

# Chapter 6

## Recent Development in Bioremediation of Soil Pollutants Through Biochar for Environmental Sustainability



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**Abstract** Soil contamination due to heavy metals has become a great concern nowadays. The main reasons for soil contamination are both natural as well as anthropogenic. Natural processes like volcanic eruption, weathering of rocks, landslides and soil erosion while anthropogenic involves several activities like smelting, mining, application of agrochemicals (pesticides, herbicides and fertilizers) and industrial wastes. Heavy metals pollution has a direct influence on the fertility of agricultural soils. The removal of heavy metals from soil is very difficult as it stored in the environment for a long time, because of its persistent nature. Several in-situ bioremediation technologies are used for removal of heavy metals from the environment. Out of that in-situ biochar application is one of the prominent technologies for remediation of heavy metals and it was found to be effective in reducing the mobility of heavy metals in soils. Biochar effectively adsorbs heavy metals and

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decreases bioavailability and toxin-induced stress to the biotic component of soil. In this chapter, the emphasis has been given on heavy metal pollution and types of biochar used for remediation of heavy metals from the soil and water.

**Keywords** Biochar · Bioremediation · Pollutants · Contaminated soil · Heavy metal

## 6.1 Introduction

Heavy metals contamination in soil and water has become an alarming issue in the recent times due to accelerated anthropogenic activities with increasing industrialization and decreasing land holdings leading to various health hazards as well as their adverse effect on the quality of soil and water (Singh et al. 2013; Bhatia et al. 2015; Matta et al. 2018; Gupta et al. 2019). Heavy metals are generally found in the soil environment in traces which are a result of weathering of rocks and minerals over the earth crust. These heavy metals become pollutant only when they cross a certain threshold limit due to anthropogenic activities which accelerate the release and addition of these metals into the environment, soils and water bodies. The sources of the heavy metals pollutions may be fertilizers, pesticides, bio solids, manures, metal mining, waste water, milling process, industrial wastes and airborne sources like dust or smoke from storage areas or waste dumps (Wuana and Okieimen 2011). The major heavy metal (loid)s pollutants commonly found in the contaminated environment are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (GWRTAC 1997). The common source of heavy metals includes cars, mining activities such as smelting, mine spoils and trailing, antiseptics, self-cleaning ovens, plastics, solar panels, mobile phones and particle accelerators (Koduru et al. 2017; Hubner et al. 2010). In addition to that the potential sources pyro-metallurgical industries, automobile exhausts, fossil fuel combustion are also the main sources of heavy metals (Lottermoser 2010; Prasad 2001), industries such as plastics, textiles, microelectronics, wood preservatives, refineries, agrochemicals (excessive use of fertilizers and pesticides) and waste disposal from sewage treatment plant, leachate from landfill and fly ash disposal some of the chief sources of the heavy metals (Singh and Kumar 2006; Kumar et al. 2016). Although, heavy metals content in domestic municipal sewage wastewater is mainly below threshold level (Sharma et al. 2014; Malla et al. 2015; Khan et al. 2019). The details about the sources of heavy metals and respective anthropogenic activities are given in Table 6.1.

Various research has been carried out all over the world towards remediation of the heavy metal contamination. This remediation may be by physical, chemical or biological means. Physical remediation is effective but cost-intensive and poses a risk of secondary diffusion while chemical methods cause secondary pollution to

