could be divided into slow, intermediate or fast depending upon the heating rate.

<b>Treatment</b> method	Feedstock used for production	Products obtained	References
Torrefaction	Rice husk, bagasse, peanut husk, sawdust, & water hyacinth	Solid	Pimchuai et al. (2010)
Combustion	Waste biomass	Solid and thermal energy	McKendry (2002), Caillat and Vakkilainen (2013)
Gasification	Lignocellulose rich plant biomass; Sedum alfredii	Gas	Pröll et al. (2007), Balat et al. (2009), Cui et al. (2018)
Flash carbonization	Woods (Oak & Leucaena); agricultural waste (corncob & macadamia nut shells)	Gas & solid	Antal et al. (2003), Asensio et al. (2013)
Hydrothermal carbonization	Agricultural waste; eucalyptus sawdust & barley straw	Solid (Hydrochars)	Sevilla et al. $(2011)$ , Titirici et al. (2012)
Slow pyrolysis	Softwood chip & grass; Crop residues	Solid	Onay and Kockar (2003), Windeatt et al. $(2014)$ , Behazin et al. (2016)
Fast pyrolysis	Corn cobs & Stover; Rice straw	Solid & liquid	Onay and Kockar (2003), Mullen et al. (2010), Eom et al. (2013)
Flash pyrolysis	Rapeseed; Sunflower oil cake	Liquid $&$ gas	Yorgun et al. $(2001)$ , Onay and Kockar (2003)
Slow steam pyrolysis	Vegetal waste, switch grass	Solid $&$ gas	Giudicianni et al. (2013)

<span id="page-4-0"></span>**Table 13.1** Various types of thermal treatment methods for production of solid (biochar), liquid (bio-oil) and gaseous (syngas) products

Feedstock is heated with moderate heating rate at 400–500 °C in slow pyrolysis. Feedstock is heated at 500–650 °C in intermediate pyrolysis. Fast pyrolysis involves very rapid heating rate, where feedstock is heated up to 800–1200 °C. Slow pyrolysis yields the maximum amount of biochar (Tripathi et al. [2016](#page-32-2)). Apart from treatment temperature and heating rate, pyrolysis also depends upon vapour residence time, pressure, feedstock particle size and the technique used for production such as burning in a kiln or electrical heating in a furnace (Asensio et al. [2013](#page-23-5)). Rate of removal of volatile gases during pyrolysis affects the vapour residence time and the occurrence of secondary reactions on the surface of biochar, which consequently affects the properties of biochar produced (Meyer et al. [2011](#page-29-4)). It must be noted that pyrolysis is considered as the most efficient and cost-effective technique for biochar production (Cha et al. [2016\)](#page-24-0).

# **13.3 Biochar Modification Methods**

Application of biochar for removal of contaminants may need improvements for better remediation results. Recently, biochar modification has received attention for improving remediation performance in char (Alam et al. [2018](#page-22-2); Shaikh et al. [2021](#page-31-4)). Some of the modification methods are digestion, oxidation, magnetization and activation. These methods affect the surface area, porosity, cation exchange capacity, pH and surface functional groups of biochar. These properties could be compared for the evaluation of heavy metal remediation efficiency in chars.

For activation of biochar, steam activation is an effective method. The pore volume is enhanced and the pore structure becomes complex after biochar activation. Hass et al. [\(2012](#page-26-4)) reported that steam activation increases the surface area and pH of biochar. They stated that steam activation of char prepared at 350 °C is similar in efficacy to char prepared at 700 °C in terms of their liming effect.

Magnetization is another efficient method reported for enhancing the sorption potential of biochar. Magnetization renders strong ferromagnetic capacity in biochar. Additionally, magnetization is beneficial in terms of the ability for its recollection by magnetic separation and reutilization. Chen et al. ([2011\)](#page-24-4) prepared magnetic biochar by chemical co-precipitation of orange peel powder with ferric and ferrous ions followed by their thermal treatment. They reported that the magnetic biochar had enhanced pore size and was more potent in removing contaminants. The ferric oxide particles on char surface aid in sorption enhancement by providing sites for electrostatic interaction. Wang et al. ([2015\)](#page-33-3) prepared magnetic biochar from pinewood and reported that the magnetized biochar could be used for removing metallic contaminants.

Oxidation is another method utilized efficiently for enhancing the sorption potential of biochar. Oxidation is achieved by the addition of oxidants in the pre- or post-treatment stages. Some of the oxidants used are hydrogen peroxide, potassium permanganate and nitric acid (Xue et al. [2012;](#page-34-4) Li et al. [2014\)](#page-27-12). Oxidation facilitates acidic functional groups to the char surface after treatment. Li et al. [\(2014](#page-27-12)) reported that nitric acid is more effective for biochar modification by oxidation treatment in comparison to potassium permanganate.

Lastly, digestion is another method used effectively for enhancing the sorption capacity of biochar. Anaerobic digestion treatment of feedstock improves the sorption capacity of char in comparison to undigested feedstocks. Inyang et al. [\(2010\)](#page-26-5) modified bagasse by anaerobic digestion and observed that the digested chars had greater cation exchange capacity, more surface area, surplus negative surface charges and higher pH than undigested chars. Similar results were reported by Yao et al. [\(2011\)](#page-34-5) in the beetroot tailings-derived biochar and Inyang et al. ([2012\)](#page-26-6) in the dairy manurederived biochar. These results are indicative of the enhanced char properties after modification by digestion treatment.

#### **13.4 Properties of Biochar**

#### *13.4.1 Composition*

Biochar composition depends on the composition of feedstock, rate of heating and treatment temperatures involved. Feedstock is generally composed of lignin and holocellulose, i.e. hemicellulose and cellulose. Thermal treatment decomposes the hemicellulose and cellulose in feedstock at 200–315 °C and 315–400 °C, respectively (Sadaka et al. [2014](#page-30-1)), while lignin decomposition occurs beyond 400  $^{\circ}$ C. Therefore, thermal treatment temperature could affect the biochar composition, which could affect the physical and chemical properties of biochar.

