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Review

Potential of biochar for clean-up of heavy metal contaminated soil and water

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Heavy metals exist in the environment naturally aside those due to anthropogenic impact. These metals are removed from effluents and water using different techniques like adsorption, oxidation/reduction, chemical precipitation, membrane separation, filtration and ion exchange. Biosorption is very effective because it is highly renewed naturally, is cheap, and can remove metals greatly because the pollutant can be recovered either by desorbing or incinerating the biomass. Therefore, this work aims to identify some biochars utilized as adsorbents to remove lead, chromium, mercury and copper in soil and water, according to different researchers. In conclusion adsorption is a very effective method to remove or recover heavy metals from the environment. These biochars can be used in place of commercial activated charcoal because, besides being cheap, they are very effective treatment in removing metal ions based on wastewater discharge standards.

Key words: Biomass, adsorbents, activated carbon, biochar, heavy metals.

INTRODUCTION

Soil and water contamination with significant metals are often attributed to several completely different sources like agricultural, mining activities, industrial and residential activities. A trending environmental downside is contamination of soil and water due to rise of harmful pollutants derived from waste effluents may be. The foremost toxic wastes are significant metals like lead, nickel and others. These might be useful in minute concentrations, but adversely affect aquatic life and human health. The existence of those elements will result in metabolic process issues, immunologic weakness, excretory organ and liver disorders, high blood pressure, genetic mutations, in a worse case death (Zhang et al., 2016). Numerous correction techniques, supported either mobilization or immobilization processes are developed preserving security of human health and also the maintenance of sustainable environment (Souza, 2009). In recent years, it has been found that more soils worldwide are contaminated with toxins, due to waste emissions from various anthropogenic processes and improper use of pesticides and chemicals for agricultural production (Mench et al., 2010). Furthermore, tailings may be characterized by a total absence or low levels of organic matter and macronutrients and will normally have an acidic pH, although some tailings may be alkaline (Krzaklewski and Pietrzykowski 2002; Gbadebo and Ekwue 2014). Aside from that, tailings are also said to be devoid of normal soil structure and support a highly

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stressed heterotrophic microbial community (Mendez et al., 2007). Further pollution of soil and tailings can be curbed by deploying pollution by employing environmentally sound technologies as alternatives (Beesley et al., 2011). For instance use of compost as soil amendment has been embraced by rural farmers due to its cost effectiveness (Umeobika and Onmonya, 2020). Many disadvantages of widespread use of chemical fertilizers include increase in soil acidity, mineral imbalance and soil degradation (Ayoola and Makinde, 2008). Also, in Europe Petruzzelli (2012) has reported that soil contamination has been known as a vital point for action within the European Economic Community, because it affects a large expanse of the available land. The economy in China has experienced progressive growth within the past few years; this has led to increased environmental problems (Xi et al., 2011). Standard strategies are enforced to reduce major metals from contaminated water. However, most of the main strategies are ineffective and undesirable due to high costs, high sludge production, and incomplete removal (Lara et al., 2016). Several studies aiming at reducing operating costs and increasing efficiency in water treatment have been conducted. Some of the biomass already worked on include: shells of aquatic animals and egg, fruit peels, vegetable oil and its residues, nuts, zeolites and husks of some roots and tuber crops cocoa and corn cobs. The efficiency of the process is hinged on the nature of the biomass used (Tejada-Tovar et al., 2016). Biochar is produced by thermochemical breakdown of biomass under restricted environments (Cha et al., 2016; Gondim et al., 2018). Temperature, type of biomass and atmosphere (often slowly oxidizing) are the most critical variables considered in this process (Kim et al., 2012). Water correction Contamination of aquatic systems may be a serious environmental issue and so the event of associate economical and appropriate technology to get rid of significant metals from binary compound solutions is important. Many strategies are often employed to remove significant metals from contaminated water. They include chemical precipitation, action, adsorption, membrane filtration; reverse diffusion, solvent extraction, and chemistry treatment with several of those strategies suffering from high capital and operational prices (Khatri et al., 2017).