**Table 6.1** Anthropogenic sources of heavy metals

S. No.	Heavy metals	Anthropogenic activities
1	Chromium (Cr)	Mining, industrial coolants, chromium salts manufacturing, leather tanning
2	Lead (Pb)	Lead acid batteries, paints, e-waste, smelting operations, coal-based thermal power plants, ceramics, bangle industry
3	Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (broken thermometers, barometers, sphygmomanometers), electrical appliances, etc.
4	Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning
5	Copper (Cu)	Mining, electroplating, smelting operations
6	Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, fuel combustion
7	Molybdenum (Mo)	Spent catalyst
8	Zinc (Zn)	Smelting, electroplating
9	Beryllium (Be)	Alloy (with Cu), electrical insulators in power transistors, moderator or neutron deflectors in nuclear reactors
10	Cobalt (Co)	Metallurgy (in super alloys), ceramics, glasses, paints
11	Iron (Fe)	Cast iron, wrought iron, steel, alloys, construction, transportation, machine-manufacturing
12	Mercury (Hg)	Extracting of metals by amalgamation, mobile cathode in the chloralkali cell for the production of NaCl and Cl <sub>2</sub> from brine, electrical and measuring apparatus, fungicides, catalysts, pharmaceuticals, dental fillings, scientific instruments, rectifiers, oscillators, electrodes, mercury vapour lamps, X-Ray tubes, solders
13	Manganese (Mn)	Production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, fungicides, antiknock agents, pigments, dryers, wood preservatives, coating welding rods
14	Molybdenum (Mo)	Alloying element in steel, cast irons, non-ferrous metals, catalysts, dyes, lubricants, corrosion inhibitors, flame retardants, smoke represents, electroplating
15	Nickel (Ni)	As an alloy in the steel industry, electroplating, Ni/Cd batteries, arc-welding, rods, pigments for paints and ceramics, surgical and dental prostheses, moulds for ceramic and glass containers, computer components, catalysts
16	Lead (Pb)	Antiknock agents, tetramethyl lead, lead-acid batteries, pigments, glassware, ceramics, plastic, in alloys, sheets, cable sheathings, solder, ordinance, pipes or tubing
17	Antimony (Sb)	Type-metal alloy, electrical applications, Britannia metal, pewter, Queen's metal, Sterline, in primers and tracer cells in munition manufacture, semiconductors, flameproof pigments and glass, medicines for parasitic diseases, nauseant, expectorant, combustion.
18	Selenium (Se)	glass industry, semiconductors, thermoelements, photoelectric and photo cells, and xerographic materials, inorganic pigments, rubber production, stainless steel, lubricants, dandruff treatment

(continued)

**Table 6.1** (continued)

S. No.	Heavy metals	Anthropogenic activities
19	Stannum (Sn)	Tin-plated steel, brasses, bronzes, pewter, dental amalgam, stabilizers, catalysts, pesticides
20	Titanium (Ti)	White pigments, UV-filtering agents, nucleation Agent for glass ceramics, alloy in aeronautics TI: Used for alloys (with Pb, Ag, or Au) with special properties, electronics industry, infrared optical systems, catalyst, deep temperature thermometers, low melting glasses, semiconductors, supra conductors
21	Vanadium (V)	Steel production, Alloys, catalyst

Singh and Kumar (2006), Kumar et al. (2016, 2019), Lottermoser (2010), Prasad (2001), Koduru et al. (2017), Hubner et al. (2010)

the environment. Biological methods, though safe to use but time consuming (Yang et al. 2019). Hence, in the last decade, the application of biochar has become the trend in addressing heavy metal contamination. Biochar based remediation are cost-effective as well as quick in action and raw material for biochar production (biomass) is easily available as biomass contributes 35% of the entire energy requirement of the world and it is the third-largest source of energy (Armynah et al. 2018). This chapter gives an insight into the action of biochar towards remediation of the heavy metal contamination.

## 6.2 Characteristics of Biochar

Biochar derived from two words, bio and char. Char means partially burnt to become blackened. So literally, biochar means charred biomass. It is carbonaceous or carbon-rich solid obtained by thermochemical conversion of biomass-derived from various sources like manure, leaves or wood at a temperature range of 300–1000 °C (Xie et al. 2015) in a partial or anaerobic condition. The products of this conversion may be heat, power, fuel and/or chemicals. The thermochemical processes involved in the production of biochar are pyrolysis, gasification, hydrothermal carbonization and microwave carbonization. Biochar when produced from woody biomass, called as charcoal. Biochar is a recalcitrant and stabilized organic C compound. Biochar is produced from a varied range of sources or biomass. Many studies have been carried out towards the characterization of biochars derived from different sources. Biochar can be produced from forest species like acacia, gmelina, eucalyptus, pine (Suárez et al. 2017; Zhang et al. 2018) and animal manures like yak manure (Zhang et al. 2018) and chicken manure (Domingues et al. 2017) and from agricultural field crop by-products like coffee husk, sugarcane bagasse and rice husk (Armynah et al. 2018; Domingues et al. 2017). Biochar also has a range of application as wide as its sources. It is used in agriculture for fertility enhancement (Domingues et al. 2017) and amendment of soil acidity (Zhang et al. 2018), C sequestration (Domingues et al. 2017), wastewater treatment and environmental

