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## Heavy Metal Remediation from Contaminated Soil Using Biochars and Modified Biochars: A Review

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### ABSTRACT

From the beginning of the industrial revolution, metal refining industries using the pyrometallurgical process are generating remarkable emissions of heavy metals. As the main objective of these pollutants, a great number of soils are now contaminated over extensive areas depending on exposure level, and duration, and pose a major risk to human health worldwide. Biochar, a co-product of the pyrolysis process, can be used to nourish soil health, and remediate heavy metals. They are nowadays modified to enhance the sorption capacity of biochar and immobilization of heavy metals. Immobilization, as an in-situ application method, is a cost-effective method for environmental remediation of heavy metals in the soils. The research statistics on biochar and modified biochar influences on heavy metal remediation from the soil are scarce. Therefore, the purposes of this review are (1) to combine modification processes of biochar (2) to offer possible mechanisms associated with the reduction of heavy metals (iii) to combine the available data on the positive effects of biochars and modified biochars on heavy metal remediation(iv) identify researchable priorities.

### INTRODUCTION

Recently, more and more soils are contaminated with organic and inorganic substances worldwide due to emissions of waste from industrial production, wastewater irrigation, byproduct application, mining activities, and improper management of pesticides and fertilizers in the agronomic system. Among inorganic pollutants, heavy metals (Cr, Cd, Hg, Pb, As, Ni, Cu, Mo, etc.) are the most alarming for our environment. Plants in polluted soils uptake heavy metals and transfer them to living beings by bioaccumulation. There are several processes throughout the world to remediate heavy metals from soils application of biochars is one of them.

Biochars' application to soil is an age-old practice. The idea of biochar for soil amendment originated in the soils, particularly in the Amazonian Basin. International Biochar Initiative said, "Biochar is a 2,000-year-old practice that converts agricultural waste into a soil enhancer that can hold carbon, increase food security and discourage deforestation." Because biochar is a basic

material, it can raise soil pH and help stabilize heavy metals. It is a fine-grained, stable, high C form of charcoal and can be used on agricultural land for agronomic or environmental management. It is produced by the process of pyrolysis. In addition to improving soil health, carbon sequestration, and plant growth, biochar may also be used to alleviate climate change, manage the environment, reduce greenhouse gases, and adsorb heavy metals. Normally, heavy metals have persistence of biodegradability. But they can be stabilized in the soil by using biochar because it has a high surface area, CEC, and capacity to absorb and retain heavy metals. Unmodified biochars can have a lower adsorbing ability to highly concentrated contaminants (Ma et al., 2014).

Biochar capacity can be enhanced by treating them with several treatments like physical treatment, chemical treatment, impregnation with mineral oxides, and magnetic treatment. These treatments increase the surface area of raw biochars and enrich surface functional groups. All these modified biochars have better properties for

supporting soil health, a more widespread impact on heavy metal remediation, and other environmental benefits. Metal sorption capacities of biochar are 2.4-147, 19.2-33.4, 0.3-39.1, 3.0-123 mg g<sup>-1</sup> for Pb, Ni, Cd, and Cr, respectively (Inyanga et al., 2016). However, they are lower than that of modified biochar, which are 255 and 91.4 mg g<sup>-1</sup> for Pb and Cd (Wilson et al., 2006).

The objective of this study is to compare the properties and effectiveness of biochar and modified biochar in the field of heavy metal remediation from the soil. This research will shed some light on the importance and effectiveness of modified biochar along with biochar and will create a greater opportunity to do future research work on it. The aims of this review study are (1) the beneficial impact of biochar and modified biochar on the environment and properties of soil; (2) the efficiency of biochar and modified biochar to remediate heavy metals; (3) the benefits of in-situ remediation of contaminated soils using both biochar and modified biochar.

## **MATERIALS AND METHODS**

This research has been prepared using secondary data from research articles, journals, books, and web-based information. Available methods that have been investigated in previous literature for biochar production were pyrolysis of biomass under different conditions (like temperature, time range, etc.) (Lehmann, 2007a) (Verheijen et al., 2010) (Table 1) and modified biochar production were several processes (i.e., chemical modifications, physical modifications, impregnation with mineral sorbents, and magnetic modifications) (Rajapaksha et al., 2016).