Soil correction was done by removal of significant metal by screening followed by Soil washing from Contaminated Soil. In this technique the contaminated soil is removed from contaminated sites (ex-situ) and washed, the limitation of this method; the operation cannot be performed for a really massive volume of soil. Benefits of excavation involve the entire removal of the contaminants and also the comparatively fast cleanup of a contaminated site. Disadvantages embrace the actual fact that the contaminants square measure merely affected to a special place, wherever they need to be monitored; the danger of spreading contaminated soil and dirt particles throughout removal and transport of contaminated soil; and also the comparatively high value. Excavation is often the foremost high-ticket choice once massive amounts of soil should be removed or disposal as risky or toxic industrial waste is needed (Khatri et al., 2017). Stabilizing metals within the soil, significant metals are often left on the site and treated during a means that reduces or eliminates their ability to adversely have an effect on human health and also the environment. This method is usually referred to as stabilization. Eliminating the bioavailability of significant metals on the site has several benefits over excavation. A technique of stabilising significant metals consists of adding chemicals to the soil that cause the chelation of minerals that contain the significant metals during a form that's not simply absorbed by plants, animals, or people. This technique is termed in-place fixation or stabilization. This method doesn't disrupt the setting or generate dangerous wastes. Instead, the significant metal combines with the additional chemical to make a less harmful compound. The significant metal remains within the soil, however in a form that is abundant and less harmful, the disadvantages is that it permits incomplete neutralization of metals (Khatri et al., 2017). Uses of plants growing plants will facilitate contain or scale back significant metal pollution often referred to as phytoremediation. It has the advantage of comparatively low value and wide public acceptance. It is often but 1 / 4 of the price of excavation or in-place fixation. Phytoremediation has the disadvantage of taking longer to accomplish than different treatments. Plants are often utilized in other ways. Generally, a contaminated site is just revegetated during a method referred to as phytostabilization (Liu et al., 2017).

EFFICIENT REMOVAL OF METALS FROM WATER BY BIOCHAR

A great number of solid substances can serve as adsorbents. Adsorbents are very important because their porous structure is suitable; it affects diffusion directly. This is seen on the surface area of solids, affecting total adsorption capacity and the values of adsorption velocity (Souza, 2009). Some works have evaluated the capacity and efficiency of adsorption to remove chromium, copper, mercury ions and lead in marine environments (Santhosh et al., 2020). Some of them are given below (Table 1), which show the biomass mostly utilized to produce biocarbons to be adsorbed to heavy metal ions.

BIOCHAR USED TO REMEDY METAL POLLUTED SOILS

Heavy metals stay for years and not easily biodegradable in soils that are polluted. For heavy metals to be removed from polluted soils it is expensive and takes a lot of time

Table 1. Copper and lead removal in aqueous environment using various adsorbents with copper activator.

Adsorbent	Dosage*	Activator	Efficiency (%)	Adsorption capacity (mg g $^{-1}$)	Reference
Conventional	0.1 g/50 ml	Nd**	99.87	4.84	Rocha et al. (2006)
Guava seed	0.1 g/50 ml	N_2	93.04	1.23	Rocha et al. (2006)
Macadamia nut	0.1 g/50 ml	N_2	99.01	3.48	Rocha et al. (2006)
Taioba-brava	0.5 g/250 ml	Physical	99.88	4.47	Lucena et al. (2012)
Saltbush	0.5 g/250 ml	Physical	98.82	8.89	Lucena et al. (2012)
Buriti lumps	1.0 g/100 ml	Physical	99.21	4.96	Pinto et al. (2013)
Sugarcane	40 mg/20 ml	HCl	99.53	3.56	Ferreira et al. (2015)
Rice husk	0.2 g/20 ml	H_3PO_4	92.9	2.20	Miguel (2017)
Rice husk	0.2 g/20 ml	KOH	99.6	3.20	Miguel (2017)
Sugarcane	0.25 g/25 ml	H_3PO_4	99.79	Nd**	Silva (2017)
Water hyacinth	100 mg/10 ml	N_2	90.8	6.31	Lima (2018)
Coffee straw	1.5 g/50 ml	N_2	85	Nd**	Oliveira (2018)

•Dosage: Refers to the amount of adsorbent / amount of adsorbate. ** Nd: parameter not determined in the study.
Source: www.revistas.ufcg.edu.br.