**Table 6.2** Characterization of biochar

Index	Value
Specific surface area (m <sup>2</sup> /g)	6.86
Micropore area (m <sup>2</sup> /g)	0.17
Total pore volume (mm <sup>3</sup> /g)	22.29
Micropore volume (mm <sup>3</sup> /g)	0.02
Ash (wt%)	42.25
pH	10.09
C (wt%)	48.45
H (wt%)	1.78
N (wt%)	1.47
S (wt%)	0.78

Brewer et al. (2009), Chen et al. (2014)

application for bioremediation. The application of biochar for any specific purpose depends upon its physicochemical properties. Physicochemical properties of biochar largely depend upon the type of feedstock from which it has been derived and the operation temperature conditions (Suárez et al. 2017; Yang et al. 2019; Armynah et al. 2018; Jindo et al. 2014; Zhang et al. 2018; Domingues et al. 2017). In most of the studies, the pyrolysis temperature has been maintained in the range of 300–800 °C (Jindo et al. 2014; Zhang et al. 2018). Many studies have used pyrolysis technique for production of biochars (Yang et al. 2019; Jindo et al. 2014; Zhang et al. 2018; Domingues et al. 2017). Other than that, the process like flash carbonization and torrefaction have also been used (Yang et al. 2019).

### 6.2.1 Characterization of Biochar

For determination of morphological and physical properties like surface area and pore size distribution of biochar, Breuner Emmet and Teller (BET) physio-sorption method is mostly used (Suárez et al. 2017; Armynah et al. 2018; Jindo et al. 2014; Zhang et al. 2018; Nartey and Zhao 2014; Askeland et al. 2019). For surface characteristics and elemental analysis, Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) can be used (Jindo et al. 2014; Jechan et al. 2017; Bouraoui et al. 2015). Chemical bonding and structural properties of biochar can be determined by Fourier Transform Infrared (FTIR) Spectroscopy (Nartey and Zhao 2014; Askeland et al. 2019). Contaminant and heavy metals in biochars are determined by Atomic Absorption Spectrometer (AAS) and Inductively Coupled Plasma Mass Spectrometer (ICP MS) (Askeland et al. 2019). For analysis of structural elements C, H and O the CHN analyzer can be used. Biochars can also be characterized and differentiated based on elemental ratios like H/C, O/C or C/N.

The specific surface area of biochar (6.86 m<sup>2</sup>/g), micropore area (0.17 m<sup>2</sup>/g), total pore volume (22.29 mm<sup>3</sup>/g), and micropore volume (0.02 mm<sup>3</sup>/g). Ash content and pH were 42.25% and 10.09, respectively. Content of C element (48.45%), H (1.78%), N (1.47%), and S (0.78%) elements as shown in Table 6.2.

**Table 6.3** The removal of heavy metals by biochar and their effects

Contaminants	Biochar type	Source	Effects	References
As and Cu	Hardwood	Soil	Mobilization due to enhanced pH and DOC	Beesley et al. (2010)
As, Cr, Cd, Cu, Ni, Pb, and Zn	Sewage sludge (500–550 °C)	Soil	Immobilization of As, Cr, Ni, and Pb due to rise in soil pH. Mobilization of Cu, Zn, and Cd due to highly available concentrations in biochar	Khan et al. (2013)
Cd and Zn	Hardwood	Soil	Immobilization due to enhanced pH	Beesley et al. (2010)
Cd, Cu, and Pb	Chicken manure and green waste (550 °C)	Soil	Immobilization due to partitioning of metals from exchangeable phase to less bioavailable organic-bond fraction	Park et al. (2011)
Cu and Pb	Oakwood	Soil	Complexation with phosphorus and organic matter	Karami et al. (2011)
Pb	Dairy manure (450 °C)	Soil	Immobilization by Hydroxyl-pyromorphite formation	Cao et al. (2011)
Pb	Oakwood (400 °C)	Soil	Immobilization by rise in soil pH and adsorption on biochar	Ahmad et al. (2012)
Pb	Rice straw	Soil	Non-electrostatic adsorption	Jianga et al. (2012)
Pb, Cu and Zn	Broiler litter (300 and 600 °C)	Soil	Stabilization of Pd and Cu	Uchimiya et al. (2012)
Cd (II)	Pine Residue 600 °C	Water	Reduction of Cd content in water by adsorption	Park et al. (2019)
Cr (VI)	Eucalyptus Bark	Soil and water	Removal from soil and ground water by sorption, electrostatic attraction, aqueous reduction by dissolved organic matter (DOM)	Choudhary et al. (2017)
Zn(II)	Wheat straw, pine needles (350 °C and 550 °C)	Soil	Immobilization in soil by OH <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> and Si released from biochar.	Qian et al. (2016)
Pb (II)	Maple wood (500 °C)	Water	Removal from water by adsorption by oxygen containing surface functional group	Wang et al. (2018)
Cd(II) and Pb(II)	Dairy manure (300 °C)	Soil	Removal from soil by precipitation as carbonate minerals complexation with surface functional carboxyl and hydroxyl groups	Chen et al. (2019)
Cr (VI)	Sewage Sludge (300 °C)	Water	Removal for aqueous solution by adsorption through electrostatic interactions between Cr(VI) anion and the positively charged functional groups on the surface of biochar	Agrafioti et al. (2014)
As(III), As(V)	Empty oil palm fruit bunch and rice husk	Soil	Surface complexes were formed between As(III) and As(V) and the functional groups (hydroxyl, carboxyl, and C–O ester of alcohols) of the two biochars	Samsuri et al. (2013)