## **RESULTS AND DISCUSSION**

### **Biochar Characterization**

The diversity of the feedstock and some chemical reactions at some stage in processing, give rise to a distinctive set of characteristics of biochar. Lehmann and Joseph (2009) confirmed that

functioning parameters, along with the rate of heating, reaction residence time, pressure, highest treatment temperature (HTT), pretreatment, reaction vessel (orientation, dimensions, stirring regime, catalysts, etc.), the flow rate of supplementary inputs, all influences the physicochemical properties of resultant biochar of any feedstocks. For example, a greater total C, lower potential CEC, lower ash content, and exchangeable cations, a lower amount of total N, S, P, K, Ca, Al, Mg, Cu, and Na content in wood-derived biochar within the manure biochars, while leaf biochars contain intermediate values. The temperature of pyrolysis likewise the main process parameter, the C content of biochar correlated to biochar production inversely, increasing from 56% to 93% between 300 and 800°C in analysis, while biochar yield reduced from 67% to 26% (Okimori et al., 2003). Biochar possesses high porosity, and crystalline structure and is exceptionally recalcitrant to decomposition, a very high surface area. It makes nutrients bioavailable and serves space for water storage, and micropores as a habitat for soil microorganisms.

Modified biochars are produced whilst unmodified ones are additionally activated for improving biochar surface area, functionality, and pore structure (Kwiatkowski, 2008). Unmodified ones can have a restricted capacity to selectively adsorb pollutants of excessive concentrations. Several methods, including functionalization, and surface oxidation have been applied for the betterment of their ability in environmental remediation (Xue et al., 2012).

For further improvement of biochar properties, there are several processes, they are further divided into 4 main types, chemical modification, physical modification, impregnation of biochar with mineral sorbents, and magnetic modification. Different modification processes bring changes in properties of unmodified biochars, changes in biochar properties are tabulated in the following table:

Table 1. Comparison of different modified biochars characteristics to unmodified biochars.

Treatments	Feedstocks	Modified/ unmodified	pH	C	Surface area	Pore Volume	References
KOH modification	Rice Husk	Unmodified	7.0	42.1	34.4	0.0028	Liu et al. (2012)
		Modified	7.0	76.4	117.8	0.073	
Steam activated biochar	Tea waste	Unmodified	7.9	70.1	2.3	0.006	Rajapaksha et al. (2014b)
		Modified	8.6	71.5	1.5	0.004	
MnO <sub>x</sub> -loaded biochar	Corn straw	Unmodified	–	85.3	61.0	0.036	Song et al. (2014)
		Modified	–	73.0	3.2	0.006	
Magnetic biochar	Orange peel	Unmodified	–	67.0	501.0	0.390	Chen et al. (2011)

**Effects of Biochar on the Environment**

There are multidisciplinary benefits of biochar on various aspects of the environment. Positive qualities of biochar depend on the properties of feedstocks and regional circumstances, including humidity, temperature, soil condition, and soil type (Zech et al., 1990). Biochar application has positive impacts on all elements of the environment (including soil, plant, microbes, climate, etc.).

**Effects on Soil Health**

Biochar amended soil shows the subsequent impacts:

1. Shows better soil structure or aggregation, aeration, and greater aggregate stability.
2. Shows a higher surface area.
3. Decreases soil bulk density.
4. Increases the soil pH (Biederman and Harpole, 2012).
5. Increases soil cation exchange capacity.
6. Acts as a direct nutrient source by impacting nutrient availability.
7. Reduces nutrient loss below the root zone.
8. Increases the bioavailability of nutrients to plants over time.

**Effects on Plant Growth**

Biochar alters the physiochemical properties of the soil which in the long run affects plant growth. Biochar increases nutrient availability to the plant. It ensures better water supply to plants by improving soil moisture-holding capacity. The effects on plant growth significantly vary with:

1. Plant species
2. Soil type
3. Dose of Biochar
4. Types of Biochar

The effect of biochar on plant growth was proved by many scientists through some experiments. Jeffery et al. (2011) observed regular a

crop productivity increase of around 10 % as an impact of biochar amendment.