(Cui and Zhang, 2004). Heavy metals are stabilized *in situ* by amending the soil with organic additives; this is mostly done to decrease the mineralization of metals and reduce absorption by plants (Komárek et al*.,* 2013). Heavy metals can be stabilized in polluted soils by biochar. Biochar can lead to the improvement of polluted soil (Ippolito et al*.,* 2012) and can greatly reduce the adsorption of heavy metals by crops. Thus, biochar has the potential of providing a novel remedy for soils polluted with heavy metals. There could be possible a large number of mechanisms involved in stabilizing heavy metals in soils using biochar. Using Pb^{2+} for instance, the research suggested different mechanisms for Pb^{2+} sorption with sludge-derived biochar as follows:

1. Heavy metal exchange with Ca^{2+}, Mg^{2+}, and other cations connected to biochar, due to co-precipitation and inner sphere complexation with complexed humic matter and biochar mineral oxides.
2. Surface complexation of heavy metals with various functional groups, and inner sphere complexation with the free hydroxyl of mineral oxides and other surface precipitation.
3. Physical adsorption and surface precipitation contributing to make Pb^{2+} stable (Lu et al., 2012).

Soils polluted with acids due to kind of biochar and levels of cation could facilitate discharge of same through sorption thus enhancing soil stabilization. Lu et al. (2012) showed that major cations often present in the sludge-derived biochar aide heavy metal exchange. However, contribution of cations with a valency of one (such as Na^+ and K^+) contributed little for heavy metal exchange. Thus, it is possible that under field condition, biochar adsorption mechanism for metal polluted soils is based on the soil types and cations in both soils and biochar; therefore results for using biochar for remedying soils polluted with metals might differ.

MERITS OF APPLYING BIOCHAR TO REMEDY SOIL AND WATER

Cheap source and waste management

Biochars are normally produced from inexpensive and abundantly existing waste biomaterials. Precisely, biochar feedstocks are mainly manufactured from the biomasses and solid wastes of agricultural works. Agricultural remains are seen in large amounts and are often difficult to dispose. For example, producing biochar from invasive plant can solve disposal problems and waste management. Also, aquatic algae are normally many and can block waterways; thus, other uses like the synthesis of biochar can benefit local people.

Nutrient

Pyrolysis of feedstock, leads to concentration of elements such as P, K, Ca, and Mg in biochar. Soluble organic substances are also formed during the pyrolysis process. Currently, using chemical fertilizers to improve soil is costly and out of reach for small farmers. Some disadvantages of the widespread use of chemical fertilizers are the soil acidity increase, mineral imbalance, and soil degradation (Ayoola and Makinde, 2008; Onmonya and Umeobika, 2020). Research has also shown that soils and residues can be characterized by total deficiency or low levels of organic matter and macronutrients and usually have an acidic pH, although some soil residues can be alkaline (Krzaklewski and Pietrzykowski, 2002; Gbadebo and Ekwue, 2014). In addition, tailings should also be without a normal soil structure and support a highly stressed heterotrophic microbial community (Mendez et al., 2007; Southam and Beveridge, 1992). The addition of biochar can provide plants and microrganisms with bioavailable nutrients. However, the nature of the starting materials and the conditions of pyrolysis determines the quality of biochar produced. The levels of C and N differed significantly in biochar when made from chicken droppings, pine and groundnut shells at 400 against 500°C. In addition, pyrolysis at 500°C yielded higher level of P, K, Ca, and Mg in biochar than at 400°C. This was due to the higher pyrolysis temperature, which decreased the CEC but enhanced mineralization of the feedstocks. In this context the goal is to maintain high quality of biomass, as well as the biochar given the right conditions for the process. In general, the nutrient content of plant derived vegetable biochar is comparatively lower than that of manure (Woolf et al*.,* 2010). In line with this, Onmonya and Umeobika (2020) recommended that researchers do more research on processed cow dung to improve soil quality.