## 6.2.2 *Morphological Characteristics*

The surface area and porosity of final biochar product depends on feedstock type and operation temperature. With increase in temperature, the surface area and total pore volume of the biochar increases and the particle size decreases for woody biochar (Suliman et al. 2017), biochar from agricultural products (Suárez et al. 2017) or from animal manures (Zhang et al. 2018). With increase in surface area the CEC of biochar also increases. Porosity and surface area of biochar material are important parameters for their use as remediation of contaminants.

## 6.2.3 *Composition of Biochar*

At low temperatures the biochar yield is higher and with increasing temperature the yield of biochar has been reported to decrease while ash and C contents have found to be increase (Jindo et al. 2014; Domingues et al. 2017). The increase in total C content of woody biochar at high temperatures may be contributed to higher degree of polymerization resulting to more condensed C structure (Lehman and Joseph 2009). Therefore, an increase in reaction temperature leads to an increase in carbon content, and decrease in the hydrogen and oxygen content (Jindo et al. 2014). In contrast, animal manure such as chicken manure (Domingues et al. 2017) and yak manure (Zhang et al. 2018) derived biochars show decrease in C content with increasing temperature which might be due to the high labile nature of organic compounds found in animal waste which are rapidly lost before biochar formation (Domingues et al. 2017). The different types of biochar on the basis of feedstock with removal of heavy metal from soil and water is given in Table 6.3. C and O are dominant elements present in biochar derived from any feedstock. Other than C and O the elemental composition varies according to feed stock and the percentage of elements also varies with operation temperatures. Apart from C and O biochar consists mostly of basic elements Ca, Mg, K (Armynah et al. 2018). For example, biochar derived from rice plant by products have Silicon as a dominant element (Armynah et al. 2018; Nwajiaku et al. 2018). With increase in pyrolysis temperature, the content of the basic elements Ca, Mg, K increases (Armynah et al. 2018; Zhang et al. 2018; Nwajiaku et al. 2018). Some studies also show that animal manure derived biochars contain traces of Fe, Cu, Mn and Zn (Zhang et al. 2018).

The amount of volatile compounds also gradually decreases with increasing pyrolysis temperature. The lignin containing biomass or woody biomass show a large change in volatile component with increasing temperature, compared to non woody species because of lignin decomposition at higher temperatures (Jindo et al. 2014).