**Effects on Microbes**

When added to soil, biochar has significantly increased microbial efficiency, and basal respiration as a measure of units of CO<sub>2</sub> released per microbial biomass carbon. And biochar when added with organic fertilizer amendments has led to a further increase in microbial biomass, population growth, CO<sub>2</sub> release per unit of microbial carbon, and decided that biochar can act as an important soil element, specifically in fertilized agriculture systems (Verheijen et al., 2010, Lehmann et al., 2011). A schematic relationship is represented below:

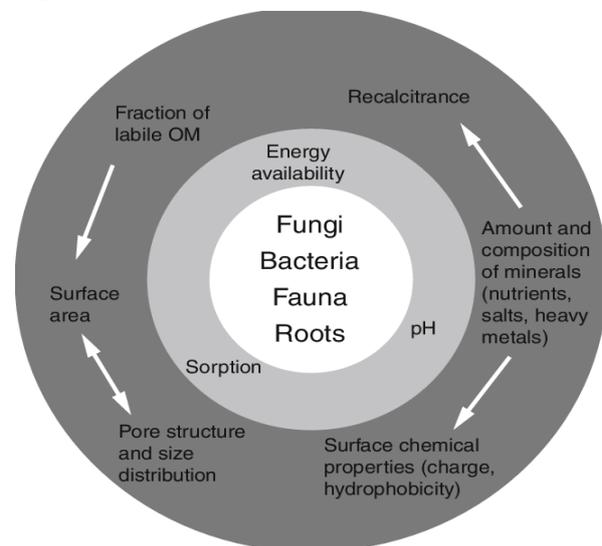


Figure 1. A schematic assessment of the connection between primary biochar properties (outer circle), the soil properties they may influence (intermediate circle), and the soil biota (the inner circle). White arrows indicate the influence of biochar properties (Lehmann et al., 2011).

### Effects on Climate Change Mitigation

Biochar, a fairly steady carbon (C) source can remain in the soil for hundreds or thousands of years, and function as an ideal C sink (Lehmann & Joseph, 2009). Biochar application, as a scheme to restore atmospheric C in soil ecosystems, has drawn considerable attention. It is being promoted that it has the potential to lessen soil GHG emissions when added to the soil. Biochar application reduces different GHG emissions like CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O significantly and separately. Among the most potent greenhouse gases, N<sub>2</sub>O possesses GWP 298 times higher than CO<sub>2</sub> and rests undyingly in the air. It has been also reported as the most significant O<sub>3</sub> reducing gas throughout the 21<sup>st</sup> century (Ravishankara et al., 2009).

Biochar can reduce N<sub>2</sub>O emissions and offset N<sub>2</sub>O. Yanai et al. (2007) applied around 150 t /ha biochar to a Typic Haplud and soil in a laboratory-based experiment. The maximum emission of N<sub>2</sub>O-N was reduced by up to 85% in biochar-added soil after watering the soil again to 73% WFPS, paralleled to the original soil. Plants capture atmospheric CO<sub>2</sub> through photosynthesis. The plant

residues can remain in the soil for up to several years of the soil aggregates size (Jha et al., 2012). Biochar amendments usually reduce CO<sub>2</sub> production by improvement of C stabilization. Sequestration of C in soils with biochar amendment, counter-balances the CO<sub>2</sub> reduced from soils through decomposition of plant remains and OM, and is considered as an offset for GHG formed by fossil fuel consumption and further origins.

### Possible routes and cycles of heavy metals in soil

Heavy metals are metals with relatively high atomic weights, densities, or numbers e.g. cadmium (Cd), chromium (Cr), uranium (U), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), nickel (Ni), zinc (Zn), cobalt (Co), etc. characterized by alike atomic electron structures in the external orbitals (Kibria et al. 2010). They are categorized as harmful (i.e. persistent, toxic, bio-accumulative), and carcinogenic (Kibria et al., 2016a) chemicals. Pathways and sources of these materials in soil are mostly industrial and agricultural. Circulation and possible routes of heavy metals are shown in figure 2.