Soil stability

Erosion effects in Nigeria is huge, especially gully erosion in the south and southeast of the country. The high water flow with the undulating topography creates a high water flow. The lack of drainage channels to control fluid flow and soil structure has contributed to the severe effects of erosion in this area (Hillili et al., 2011). Moreso, wind erosion predominates in some parts of the northern states. In 1995 it was estimated that over 700 million kg of metals were dumped in land mine debris each year (Warhurst, 2000). The global impact of such tailings dumps is enormous, since unused tailings piles typically lie fallow for several decades and exposed tailings piles can spread over several tens of hectares due to aeolian dispersion and water erosion (González and González-Chavez, 2006). This has the potential to contaminate nearby communities and ecologically sensitive areas (Gbadebo and Ekwue, 2014). It is therefore imperative to research for alternatives such as biochar for promotion of stable soils (Trazzi et al., 2018). Biochar acts as an isolated particle, distinct from other stable organic matter that trapped in aggregates, soil pores or adsorbed on mineral surfaces. Biochar makes it easier for carbon to be sequestrated in the soil, because it is highly stable in its organic form. Sun et al. (2018) reported a half-live of 102 – 107 years for carbon in biochar and stated that biochar mineralizes very slowly. Woolf et al. (2010) also reported that fine particles of biochar have been in soils in climates with low heat levels, like Amazon.

Effect of biochar on heavy metal mobility

Biochar can reduce the movement of heavy metals in polluted soils, resulting in a low risk uptake by plants. Research has shown that bamboo-derived biochar can absorb Cu, Hg, Ni and Cr from soil and water and Cd in contaminated soils. Cao et al. (2009) reported that biochar derived from dairy manure at 200 °C pyrolyzes Pb more effectively than biochar produced at 350°C due to the higher concentration of soluble phosphate in the biochar at 200°C. A remediation process can utilize different biochar and mechanism for multi-element polluted soils.Therefore, when using biochar to improve soils polluted with heavy metals, the types of heavy metals in the polluted soil and the temperature used in the production of biochar must be considered because their properties depend on the pyrolysis conditions such as the water content of the feedstock, highest treatment temperature, type of starting material used and residence time. The influence of biochar on the bioavailability of metals varies depending on the type of biochar products and heavy metals. The ratio of Cd and Zn in pore water of contaminated soil was reduced when biochar from hardwood was applied (Beesley et al., 2010). Similarly, addition of biochar to contaminated soil reduced the concentrations of Cd and Zn in the pore water by 300 and 45-fold in a column leaching experiment (Beesley et al., 2011). Namgay et al. (2010) showed that the ratios of As and Zn that can be extracted in soil became high with the application of biochar; extractable Pb reduced; Cu was unchanged and Cd was not constant. They also described that there was sorption of trace elements on biochar with initial loadings up to 200 mol at pH 7 in the order: Pb > Cu > Cd > Zn > As. Biochar can decrease the leakage of metals via its effect of redox reactions of metals (Choppala et al., 2012). The significant reduction in the leaching of Cr(III) is due to the uptake of Cr(III) onto cation exchange sites and precipitation as $Cr(OH)_3$ resulting from the discharge of OH ions during the process of Cr(VI) reduction (Bolan et al*.,* 2013) as illustrated in Figure 1.

Biochar production and identification of the main biomasses used in this process

The two main techniques for converting biomass are: the use of enzymes and microorganisms (biochemical conversion) which is less expensive and environmentally friendly, although has a lower yield (Tripathi et al., 2016); and break down of biomass using heat (thermochemical conversion) (Kubilay et al., 2014). The thermochemical process includes conventional carbonization or pyrolysis, hydrothermal carbonization, incineration and gasification (Kubilay et al., 2014). The processes in this type of biochar production are mainly determined by the pyrolysis temperature, the residence time of the material in the reactor and the heating rate (Trazzi et al., 2018). Using biomass in combination with thermochemical synthesis has advantages in obtaining new carbonaceous