Thermal treatment of the biomass results in detachment of oxygen and hydrogencontaining surface functional groups, resulting in the decrease in their ratios with respect to carbon. Hydrogen, oxygen and nitrogen contents decrease with an increase in treatment temperature (Sun et al. [2014\)](#page-32-3). Carbon contents increase in biochar at high treatment temperatures (Vassilev et al. [2010](#page-33-4)). The increase in treatment temperature increases the loss of volatile matter by enhancement of devolatilization and decomposition of the char matrix. Therefore, the volatile matter decreases at higher treatment temperatures in biochar (Pimchuai et al. [2010;](#page-30-2) Weber and Quicker [2016](#page-33-5)). Elements such as magnesium, calcium and potassium increase in biochar with an increase in the treatment temperature (Sun et al. [2014\)](#page-32-3).

Addition of biochar to soil enhances dissolved organic carbon content. Such an enhancement stimulates the activity of micro-organisms in soils. Additionally, there is an alteration in redox processes and biochemical reactions. These changes affect the impact of biochar on soil contaminants (Beesley and Dickinson [2011;](#page-23-9) Choppala et al. [2012](#page-24-5); Qian et al. [2016\)](#page-30-4). Park et al. ([2011b](#page-29-9)) reported that the dissolved organic matter increases the mobilization of copper, which could be indicative of a detrimental effect of biochar addition.

With an increase in the treatment temperatures, aromaticity in the char enhances. This could be due to thermodynamic stability of aromatic carbon at high treatment temperatures (Conti et al. [2014](#page-24-6)). The aromatic structures help in increasing the heavy metal remediation efficiency by enhancing the sorption potential of organic and inorganic contaminants (Wang et al. [2016\)](#page-33-6).

#### *13.4.2 pH and Ash Content*

The removal of the acidic functional groups on the surface of char enhances its alkalinity (Fidel et al. [2017\)](#page-25-6). The increase in alkalinity is accompanied by an increase in pH of the char. pH values as high as 10–12 are obtained for thermal treatment at high temperatures. A high pH enables the char to neutralize acidic soils, thereby increasing the availability of arable lands, which could be extremely significant in

the present context, comprising of a rise in pollution and the need for more food crop production.

Increase in pH of the char could also be an outcome of the rise in the ash content at high treatment temperatures. Ash contributes in increasing the alkalinity in animal manure biochar. Volatilization of organic acids and removal of acidic functional groups contributes in the high pH in the agricultural waste biochar (Wang et al. [2019](#page-33-7)). In comparison to plant biomass-derived biochar, animal-derived biochar has a higher carbonate and ash content which could be responsible for the high pH (Rajkovich et al. [2012\)](#page-30-5). Therefore, feedstock composition affects the pH of char (Wang et al. [2019\)](#page-33-7). Ash could be composed of oxides of alkaline and alkali metals such as silicon, aluminium, potassium, calcium and magnesium (Vassilev et al. [2013b](#page-33-8)). High ash content could be detrimental for the applicability of the char in industrial applications due to the health problems related to ash.

Ash content regulatesion exchange in the soil matrix, while soil pH and alkalinity regulate co-precipitation (Wang et al. [2018a](#page-33-9)). Heavy metals are stable in an alkaline environment while unstable in an acidic environment. Addition of biochar to soil facilitates the carbonates and oxygen-containing functional groups, thereby increasing the pH in the soil making it alkaline. Such alkaline conditions enhance the stability of heavy metals. Further, the functional groups provide negative charges on the char surface, aiding in heavy metal removal (Yuan et al. [2011](#page-34-6)).

# *13.4.3 Cation exchange capacity*

Majority of the functional groups on surface of the char provide a negative charge, indicating its anionic nature. It enables the char to attract the cations. Therefore, char produced at low treatment temperature has a high cation exchange capacity (Mukherjee et al. [2011](#page-29-5)). Rajkovich et al. [\(2012](#page-30-5)) reported that cation exchange capacity is greater in biochar derived from oak, corn stover, or manure than compared to biochar derived from hazelnut shells, paper mill waste, or food waste. Cow manurederived char has a low cation exchange capacity in comparison to plant biomassderived char due to their high ash content and low carbon/nitrogen content (Wang et al. [2019](#page-33-7)). Further, it helps in capturing the contaminants, thereby assisting in the remediation of polluted lands. It could also help in reducing the contaminant levels in the plants by reducing their availability for plant uptake (Cushman and Robertson-Palmer [1998](#page-24-7); Liang et al. [2006](#page-28-6)).

## *13.4.4 Surface Area, Porosity and Pore Volume*

The porosity and surface area of char depends on the feedstock used, the treatment temperature involved and the rate of heating (Manna et al. [2020\)](#page-28-7). The thermal treatment of feedstock produces a porous biochar by releasing volatile gases and

decomposition of the biomass matrix. With an increase in treatment temperature, porosity of the char increases. However, treatment temperatures above 800–1000 °C break the cell structures in the biomass, leading to a reduction in porosity at high treatment temperatures (Cetin et al. [2004\)](#page-24-8). Treatment temperatures increase the pore volume in biochar (Fu et al. [2012\)](#page-25-7). Furthermore, micropores  $(0.05-0.0001 \,\mu m)$  form volume above 80% in the char. The abundance of pores in biochar helps in sorption of heavy metals on the outer sphere and its transport to the inner sphere (Houben et al. [2013](#page-26-7); Yin et al. [2016](#page-34-7)).

With an increase in treatment temperature, surface area of the char increases. Similar to the porosity, surface area of biochar decreases at temperatures above 800–1000 °C (Cetin et al. [2004\)](#page-24-8). The decrease in surface area could be a result of shrinking solid matrix (Pulido-Novicio et al. [2001\)](#page-30-6). Cao and Harris [\(2010](#page-24-9)) stated that the surface area of a char derived from dairy manure is less than a char obtained from plant biomass due to the abundance of carbon in its matrix. The abundance of organic carbon also enables the char derived from plant biomass to have a very high porosity. High porosity and surface area increase the heavy metal removal capability of biochar by enhancing the adsorption capacity (Rouquerol et al. [1999](#page-30-7)). A high surface area aids in increasing the cation exchange capacity, water holding potential and nutrient retention capacity of biochar (Weber and Quicker [2018\)](#page-33-1). Surface area also plays a vital role in affecting the microbial community present in the soil matrix by providing pores to the microbes for survival (Igalavithana et al. [2017\)](#page-26-3). The surface of biochar could develop both positive and negative charges, which could help in the sorption of both positively and negatively charged metal species such as chromium and arsenic. This is brought about by the stimulation of microbial processes which helps in the promotion of redox reaction in the soil (Solaiman and Anawar [2015](#page-31-5)).