### 6.2.4 Acidity/Alkalinity

The pH of biochar is an important property with regards to its use as soil amendment or as remediation of contaminated soils (Zhang et al. 2018). Because the changes in pH greatly influence some of the soil processes such as precipitation of minerals, nitrogen mineralization and ion exchange (Novak et al. 2016; Dai et al. 2018; Fidel et al. 2017). The resultant pH of biochar is dependent upon the temperature and type of feedstock. Generally, the pH value of biochar increase with increasing pyrolysis temperature (Jindo et al. 2014; Zhang et al. 2018; Suliman et al. 2017). Increase in pH at higher temperature may be due to increase in concentration of inorganic elements which are not pyrolysed and basic oxides formed at the surface under high temperature of pyrolysis (Zhang et al. 2018). The other reason may be the detachment of functional group during pyrolysis which is principally acidic in nature, such as hydroxyl, formyl or carboxyl groups (Weber and Quicker 2018; Tiwari et al. 2019a, b; Singh et al. 2019; Kour et al. 2019). Therefore removal of acidic functional group during pyrolysis shifted the pH to more basic condition. Hence, an increased pH-value is mainly contributed to increasing degree of carbonization (Quicker et al. 2016).

## 6.3 Mechanism of Biochar Interaction with Heavy Metals in Soil

The main reason behind application of biochar in soil is increasing the population of hydrocarbon-degrading microbes (Karppinen et al. 2017). Heavy metals cannot be degraded completely from the soil and water, but it can be transformed from more toxic to less toxic form. It can also be accumulated in plants and animals. Therefore, there are mainly four commonly used strategies for bioremediation of heavy metals.

1. Passive adsorption of ionic cations on the surface of biochar from the soil
2. Precipitation of anions like phosphate, carbonates, silicate, and chloride
3. Complexation with functional groups on the surface of biochar
4. Nutrients release such as N, P, K, Ca, Mg, S etc.

The processes passive adsorption, precipitation and complexation can reduce the bioavailability of heavy metals in the soil and further reduce the phytotoxicity to plants, on the other hand the nutrient release mechanism can increase the availability of nutrients to plants and microorganism in rhizosphere. The different mechanism of bioremediation and phytoremediation are given in Fig. 6.1. The mechanism of biochar application in phytoremediation is shown in Fig. 6.2. The mechanism of biochar application in phytoremediation is shown in Fig. 6.1. Phytoremediation includes the phytostabilization, phytoextraction, phytodegradation and phytovolatilization. Phytostabilization and phytoextraction are the commonly used