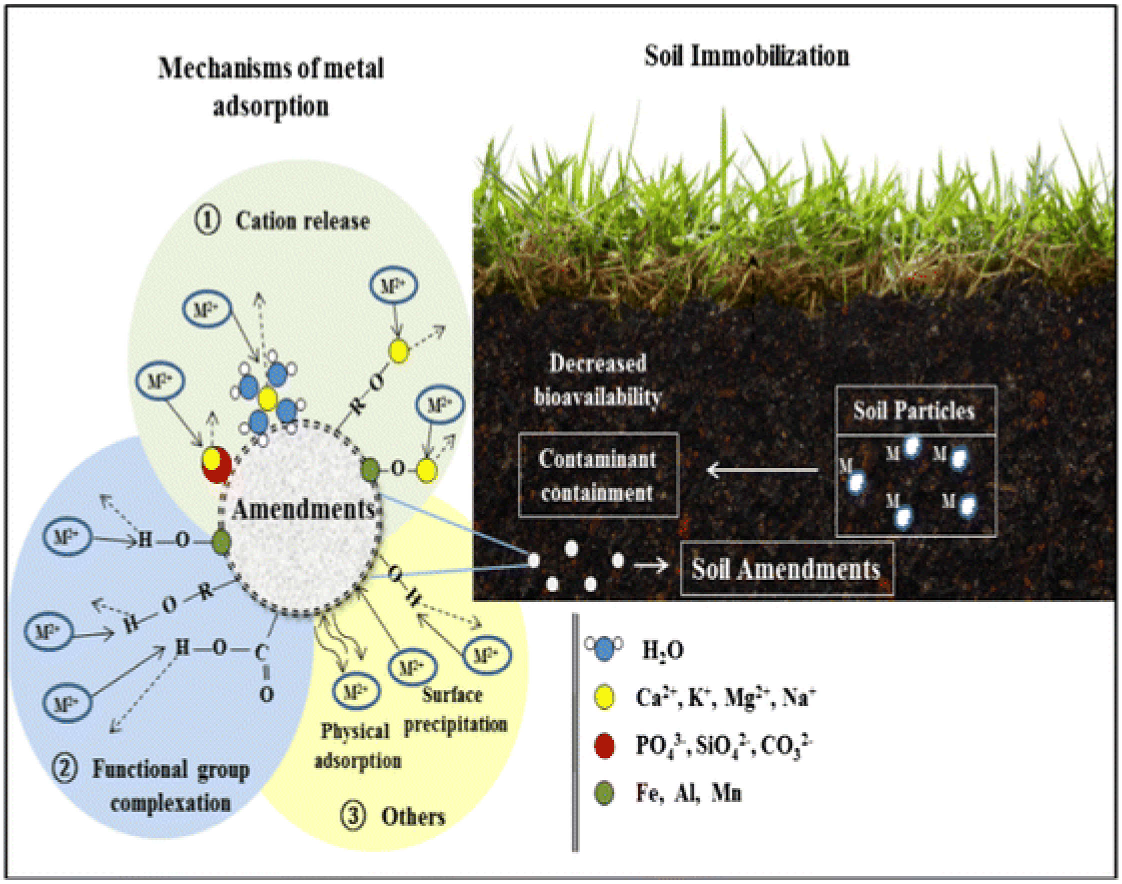

Figure 1. Mechanisms of metal Adsorption in Soil.

Table 2. Copper and lead removal in aqueous environment using various adsorbents chromium activator.