### *13.4.5 Mechanical Stability and Grindability*

Thermal treatment of feedstock decreases its mechanical stability due to an increase in the porosity and a decrease in structural complexity of char, i.e. the solid product formed after thermal treatment of feedstock (Byrne and Nagle [1997](#page-24-10)). Biochar becomes brittle and grindable due to the decrease in mechanical stability. High hemicellulose content in feedstock produces a highly grindable char. On the contrary, high lignin content in the feedstock produces biochar which is less brittle and has high mechanical stability (Emmerich and Luengo [1994](#page-25-8)).

High mechanical stability could assist the char in replacing coal for industrial applications. High stability is also significant for the carbon sequestration for a long period of time. The extended stability of biochar in the soil does not have any negative impact on the heavy metal removal. In a study by Li et al. ([2016\)](#page-28-8), biochar prepared from hardwood was applied to cadmium and copper contaminated soils and incubated for 3 years. The biochar application reduced the concentration of cadmium and copper by 58% and 64% in the 1st year, followed by a further decrease in the 2nd and 3rd years. These results are indicative of heavy metal removal from the soil and absence of negative impacts of biochar ageing on the soil.

Grindable nature of char affects its particle size distribution. Particle size affects the interaction between the char particles and the soil matrix (Liao and Thomas [2019\)](#page-28-9). Smaller particle size enhances the surface area and micro-porosity of the char, thereby increasing the interaction between char particles and soil (Valenzuela-Calahorro et al. [1987](#page-32-4); Sun et al. [2012a;](#page-32-5) Xie et al. [2015\)](#page-34-8). It helps in increasing the nutrient availability for the plants grown in these soils (Xie et al. [2015\)](#page-34-8).

## *13.4.6 Energy Content and Thermal Conductivity*

The increase in carbon content in biochar helps in increasing the energy content (Weber and Quicker [2018\)](#page-33-1). The energy content in char (30–35 MJ/kg) produced at 700 °C is nearly double the value of the energy levels of the feedstock (15– 20 MJ/kg) from which the char is prepared. The high energy content could assist in its applicability as a source of bioenergy.

Thermal conductivity of biochar increases with a rise in its density. Increase in porosity decreases the thermal conductivity of the char by trapping air in the pores. The decrease in thermal conductivity helps the soil in providing soil insulation in colder areas. biochar could be used in the construction materials to assist in heat insulation and electromagnetic shielding (Usowicz et al. [2006\)](#page-32-6).

#### *13.4.7 Interaction with Water*

Previous studies have reported contrasting results of the interaction between biochar and water. Chun et al. ([2004\)](#page-24-11) reported a rise in water-repelling tendency of biochar produced at high temperatures. This is seen due to the detachment of oxygencontaining surface functional groups, polar in nature. As a result of polar group detachment, hydrophobicity increases. However, Zornoza et al. [\(2016](#page-35-2)) reported that low-temperature chars are more hydrophobic in comparison to the high-temperature chars.

Rise in the treatment temperature increases the porosity of char which assists in enhancing its water holding capacity (Zhang and You [2013;](#page-34-9) Gray et al. [2014](#page-25-9)). Such an enhancement of water holding capacity increases the water retaining capability of soil. This helps in reducing the water lost due to leaching and increasing the water available to plant roots.

#### **13.5 Heavy Metals and Their Removal**

Metals or metalloids with a potential to affect human and environmental health negatively and possesses a specific density above 5 g/cm<sup>3</sup> are called heavy metals (Järup [2003](#page-26-8)). Lead, mercury, chromium, arsenic, cadmium, etc. are certain examples of heavy metals. They have been involved in vital processes such as cell division, redox reaction, enzymatic functioning, protein synthesis and regulation, etc. in the living organisms (Pilon-Smits et al. [2009\)](#page-30-8). Additionally, they have been widely used by human beings for various domestic and industrial applications (Tchounwou et al. [2012\)](#page-32-7).

The excessive use of the heavy metals has resulted in the pollution of land and water bodies. The non-biodegradability, high bioavailability and enhanced mobility of heavy metals make them toxic to the living beings (Zhang et al. [2013](#page-34-0)). Heavy metals enter the environment by natural (e.g. weathering) and anthropogenic routes (e.g. Industrial release, agricultural discharge, metal mining, etc.) and penetrate the soil and water bodies equally (Young [1995;](#page-34-10) Tchounwou et al. [2012\)](#page-32-7). They are transported from soil to water and water to soil and do not get self-purified.

Heavy metals could be taken up by plants and microbes through which they enter the animal bodies upon ingestion (Mohammed et al. [2011;](#page-29-10) Tangahu et al. [2011](#page-32-8)). They trigger chlorosis, necrosis, growth stunting, enzymatic inhibition, photosynthetic stress and reactive oxygen species formation in plants (Stadtman [1990\)](#page-32-9). Heavy metals affect the reproductive system, circulatory system, nervous system, digestive system and excretory system. Further, they damage the genetic material and could be mutagenic (Patra et al. [2006](#page-30-9); Tchounwou et al. [2012](#page-32-7)).

The persistence and toxicity of the heavy metals have made it impertinent to look for remediation methods. The various methods developed are physical, chemical and biological in nature (Gunatilake [2015;](#page-26-9) Khalid et al. [2017](#page-26-0)). Biochar-based remediation has gained attention in the previous decades because of the low costs involved, simplicity, high efficacy and efficiency, to minimize the damage caused by the heavy metals (Ahmad et al. [2014;](#page-22-0) Dwibedi et al. [2022](#page-25-0)). The fate of heavy metals, their toxicity manifestations in plants and human beings and their removal from soil have been depicted in Fig. [13.1](#page-11-0).