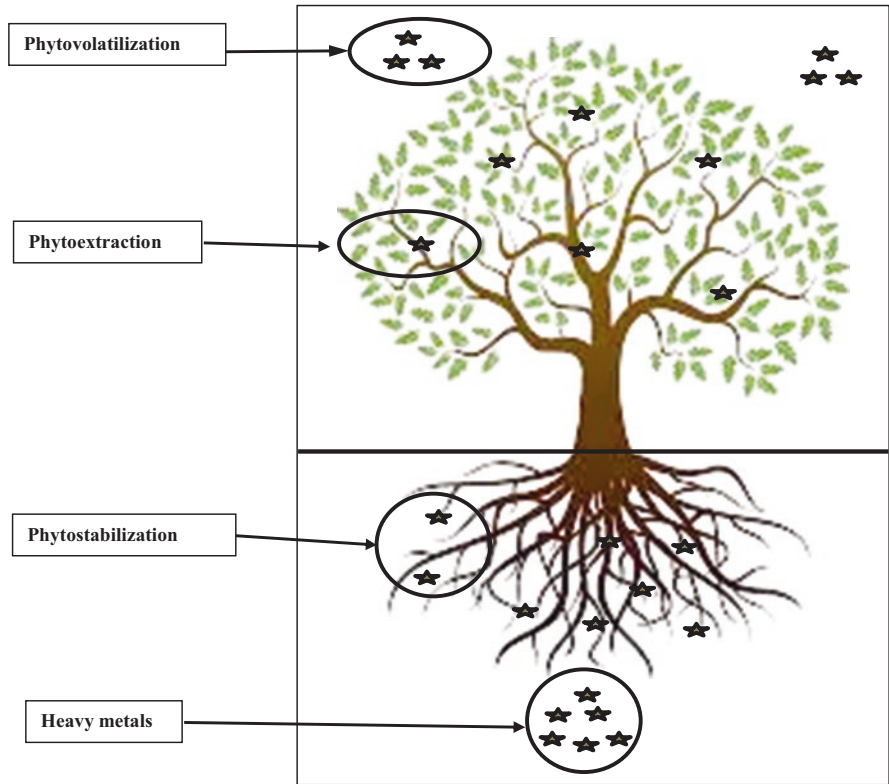


Fig. 6.1 Mechanism of remediation of heavy metals absorbed from soil in plants

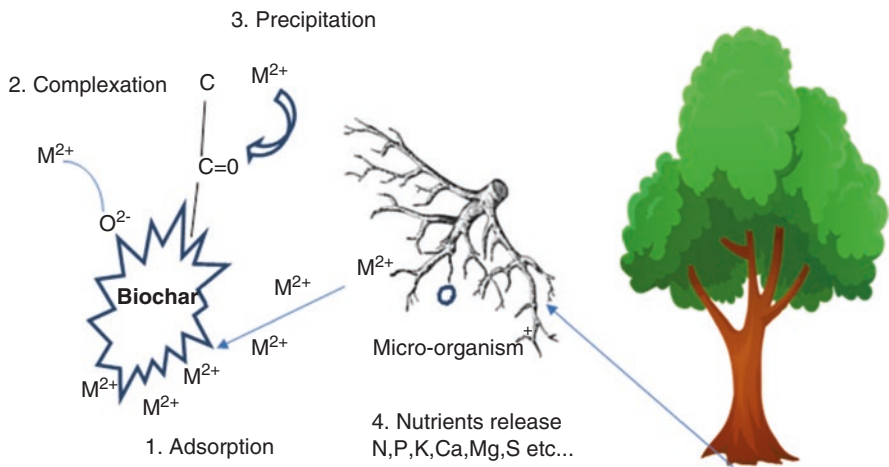


Fig. 6.2 Mechanism of combining effects of phytoremediation and biochar for bioremediation of heavy metal contaminated soil. Cationic metal ions expressed as M<sup>2+</sup>. (Source: Wenjie et al. 2018)

technologies for the bioremediation of the contaminated agricultural soils. In phytoextraction, generally used the fast-growing hyper-accumulators or energy plants to uptake the heavy metals. The biochar amended phytoremediation from agricultural soils was performed using *Brassica napus* (Houben et al. 2013), *Anthyllis vulneraria* and *Noccaea rotundifolium* (Fellet et al. 2014), *Brassica juncea* (Rodriguez-Vila et al. 2014), *Spinacia oleracea* and *Brassica napus* (Kelly et al. 2014), *Amaranthus tricolor* (Lu et al. 2015), *Clitocybe maxima* (Wu et al. 2016), *Cassia alata* (Huang et al. 2018), *Solanum nigrum* (Li et al. 2019) and *Lycopersicon esculentum* (Bandara et al. 2017). The impact of various dose of biochar and different plant species in bioremediation are mentioned in Table 6.4.

The alkaline nature and negatively charged surface of biochar help it to adsorb and retaining the heavy metals ions. In spite of this, biochar also provide support and favourable micro environment for beneficial microbes, nutrient supply to plant roots and contributes in the soil structure development. Namgay et al. (2010) reported that application of biochar in contaminated soil reduces the availability of heavy metals which lead to reduction of absorption of heavy metal to plants. Apart from that biochar also increases the soil pH (Novak et al. 2009) hence might have improved sorption of these metals, consequently decreasing their bioavailability for plant uptake.

## 6.4 Interactions Between Biochar and Metals

These metals occur as their cations, anions or complexes. The form of occurrence depends upon the reaction (pH) (Park et al. 2019) and the aeration status (aerobic or anaerobic) of the environment. The mechanism of interaction of these metal (loid)s with biochar depend upon the form of their occurrence and the biochar characteristics (Ahmed et al. 2014) like surface area, porosity, content of exchangeable cations or anions and elemental composition of biochar which ultimately depends upon the feedstock type and operation temperature. Ion-exchange, electrostatic attraction and precipitation are predominant mechanisms for the remediation of inorganic contaminants by biochar (Ahmed et al. 2014). The increase in soil pH due to application of biochar also results in the immobilization of the metal cations (Egene et al. 2018).