Adsorbent	Dosage*	Activator	Efficiency (%)	Adsorption capacity (mg g $^{-1}$)	Reference
Conventional	0.35 g/50 ml	Nd**	98	0.54	Souza et al. (2009)
Water hyacinth	7 g/L	Physical	92.24	36.34	Giri et al. (2012)
Acerola seeds	1 g/50 ml	Nd**	66	Nd**	Resende et al. (2014)
Sugarcane	10 mg/20 ml	HCl	99.97	5.26	Ferreira et al. (2015)
Yam peel	40 mg/200 ml	$C_6H_8O_7$	88.7	25.01	Tejada-Tovar et al. (2015)
African palm bagasse	40 mg/200 ml	$C_6H_8O_7$	58.8	41.57	Tejada-Tovar et al. (2015)
Walnut shells	Nd**	Physical	80.47	36.55	Altun and Kar (2016)
Rice residues	3 g/20 ml	H_3PO_4	72	6.67	Miguel (2017)
Sugarcane	0.5 mg/100 ml	H_2SO_4	29.13	0.2884	Ferreira (2018)
Corn cob	10 g/50 ml	H_3PO_4	93	25.69	Gupta et al. (2018)

•Dosage: refers to the amount of adsorbent / amount of adsorbate. ** Nd: parameter not determined in the study.
Source: online at www.revistas.ufcg.edu.br.

materials with different applications, low cost, high availability in nature and fast regeneration (Santos, 2016). For (Novotny et al., 2015) various organic materials are suitable as raw materials in thermal processing, from agricultural and wood biomass to all available agricultural and industrial waste (husks, straw, seeds, bagasse, nut shells, wood chips, etc.) and even municipal waste (Table 2). The biochar produced in the

Table 3. Copper and lead removal in aqueous environment using various adsorbents mercury activator.

Adsorbent	Dosage*	Activator	Efficiency (%)	Adsorption capacity (mg g $^{-1}$)	Reference
Conventional	0.3 g/50 ml	Nd**	99.9	4.77	Tan et al. (2016)
Apricot	10 mg/50 ml	HCl	99.6	153	Ekinci et al. (2002)
Soybean stem	0.01 g/35 ml	Physical	74.5	86.4	Kong et al. (2011)
Bamboo	0.6 g/L	H_2O	99.13	248.05	González and Pliego-Cuervo (2014)
Cocoa husk	0.05 mg/50 ml	$ZnCl_2$	99.8	10	Kede et al. (2015)
Wheat straw	5 g/50 ml	N_2	98.1	10.47	Tang et al. (2015)
Hops	0.8 g/200 ml	Physical	>95%	Nd**	Liu et al. (2016)
Corn cob	0.8 g/200 ml	Physical	>95%	Nd**	Liu et al. (2016)
Cotton seed	0.8 g/200 ml	Physical	>95%	Nd**	Liu et al. (2016)
Corn cob	0.3 g/50 ml	N_2	99.8	3.23	Tan et al. (2016)

•Dosage: refers to the amount of adsorbent / amount of adsorbate. ** Nd: parameter not determined in the study.

Table 4. Copper and lead removal in aqueous environment using various adsorbents lead activator.

Adsorbent	Dosage*	Activator	Efficiency (%)	Adsorption capacity (mg g $^{-1}$)	Reference
Commercial	1 g/100 ml	Nd**	98.69	4.32	Nogueira (2010)
Babassu coconut shell	0.1 g/200 ml	H_2O	98.87	30.3	Golin (2007)
Moringa seed husk	1 g/100 ml	H_2O	98.21	136.98	Nogueira (2010)
Moringa seed husk	1 g/100 ml	CO_2	99.14	15.22	Nogueira (2010)
Green coconut	17 g/1 L	NaOH	98.79	Nd**	Ferreira et al. (2012)
Sugarcane	1 g/20 ml	HNO_3	96	20.77	Figueredo et al. (2017)
Pine nut shell	90 mg/30 ml	N_2	98.5	73.99	Lage Junior (2016)
Cocoa husk	8 g/8 L	Physical	91.32	0.07	Lara et al. (2016)
Yam peel	40 mg/200 ml	$C_6H_8O_7$	98.04	98.36	Tejada-Tovar et al. (2016)
Cassava peel	40 mg/200 ml	$C_6H_8O_7$	95.57	52.34	Tejada-Tovar et al. (2016)
Orange peel	1 g/100 ml	$ZnCl_2$	96	Nd**	Ali and Abdel-Satar (2017)
Sugarcane	0.5 mg/100 ml	H_2SO_4	54.74	0.4486	Ferreira (2018)