It is also important to distinguish the applicability of biochar for heavy metal removal in comparison to activated carbons. Activated carbons are prepared by oxygen activation of char, which renders them high porosity and surface area. However, the properties of porosity and surface area in activated carbons are comparable to biochar (Cao et al. [2011](#page-24-12)). Further, biochar does not need an additional treatment stage unlike activated carbons and contains surface functional groups rich in oxygen, possesses a non-carbonized fraction and a high cation exchange capacity for contaminant removal (Ahmad et al. [2012a](#page-22-3)). Additionally, biochar aids in soil quality enhancement, climate change mitigation, energy production and waste management (Atkinson et al. [2010](#page-23-10); Sohi [2012;](#page-31-6) Lee et al. [2017b](#page-27-13); Sophia Ayyappan et al. [2018](#page-31-7)). The advantages associated with biochar application are indicative for its preferability to activated carbons.



<span id="page-11-0"></span>**Fig. 13.1** Fate of heavy metals in the environment, their toxic effects in plants and human beings and their removal from soil by biochar amendment and phytoremediation

## *13.5.1 Heavy Metal Remediation Mechanisms*

The properties of high porosity, adequate surface area, alkaline pH, aromaticity and oxygen-containing surface functional groups enable biochar remediating heavy metals from soil. The various mechanisms are summarized in Fig. [13.2.](#page-12-0) These mechanisms are elaborated in the following passages:

(1) Physical adsorption

It is also called as van der Waals adsorption and is an outcome of the intermolecular interaction between the adsorbent particles and the adsorbate. The heavy metals in soil get sorbed on the char surface (Yu et al. [2009;](#page-34-11) Lou et al. [2011\)](#page-28-10). The process is reversible in general. High porosity, pore volume, large surface area, surface energy, high pH and adequate ionic strength affect heavy metal sorption (Zhang et al. [2009;](#page-34-12) Xie et al. [2011\)](#page-34-13). A high surface area and large pore volume facilitate a greater contact between the heavy metals and biochar. An increase in pyrolysis temperatures increases the surface area and pore volume and consequentially contributes in a greater remediation of heavy metals. Liu et al. [\(2010](#page-28-11)) prepared chars from switchgrass and pine wood at 300 °C and 700 °C, respectively. They reported that these chars could immobilize uranium



<span id="page-12-0"></span>**Fig. 13.2** Various mechanisms involved in removal of heavy metals

and copper effectively. Beesley and Marmiroli [\(2011](#page-23-3)) stated that biochar could immobilize zinc, cadmium and arsenic by physisorption remarkably.

(2) ion exchange

Exchange of metal ions such as magnesium, potassium and sodium on char surface by heavy metal ions is called as ion exchange. It is dependent on the chemical properties of char surface. The high cation exchange capacity of biochar assists in the process of ion exchange. Cation exchange capacity decreases with an increase in pyrolysis temperature and maximum cation exchange capacity is seen in chars produced at 250–300 °C (Lee et al. [2010](#page-27-14)). El-Shafey [\(2010](#page-25-10)) prepared biochar from rice husks at 175–180 °C and reported that mercury and zinc were effectively removed by these chars via ion exchange mechanism. Liu et al. [\(2010\)](#page-28-11) observed that char prepared by pyrolysis possess greater surface area in comparison to hydrothermal chars. The greater surface area assists in copper removal by ion exchange and sorption. They also stated that ion exchange removes heavy metals more effectively in comparison to sorption. Sánchez-Polo and Rivera-Utrilla ([2002\)](#page-31-8) demonstrated that ion exchange is related to soil pH. When soil pH is less than biochar pH at point of zero charge, greater amount of heavy metals are removed via ion exchange.

(3) Electrostatic attraction/repulsion

Electrostatic interaction between cations (metal pollutants) and anionic char surface is involved in heavy metal remediation (Xu et al. [2011\)](#page-34-14). Metal exchange between cations on char surface and heavy metals results in electrostatic outer sphere complex formation thereby aiding in heavy metal remediation (Ahmad et al. [2014\)](#page-22-0). Electrostatic interaction depends on factors such as soil pH, point of zero charge of biochar, valency and ionic radius of the metallic contaminant (Dong et al. [2011;](#page-25-11) Mukherjee et al. [2011\)](#page-29-5). Qiu et al. ([2008\)](#page-30-10) reported that chars derived from rice and wheat straw is more effective remediator than activated carbon as a result of the electrostatic interaction between lead ions and the char surface. Peng et al.  $(2011)$  $(2011)$  stated that the increase in soil pH and cation exchange capacity after biochar addition results in enhanced electrostatic interaction consequentially boosting heavy metal remediation.

(4) diffusion

A significant distinguishing feature between biochar and activated carbon is presence of non-carbonized phase in biochar. The contaminants diffuse not only into the non-carbonized portions of the char but also in the carbonized portions (Xu et al. [2012\)](#page-34-15).

(5) Complexation

Biochar surface has abundant oxygen-containing functional groups such as hydroxyl and carboxylic groups. These functional groups form surface complexes with heavy metals (Park et al. [2011a](#page-29-11); Tong et al. [2011](#page-32-10)). Biochar prepared at lower treatment temperatures consists of greater number of these functional groups. Further, oxidation of the char surface could result in an increase in the surface functional groups (Harvey et al. [2011](#page-26-10)). Stable complexes could be formed between lead ions and hydroxyl/carboxyl groups (Cao et al.  $2011$ ; Lu et al.  $2012$ ). Dong et al.  $(2011)$  $(2011)$  reported surface complexation as the main mechanism in chromium removal by biochar derived from sugar beet tailings. Further, smaller ionic radius of the metals aid in the enhancement of remediation (Wan Ngah and Hanafiah [2008](#page-33-10)).

(6) precipitation

precipitation is another mechanism through which biochar immobilizes the heavy metals and insoluble precipitates such as carbonates and phosphates are formed (Shen et al. [2015,](#page-31-9) [2017](#page-31-10)). Cao and Harris ([2010\)](#page-24-9) prepared biochar by thermal treatment above 300 °C and observed that these chars could be used for heavy metal removal by precipitate formation. In the study, lead formed lead-phosphate-silicate precipitates in the alkaline biochar. Cao et al. [\(2011\)](#page-24-12) investigated lead immobilization by cow manure-derived biochar. These chars have high ash content, which is rich in magnesium, silicon, potassium, phosphorus and sodium. The phosphates could form insoluble precipitates with heavy metals, such as pyromorphite is formed with lead. Xu et al. [\(2013b](#page-34-16)) investigated cadmium, zinc, copper and lead removal by biochar derived from cow manure and rice husk and observed that precipitation, in the form of carbonate and phosphate precipitates, is the main mechanism involved in their removal.