Cd interacts by mechanisms of chemisorption, cation exchange, precipitation by carbonate ( $\text{CO}_3^{2-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ) and complexation with surface functional groups like carboxyl ( $\text{COO}^-$ ) and hydroxyl ( $\text{OH}^-$ ) groups (Singh et al. 2017a, b, c, 2018; Tiwari et al. 2018; Park et al. 2019; Chen et al. 2019). In its compounds Cd occurs as divalent Cd (II). Adsorption of  $\text{Cd}^{2+}$  is reported to be dominated by boundary layer diffusion and very small amount of intraparticle diffusion or adsorption due to diffusion by pores (Park et al. 2019). At the surface, the interaction is mainly by exchange with cations of Ca, Mg and K but intra particle interaction is due to precipitation by  $\text{PO}_4^{3-}$  (Park et al. 2019; Chen et al. 2019).  $\text{Pb}^{2+}$  follows similar sorption mechanism as  $\text{Cd}^{2+}$  and interacts with biochar by mechanisms of

**Table 6.4** Effects of biochar application on bioremediation and phytoremediation of contaminated soils

Feedstock	Biochar dose	Contaminants	Experiment type	Mechanism/Effect	Microbial/Plant species	References
Corn cob biochar	0%, 1% and 5%	Cd	Pot experiment	Phyto extraction	<i>Solanum nigrum</i> L.	Li et al. (2019)
Pruning residues Manure biochar	0%, 1.5%, and 3%	Cd and Pb	Pot experiment	Phytostabilization	<i>Anthyllis vulneraria</i> and <i>Noccaea rotundifolium</i> ,	Fellet et al. (2014)
Miscanthus biochar	1%, 5% and 10%,	Cd, Zn and Pb	Greenhouse pot experiment	Phytostabilization	<i>Brassica napus</i> L.	Houben et al. (2013)
Sewage sludge biochar	0.4%, 1%, and 3%	Pb, Zn, Cu, Cd and As	100-day pot experiment	Immobilization	<i>Cassia alata</i> L.	Huang et al. (2018)
Pine wood biochar	0%, 10%, 20%, and 30%	Cd and Al	Pot experiment	Phytostabilization	<i>Spinacia oleracea</i> and <i>Brassica napus</i>	Kelly et al. (2014)
<i>Hordeum vulgare</i> straw biochar	0%, 3% and 6%	Cd and Cu	Pot experiment	Mycocoextraction	<i>Clitocybe maxima</i>	Wu et al. (2016)
Biochar with compost	1%, 2%, 4% and 8% biochar in 20% 40% 80% and 100 % amendment	Co, Cu and Ni	Greenhouse experiments	Phytostabilization	<i>Brassica juncea</i> L.	Rodriguez-Vila et al. (2014)
Woody biochar	1%, 2.5% and 5%	Cr, Ni and Mn	–	Phytostabilization	<i>Lycopersicon esculentum</i> L.	Bandara et al. (2017)

chemisorptions, cation exchange, precipitation by carbonate ( $\text{CO}_3^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ) and silicate ( $\text{SiO}_4^{2-}$ ) (Wang et al. 2018; Chen et al. 2019). Pb is released as  $\text{Pb}^{2+}$ , metal oxyanion complexes and its oxides and hydroxides in to the soil and water environment. But most stable forms are  $\text{Pb}^{2+}$  and lead hydroxy complexes (Wuana and Okieimen 2011). However, due to easy hydrolysis of Pb at low pH, biochar has been reported to have a higher affinity for Pb than Cd (Chen et al. 2019). In aqueous solution, the sorption of these divalent metal cations is pH dependant due to their strong tendency to be hydrated in aqueous solution (Dong et al. 2017). According to a study, adsorption of Cd increased with increasing pH up to 5 and maximum adsorption occurred at pH from 5–8 and the adsorption decreased gradually from pH 9 (Park et al. 2019). Similar behaviour has been reported for Pb adsorption with increasing pH. This behaviour is due to formation of hydroxide or carbonate complexes at higher pH (Park et al. 2019; Wang et al. 2018).

The dominant and toxic form of Cr found at contaminated sites is Cr (VI) and major species are chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ). At reduced condition it may occur as Cr (III) (Wuana and Okieimen 2011). The mechanism of Cr (VI) removal by biochar is governed by sorption due to electrostatic attraction of anionic Cr (VI) by protonated biochar surface, where it is reduced to Cr (III) by carboxylic and phenolic hydroxyl group. Other mechanism is sorption and reduction mediated by surface organic complexes (Cr (III) - DOM complex) of biochar, and direct aqueous reduction by dissolved organic matter (DOM), derived from biochar (Choudhary et al. 2017).