*Dosage: refers to the amount of adsorbent / amount of adsorbate. ** Nd: parameter not determined in the study.

pyrolysis process is high in energy comparable to the coal used in industry, owing to its microporous structure and high carbon content. In agriculture, it is used to improve soil quality and increase carbon storage. It slows down nutrient degradation and consequently improves soil quality. In the adsorption industry it is used to remove heavy metals such as Cr, Cd, Ni, Hg, Pb and organic compounds (Tripathi et al., 2016). Accordingly, low-cost alternative sources for the production of biochar are being researched into. Sofar agricultural residues such as rice husk (Doria et al., 2016), orange peel (Tejada-Tovar et al., 2015), corn cobs (Lopes et al., 2013), sugar cane bagasse (Ferreira et al., 2015) (Table 3) orange peel (Tejada-Tovar et al., 2015) (Table) 4 and the coir-chitosan composite (Costa et al., 2017) have shown great potentials for adsorption of pollutants.

HOW BIOCHAR AFFECT HEAVY METAL BIOAVAILABILITY

Heavy metals are generally found in small amounts in agricultural soils. However, due to their cumulative behavior and toxicity, they not only have a potentially harmful effect on crops but also on human health (Ekwue et al., 2012; Das et al., 1997). Heavy metal contamination of soil, water and crops and its health impact on local residents is an ongoing social problem, and several studies have identified health risks for local residents living near abandoned mines (Chung et al., 2005). Man-made pollutants can threaten human health and harm the natural ecosystem and environment (Hilli et al., 2021). The bioavailability of heavy metals determines toxicity in soil and potential risk upon entry into the environment. Fellet et al. (2011) reported that increased application of biochar resulted in increased pH, cation exchange capacity, and water-holding capacity and decreased bioavailability of some metals in mine tailings. In a study Zhou et al. (2008), used biochar derived from cotton stalks to improve Cd-contaminated soil, the biochar decreased the bioavailability of Cd in the soil. Mendez et al. (2012) also reported that biochar treatments reduced the plant availability of Ni, Zn, Cd and Pb compared to sewage sludge treatments in a Mediterranean agricultural soil. A reduced Cd, Cu and Pb uptake by Indian mustard was reported by Park et al. (2011) when they applied chicken manure and green waste derived biochar. The study also recorded reduced metal concentrations in plant except for Cu, with increased biochar application. Furthermore, biochar is highly effective in adsorption of many natural and anthropogenic sourced organic compounds (Sarmah et al., 2010). Owing to its highly aromatic nature, large surface area, micropore volume and abundant polar functional groups, biochar is effective in absorbing a wide range of organic chemicals including pesticides, PAHs and new emerging contaminants such as steroid hormones (Kookana et al., 2011). The level of aromaticity, type of biochar and organic carbon play a major role for effective removal of contaminants (irrespective of the other properties of the biochar) (Sarmah et al., 2010).

CONCLUSION

Bioremediation supplemented with biochar is one of the most important remediation technologies for the remediation of soil and water bodies contaminated with heavy metals. Biochar-enhanced remediation has great potential for immobilizing cationic heavy metals in mining tailings, tailings piles and water bodies, especially those with high acidity. Biochar can reduce the bioavailability and leachability of cationic heavy metals in soil and water, improve soil fertility and greening, and create a suitable environment for soil microbial diversity. To reduce the bioavailability of the organic pollutants and the risk of the pollutants entering the human food chain or leaching into groundwater, biochar could be of immense benefit. However, the long-term environmental fate of the deposited pollutants is still unknown and further research is warranted to fill this gap, especially under realistic field conditions through biochar-mediated remediation trials. Furthermore, it is important to select appropriate biochar to develop an effective strategy to immobilize anionic metals in situ. Future research should focus on: biochar stability and its impact on the fate and transport of metals in mining tailings and large-scale soils and waters; and understand the mechanisms of biochar-assisted bioremediation.

CONFLICT OF INTEREST

The authors have not declared any conflict of interest.

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