(7) Hydrogen bond formation

Formation of hydrogen bonds could also be involved in the removal of heavy metals. Contaminants form hydrogen bonds with the oxygen-containing functional groups present in abundance on the surface of biochar. Some of these functional groups are phenol, hydroxyl and carboxyl. Sun et al. ([2011,](#page-32-11) [2012b\)](#page-32-12) stated that organic contaminants could form hydrogen bonds with the surface functional groups available on the char.

The properties of biochar are dependent upon the feedstock type and thermal treatment conditions, as previously stated. Different types of biochar could be used for different remediation performances and it would be difficult to pinpoint a biochar for universal heavy metal removal. Some of the biochars used for removal of heavy metals have been represented in Table [13.2.](#page-15-0) Further, biochar incorporates different types of mechanisms for removal of heavy metals from contaminated soil as previously discussed, and a universal specific mechanism cannot be pointed. Biochar could affect the mobility and bioavailability of different heavy metals when amended to the contaminated soils. Therefore, heavy metal type and biochar properties must be considered before using the biochar for soil amendment to remove heavy metals. The impact of biochar on mobility and bioavailability of heavy metals in soil is discussed in the following sections.

#### **13.6 Impact of Biochar on Mobility of Heavy Metal**

Applying biochar to contaminated soils decreases the mobility of heavy metals present in these soils. This helps in decreasing the metal taken up by the plants grown in contaminated soils. Previously, it has been reported that bamboo-derived biochar could help in adsorption of heavy metals such as cadmium, copper, chromium, mercury and nickel from contaminated soils (Skjemstad et al. [2002](#page-31-11); Cheng et al. [2006\)](#page-24-13). In a study by Cao et al. [\(2009\)](#page-24-14), biochar prepared from dairy manure at 200 °C was more effective in lead sorption when compared to biochar prepared from dairy manure at 350 °C. They stated that this could be an outcome of higher soluble phosphate concentration in biochar prepared at 200 °C.

Beesley et al. [\(2010](#page-23-11)) investigated the impact of biochar prepared from hardwood on mobility of cadmium and zinc in contaminated soils and reported that the chars reduced the heavy metals in pore water. In another study by Beesley and Marmiroli ([2011\)](#page-23-3), biochar amendment immobilized zinc and cadmium in the contaminated soils. The concentration of zinc and cadmium decreased by 300 and 45 times, respectively in the pore water. Namgay et al. [\(2010](#page-29-12)) investigated impact of biochar application on mobility of heavy metals and reported an increase in zinc and arsenic concentration, a decrease in lead concentration, an irregular trend in cadmium concentration and an absence of change in copper concentration.

There could be involvement of redox processes between biochar and heavy metals, which could help in decreasing leaching of the heavy metals. Choppala et al. [\(2012](#page-24-5)) prepared biochar using chicken manure as feedstock and applied the chars to chromium-contaminated soils. They reported that chromium (III) ions are sorbed on cation exchange sites on biochar. Additionally, chromium precipitates as chromium hydroxides which help in chromium reduction. Therefore, biochar helps in

Feedstock	Treatment temperature $(^{\circ}C)$	Remarks	References
Bamboo	500	Cadmium, Lead, Zinc, Copper (maximum removed-49%)	Lu et al. $(2014)$
<b>Broiler litter</b>	700	Cadmium, Nickel, Zinc, Copper (maximum removed-75%)	Uchimiya et al. (2011a)
Chicken manure	550	Cadmium, Lead (maximum removed-94%)	Park et al. $(2011a)$
Dairy manure	450	Lead (sorption capacity- $-132.81$ mg/g)	Cao et al. (2011)
Miscanthus	600	Cadmium, Zinc, Lead (maximum removed-92%)	Houben et al. $(2013)$
Rice straw	500	Zinc, Copper, Cadmium, Lead (maximum removed-71%)	Lu et al. $(2014)$
Sewage sludge	500-550	Lead, Nickel, Cobalt, Chromium, Arsenic immobilization; Cadmium, Zinc, Copper mobilization	Khan et al. (2013)
Cottonseed hulls	$200 - 800$	Cadmium, Lead, Nickel, Copper removed by sorption, complex formation, precipitation and electrostatic interaction	Uchimiya et al. $(2011b)$
Hard wood	<b>NA</b>	Cadmium and Zinc removal; Arsenic mobilization	Beesley and Marmiroli (2011)
Oak wood	400	Bioavailability reduction of Lead by 76%	Ahmad et al. (2012b)

<span id="page-15-0"></span>**Table 13.2** Variation in feedstock and treatment temperature for removal of heavy metals

reducing chromium (VI) ions to chromium (III) ions, thereby resulting in a decrease in chromium leaching (Bolan et al. [2013\)](#page-23-12). The long-term existence of biochar in soil as a result of its excellent stability triggers changes in physicochemical properties of the char. Biochar ageing results in the oxidation of its surface, thereby increasing in the presence of oxygen-containing functional groups. Such a process could be accompanied by an increase in the cation exchange capacity and surface negative charges in biochar. These processes help in heavy metal immobilization (Wang et al. [2019\)](#page-33-7).

Biochar application to soil could need amendments in certain cases. For example, arsenic (V) could get reduced to arsenic (III) by biochar application, consequentially increasing its mobility (Ahmad et al. [2014\)](#page-22-0). Therefore, such a scenario could ask for amendments in biochar. Warren et al. ([2003\)](#page-33-11) stated that magnetization of biochar by iron oxide treatment could help in anion exchange thereby reducing the arsenic mobility in soil. Interestingly, reduction of heavy metals by biochar addition could be helpful in decreasing its toxicity in most of the cases. Choppala et al. ([2016\)](#page-24-15) reported that chromium (VI) is reduced to chromium (III) by biochar addition, which helps in decreasing their toxicity and bioavailability. The study also observed an increase in mobility of arsenic by its reduction from arsenic (V) to arsenic (III) when biochar was added to the soil.