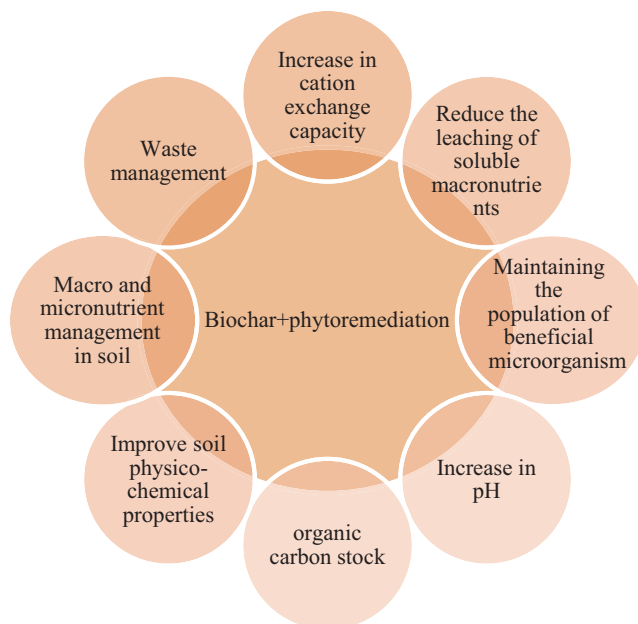
Arsenic is a metalloid contaminant. In aerobic environments the dominant form is As (V) and it occurs as arsenate ion. Cr and as occur as their anions ( $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{AsO}_4^{3-}$ ) and hence, the positively charged biochar surfaces are important for their adsorption. Under reducing condition, dominant form is As (III). As may interact with biochar by anion exchange at surface with anions like  $\text{PO}_4^{2-}$ , surface complexation with carboxylic and phenolic groups, adsorption on surface by metal bridging and DOM mediated reduction and physical adsorption (Vithanage et al. 2017).

## 6.5 Impacts of Biochar on Agriculture Productivity

The application of biochar has resulted in to improve in soil fertility, increase crop productivity, and water holding capacity of soil etc. as given below.

### 6.5.1 Soil Property and Crop Productivity

The excess use of fertilizer lead to leaching of excess nutrients, runoff losses of nutrients especially nitrogen to nearby water bodies, reduce soil fertility, acidification of soil, etc. On the other hand application of biochar in soil increases the organic



**Fig. 6.3** A summary of the potential positive effects achieved by combining phytoremediation and biochar in heavy metal pollution remediation

carbon stock, helpful for maintaining the population of beneficial microorganism, improves physico-chemical properties, cation exchange capacity of soil, reduce the leaching of soluble macronutrients and therefore enhancing the soil fertility and crop yield. Biochar application also improves the water holding capacity of soil by improving soil quality in terms of physical chemical and biological properties of soil. An overview of combining biochar application with phytoremediation is given in Fig. 6.3.

### 6.5.2 Carbon Sequestration

As biochar is rich source of organic carbon, so have a potential role in carbon sequestration in soil. Biochar degrade slowly in soil, hence play an important role in built up of organic carbon in soil. Carbon sequestration improves the organic carbon status of soil. As organic carbon is tightly bound to soil particle, results in to less emission of  $\text{CO}_2$  to the atmosphere from agriculture. Therefore biochar has an effective role in mitigating greenhouse gases emission and climate change.

### 6.5.3 Waste Management

Biochar is produced from waste material (municipal sewage waste, biomass, chicken waste etc.). Since the waste material is reuse for production of biochar, therefore the biochar production process is sustainable technique and economically viable.

## 6.6 Conclusions

Globally, heavy metal pollution is a severe problem. Several in-situ bioremediation methods are used for treating contaminated soil and water. Biochar application is one of the environment friendly and sustainable technology for treating heavy metal contaminated soil. Various types of biochar on the basis of feedstock used are hardwood, chicken manure, oak wood, rice straw, dairy manure etc. The heavy metals such as Cr, Zn, Pb, Cu, As are removed by biochar from contaminated soil and water through mechanism such as complexation, adsorption, precipitation and stabilization. In spite of decreasing bioavailability of heavy metal to soil, biochar application also improve soil physicochemical properties, organic carbon content, increase in pH and CEC of soil, maintaining the population of beneficial microorganism and waste management. Hence, it can be concluded that biochar application to contaminated soil and water plays a dual role of controlling soil and water pollution and improving the soil fertility.

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