Furthermore, efficiency and efficacy of biochar application could be affected by the soil type. In a study by Shen et al. ([2016a,](#page-31-12) [b](#page-31-13)), biochar prepared from hardwood was applied to contaminated sandy soil and lead-contaminated kaolin. They reported that the biochar application reduced zinc and nickel concentrations in sandy soil. However, no major effect was observed on lead mobility in kaolin.

#### **13.7 Impact of Biochar on Bioavailability of Heavy Metal**

The bioavailability of heavy metals regulates its potential to cause toxicity in soil the risks associated with its entry in food chain and its accessibility by the organisms thriving in the soils (Naidu et al. [2008\)](#page-29-13). Additionally, the bioavailability of heavy metals determines their degradation potential and ecotoxicology (Zhang et al. [2013](#page-34-0)).

Application of biochar aids in immobilization of heavy metals in soils, which decreases their phytotoxicity and bioavailability. In a study by Fellet et al. [\(2011](#page-25-12)), biochar was prepared from orchard prune residues and applied at rates varying from 1 to 10% to decrease the toxicity caused due to heavy metals in the mine tailings. They reported that there was an increase in water retention, cation exchange capacity and pH in the soils. Further, there was a decrease in bioavailability of cadmium, zinc and lead, with maximum decrease in cadmium. Zhou et al. [\(2008](#page-35-3)) prepared biochar using cotton stalks and applied them in contaminated soils to reduce cadmium uptake in cabbage plants. They reported that bioavailability of cadmium in soil was reduced by using co-precipitation and sorption.

Méndez et al. [\(2012](#page-29-14)) prepared biochar using sewage sludge and used them to decrease the solubility and bioavailability of heavy metals in soils. They reported that biochar diminished the bioavailable nickel, zinc, cadmium and lead in the agricultural soils. Park et al. [\(2011a,](#page-29-11) [b](#page-29-9)) prepared biochar using green waste and chicken manure and reported that they decreased copper, lead and cadmium uptake in mustard plants. In a study by Jiang et al. [\(2012](#page-26-12)), biochar prepared using rice straw immobilized copper and lead more efficiently than cadmium. It is, therefore, clear that biochars prepared from different feedstock at different treatment temperatures are differently potent in immobilization of heavy metals. Namgay et al. ([2010\)](#page-29-12) prepared biochar using activated wood and applied them to heavy metal contaminated soils. They observed that there is a decrease in arsenic, cadmium and copper concentrations in the shoots of maize plants. However, the results on lead and zinc removal were inconclusive in the study.

pH of soil has been reported to be correlated to heavy metal bioavailability. Uchimiya et al. [\(2010](#page-32-15)) investigated the impact of biochar amendment in soils and reported that biochar increases the pH and cation exchange capacity of soil, thereby increasing heavy metal immobilization in soils. Ahmad et al. [\(2012b\)](#page-22-4) reported a decrease in bioavailability of lead by 76% from contaminated soils in military shooting ranges by biochar application. They stated that biochar increases the pH of soil and the sorption potential, thereby aiding in heavy metal remediation. Beesley and Marmiroli ([2011](#page-23-3)) investigated the impact of biochar prepared from fruit trees to remediate a naturally contaminated soil. They stated that biochar effectively decreased the heavy metal concentrations in soil and organic carbon content could have an important impact on decreasing heavy metals bioavailability.

# **13.8 Remediation of Polluted Sites by Application of Biochar**

Studies have been conducted in various parts of the world to determine the efficiency and efficacy of biochar amendment for heavy metal removal from polluted soils. Koetlisi and Muchaonyerwa ([2019\)](#page-27-15) prepared biochar from different feedstocks such as pine bark and human faecal products. They reported that these chars could be used to effectively remove copper, chromium and zinc from industrial effluents in South Africa so that soil contamination could be reduced. Gwenzi et al. [\(2016](#page-26-13)) prepared biochar by using sewage sludge to study their impact on soil properties, plant growth, nutrient uptake and heavy metal removal from tropical clayey soils in Zimbabwe. They reported that biochar could decrease the copper, lead and zinc concentrations in these soils.

In a study by von Gunten et al. [\(2019](#page-33-12)), biochar was prepared from Tibouchina wood and applied to ferralsol in Brazilian forests. They observed that mobility of magnesium, calcium, potassium, barium and zinc concentrations in soil increased after biochar application. Puga et al. ([2015](#page-30-12)) prepared biochar using sugar cane straw at 700 °C for amending Brazilian mine soils contaminated with heavy metals. They reported that biochar application reduced cadmium, lead and zinc concentrations in the pore water and the plants grown on these soils. Rodriguez et al. ([2019\)](#page-30-13) prepared biochar from corncobs for utilization as a lead-contaminated soil amendment. They observed that the biochar could immobilize lead in these Colombian soils. However, the immobilization is not that effective due to the extreme contamination of the soils.

Rees et al. ([2014](#page-30-14)) investigated the short-term impact of biochar produced in Germany on heavy metal mobility in French soils. They concluded that biochar could immobilize lead, copper, zinc and cadmium in soils by increasing the pH of the soil and intra-particle diffusion in the biochar matrix. In a study by Beesley et al. [\(2014](#page-23-13)),

biochar was prepared from orchard prunings at 500 °C and applied to contaminated mine soils in Spain. They reported that biochar could effectively remediate heavy metals from the soils. Further, they stated that mixing biochar with compost could enhance the efficacy of heavy metal immobilization and toxicity reduction.

In a review by He et al. [\(2019\)](#page-26-14), it was concluded that biochar could be applied to Chinese soils to effectively minimize heavy metal contamination. The remediation potential is dependent on the properties of biochar and soil used. Further, biochar application could reduce the heavy metal accumulation in plants. Mohan et al. ([2018\)](#page-29-15) prepared biochar using corn stover and rice husk at 550 °C and 650 °C and observed that biochar could be applied in Indian soils to improve their productivity and remove heavy metals from the soil sustainably. Choudhary et al. [\(2017](#page-24-16)) prepared char using eucalyptus bark at 500 °C and highlighted their potential in effective chromium remediation from groundwater, wastewater and soil in India. Hina et al. ([2019\)](#page-26-15) prepared biochar using rice husk and plant waste as feedstock to immobilize arsenic from soils in Pakistan. Rice husk char was more effective for lower arsenic contamination, while plant waste char was more efficient in higher arsenic concentrations. Mazhar et al. ([2020\)](#page-28-13) reported that biochar could be applied to soils in Pakistan to improve the plant growth parameters and effective removal of chromium. Bandara et al. ([2017\)](#page-23-14) prepared biochar using wood as feedstock and applied them to soils in Sri Lanka to effectively remove chromium, nickel and manganese from the soils.

Samsuri et al. [\(2013](#page-30-15)) prepared biochar from rice husk and empty oil palm fruit bunch and used them to remove arsenic from Malaysian soils. Fahmi et al. [\(2018](#page-25-13)) used biochar derived from empty fruit bunch and demonstrated that they could remove cadmium and lead from soils in Malaysia. Mulder ([2014\)](#page-29-16) used biochar to remove heavy metals from Malaysian and Indonesian soils. Dang et al. [\(2019](#page-25-14)) prepared biochar from rice straws and applied them to contaminated soils in Vietnam. They reported that these chars could be used to remove zinc, cadmium, and lead from these soils. Saengwilai et al. ([2020\)](#page-30-16) used organic amendments to immobilize cadmium from the polluted soils in Thailand. Therefore, various studies across the globe have prepared biochar using different types of feedstocks at varying thermal treatment conditions. These chars have effectively decreased the mobility and bioavailability of heavy metals from polluted soils across the globe.

# **13.9 Applications of Biochar Other Than Heavy Metal Removal**

The char properties of oxygen-containing surface functional groups, good porosity, surface area, high carbon content and remarkable energy content facilitate its wideranging applications, which could help in tackling the issues of climate change, energy security, food security and waste management simultaneously.

Waste biomass could be used as feedstock for biochar production. Examples of waste biomass include agricultural residues, food waste, kitchen waste, animal

manure, sewage sludge, municipal solid waste and others (Cao and Harris [2010](#page-24-9); van Zwieten et al. [2010](#page-33-13); Yargicoglu et al. [2015;](#page-34-17) Kumar et al. [2016;](#page-27-16) Lee et al. [2017b](#page-27-13)). Further, the biochar could be used for decreasing the mobility and bioavailability of heavy metals consequently reducing their plant uptake and toxicity (Cui et al. [2012](#page-24-17); Hmid et al. [2014\)](#page-26-16). Thermal treatment of the waste biomass would also help in killing the prevalent microbes which could be harmful to the environment and human health (Dahal et al. [2018\)](#page-24-18). Therefore, biochar production would help in waste management and risk reduction at the same time.

Biochar helps in carbon sequestration. The carbon content available in biomass is converted to stable forms by thermal treatment in biochar. Carbon captured in biochar could check carbon dioxide release by 0.3 billion tonnes every year (Liu et al. [2015](#page-28-14)). Biochar has a very high stability in soil (Singh et al. [2012](#page-31-14)). Further, biochar could capture methane and nitrous oxide thereby helping in their emission reduction (van Zwieten et al. [2010](#page-33-13); Yaghoubi et al. [2014](#page-34-18); Edwards et al. [2018\)](#page-25-15). It has also been reported that biochar could stimulate the activity of micro-organisms and help in suppressing the greenhouse gas emissions (Castaldi et al. [2011](#page-24-19); Liu et al. [2014a,](#page-28-15) [b](#page-28-16)). In a study by Spokas et al. [\(2009](#page-31-15)) and Al-Wabel et al. ([2013\)](#page-22-5), it was observed that biochar prepared at thermal treatment temperatures of 500  $^{\circ}$ C and above decreases the greenhouse gas emissions, consequentially mitigating climate change.

Thermal treatment of biomass produces syngas, bio-oil and biochar in different concentrations depending on the feedstock variation and thermal treatment conditions. Bio-oil is produced in large quantities in fast pyrolysis, while gasification produces syngas in abundance (Mohan et al. [2006;](#page-29-17) Lombardi et al. [2015](#page-28-17)). Biochar could be utilized as catalyst for biodiesel production (Lee et al. [2017a](#page-27-17)). The presence of surface functional groups in char help in metal sorption and aid in the functioning of biochar as catalysts (Titirici et al. [2012](#page-32-1); Cheng and Li [2018](#page-24-20)). The various sources of bioenergy could be used to replace fossil fuels, consequentially decreasing the greenhouse gas emissions and aid in climate change mitigation. Biochar production could, therefore, help in solving energy security issues to a certain extent.

The properties of high carbon content and remarkable water retention capacity in biochar promote its utilization as soil conditioner to tackle water deficit situations (Bryant [2015;](#page-23-15) Nichols [2015\)](#page-29-18). Biochar application minimizes the nutrient loss from soil (Sohi et al. [2010\)](#page-31-16). Alkaline conditions introduced by biochar into soil help in neutralizing the acidic conditions. Further, biochar application stimulates microbial communities in soil and the associated microbial activity (Lehmann et al. [2011](#page-27-6)). Microbes oxidize the char surface thereby increasing oxygen-containing functional groups and the cation exchange capacity of the soil matrix. These changes help in increasing nutrient retention by soil, correspondingly enhancing the growth in plants. Various studies have stated that biochar application increase crop yield by facilitating nutrients to the plant roots (Steiner et al. [2009](#page-32-16); Vassilev et al. [2013a](#page-33-14); Houben et al. [2014](#page-26-17); Siebers et al. [2014](#page-31-17)). Biochar could be used to decrease the time needed for composting and increase the value of compost (Awasthi et al. [2017](#page-23-16); Sanchez-Monedero et al. [2018\)](#page-30-17). All of the aforementioned changes help in improving crop yield, consequently solving the problem of food security partially.

Apart from removal of heavy metals from soil, biochar could also help in removing organic contaminants from environment (Beesley et al. [2011](#page-23-17); Ahmad et al. [2014](#page-22-0)). Soils contaminated with oil and petroleum could be treated by biochar amendment (Wang et al. [2017;](#page-33-15) Kandanelli et al. [2018](#page-26-18)). Biochar supports microbial population growth in its pores and on its surface, which assists in hydrocarbon degradation. Biochar could also be utilized for dye degradation and remediation (Nautiyal et al. [2016;](#page-29-19) Sophia Ayyappan et al. [2018\)](#page-31-7). The surface area and high pH of biochar could help in removing hydrogen sulphide from biogas (Sahota et al. [2018](#page-30-0)).

# **13.10 Advantages and Risks Associated with Biochar Production and Application**

Apart from the various applications, biochar production and its use has a number of advantages. Biochar is cheaper than activated carbons and does not require additional activation steps. Additionally, biochar has a rich surface oxygen-containing functional groups, a non-carbonized fraction and a great cation exchange capacity, as stated previously. These enhanced properties aid in enhanced contaminant removal (Cao and Harris [2010;](#page-24-9) Ahmad et al. [2012a](#page-22-3); McCarl et al. [2012\)](#page-28-18). Further, biochar supports the growth of microbial colonies, consequently enhancing food chain in the soil (Pietikäinen et al. [2000\)](#page-30-18). Additionally, they enhance the water retention capacity in soil aiding in nutrient retention and crop growth (Ventura et al. [2013;](#page-33-16) Yu et al. [2013\)](#page-34-19).

However, there could be risks associated with biochar production and application. There could be presence of contaminants such as heavy metals and polycyclic aromatic hydrocarbons in the feedstock used for biochar production (Hossain et al. [2007\)](#page-26-19). Risks associated with these contaminants could, however, be removed by thermal treatment at 500 °C and above (Verheijen et al.  $2010$ ). Interestingly, in a study by Gong et al. ([2018\)](#page-25-16), it was observed that heavy metals in plants used for phytoremediation could be stabilized by charring. Further, chars prepared from such plants could be used for remediation of polluted sites. The ash content in chars could be a threat to human health (De Capitani et al. [2007](#page-25-17)). However, health safety guidelines, during production and application of char, could be enforced to minimize and remove the risks associated with ash. Biochar could sorb agro-chemicals, such as pesticides and herbicides, thereby decreasing their potential to increase the crop yield. However, such a sorption could help in immobilizing excess agrochemicals in soil (Sun et al. [2012b](#page-32-12)). In a few studies, biochar has been reported to negatively affect earthworms and increase nitrous oxide emissions (Topoliantz and Ponge [2003](#page-32-17); Warnock et al. [2007;](#page-33-18) Angst et al. [2014;](#page-22-6) Verhoeven and Six [2014\)](#page-33-19). However, wet biochar could be applied to minimize the damage to earthworms (Li et al. [2011\)](#page-27-18). Therefore, risks associated with biochar production and application do prevail, but the risks could be minimized by appropriate steps taken and guidelines properly enforced. Further,

the need for extensive research arises with regard to biochar production and their application.

# **13.11 Future Research**

Although biochar has been used for remediation of heavy metals from a number of polluted sites, there is a lot of scope for future research. These opportunities are mentioned in the following points:

- (1) Due to the variation in properties and performance of biochar produced from different feedstock and thermal treatment conditions, there is a need to establish a global standard for obtaining maximum advantage in terms of remediation of polluted sites.
- (2) Most of the studies have been small-scale and limited to laboratories and tiny agricultural lands. Further, the experiments have been focussed on single heavy metal removal. However, real-time metal pollution involves multiple heavy metals and occurs on large areas of land. Therefore, there is a need for extensive research involving multiple heavy metal contamination.
- (3) The complexity of soil systems brings about variation in biochar efficiency from remediation. The mechanisms involved in the metal removal could be studied extensively to bring clarity in remediation of polluted sites by biochar application.
- (4) The dose and rate of biochar application in metal-polluted sites need further optimization. Additionally, the suitability of biochar could be determined for targeted and specific removal of heavy metals.
- (5) Emergence of extreme weather events in the scenario of climate change, enquire for identification and confirmation of their impact on the efficacy and efficiency of biochar performance for heavy metal removal.

## **13.12 Conclusion**

Biochar could be a sustainable alternative for effective and long-term removal of heavy metals from polluted lands. Biochar could be produced from wide-ranging biomass sources and a number of thermal treatment methods are employed for its preparation. Biomass type and thermal treatment conditions affect the properties of char produced. Properties of alkaline pH, high cation exchange capacity, high surface area, high porosity, abundant oxygen-containing surface functional groups and a non-carbonized fraction, enable the biochar to remove heavy metals from the soil. Biochar incorporates mechanisms such as ion exchange, precipitation, diffusion, complex formation, electrostatic interaction and sorption, for the removal of metal pollutants from soil. Biochar decreases the mobility and bioavailability of heavy metals, thereby minimizing their toxic effects. The potential of biochar for heavy

metal removal has been tested in different studies conducted across the various parts of the globe and biochar was found to be effective in the remediation of heavy metal polluted sites.

Biochar could also be used for removing the organic contaminants from soil. Utilization of waste biomass assists in waste management and waste reduction. Enhancement of crop production can help in tackling issues of food security. Removal of contaminants from soil and water makes it safe for the animals and human beings. Extended stability of biochar in soils reduces the safety concerns. Biochar production could help in producing bioenergy which could be used as an alternative to fossil fuels. Biochar production would help in solving the problem of energy security and depleting fossil fuel reserves. Biochar would help in the mitigation of climate change by carbon sequestration and reduction in emission of greenhouse gases. Therefore, biochar could be a promising method for remediation of polluted sites and tackling the various problems endangering the environment and human health. Government of various countries could assist the scientists by providing them grants for research and they could commence policies to boost the production and application of biochar. Lastly, the risks associated with biochar production and application should be acknowledged and minimized for helping the society in the longer run.

**Acknowledgements** One of the authors (Abhishek Kumar) is thankful to the University Grants Commission, New Delhi, for providing NET-JRF Fellowship [Ref. No.—3635/(OBC)(NET-DEC.2015)].

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