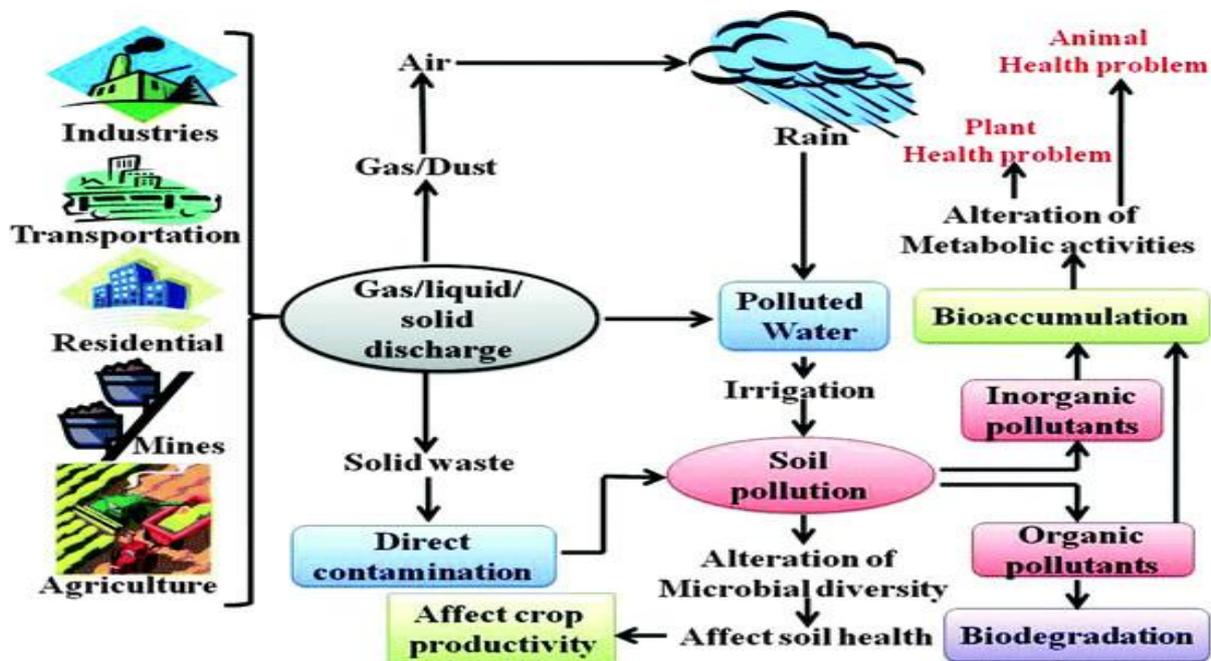


Figure 2: Routes and cycles of heavy metals in soil (Oves et al., 2012)

### Maximum Permissible Limits of Heavy Metals in Soil

Various soil characteristics, soil composition, and many other factors affect the mobility, distribution, and accessibility of heavy metals in

soil. They are present in almost all soils as a result of their parent materials weathering. Each metal has an allowable concentration in the soil which is called the maximum allowable concentration. Beyond these levels, the soil will be considered

contaminated. The maximum allowable concentration of various heavy metals in soil is bellowed.

Table 2. Heavy metals maximum allowable concentration in soil (Chiroma et al., 2014).

Elements	Maximum permissible limit (µg/g)
As	20
Cd	3
Cr	100
Co	50
Cu	100
Mn	2000
Pb	100
Se	10
Ni	50
Zn	300

**Effects of Heavy Metals**

Heavy metal contamination results in various adverse environmental impacts on soil and living organisms.

**Effects on Soil**

Heavy metal contamination of soil is one of the most significant apprehensions in the developed world (Kibria et al., 2012). They not only adversely impact soil physicochemical properties but also alternate the size of microbial community, activity, and composition (Lehmann et al, 2011). That’s why they are considered one of the major soil pollutants. Different metals particularly Cu, Ni, Cd, Zn, Cr, Pb, etc. pollute the soil (Kibria et al., 2012).

1. They affect soil's biological and biochemical properties adversely. Soil properties like organic matter, pH, and clay contents have the main impacts on the level of influences on genetic and biochemical properties.
2. Heavy metal pollution adversely affects on various plant parameters like quality and yield.
3. Heavy metals shift the microbial community and indirectly affect soil enzymatic activities.
4. Heavy metals decline the quantity and activity of soil microbes.

**Effects on living beings**

Heavy metals from contaminated soil pass in the food chain by plant uptake, bioaccumulation and result in bio-magnification which has several

adverse impacts on plants, microbes, and human health, which are:

1. Plant growth reduction due to changes in physiological and biochemical activities.
2. Oxidative stress, cellular damage, and disruption of cellular ion homeostasis in plants.
3. Decreases plant biomass including roots, shoots, and fruits.
4. Wilting of plants.
5. Causes plant leaf necrosis.
6. Reduces germination percentage and bud sprouting.
7. Degradation of photosynthetic pigments.
8. Yields reduction.
9. The reduction of growth rate and increase in lag time reflect a severe reduction of microbial activity (Web 1).
10. Microbes also suffer from transcription inhibition, enzyme activity reduction, and cell membrane disruption.
11. Effects of heavy metals on the human immune system eventually lead to death. In addition to their health impacts, heavy metal toxicity also creates social problems like social instability, superstition, marriage-related problems, an increase in poverty, etc. Consequences of heavy metal contamination on humans are shown in the following figure 3.

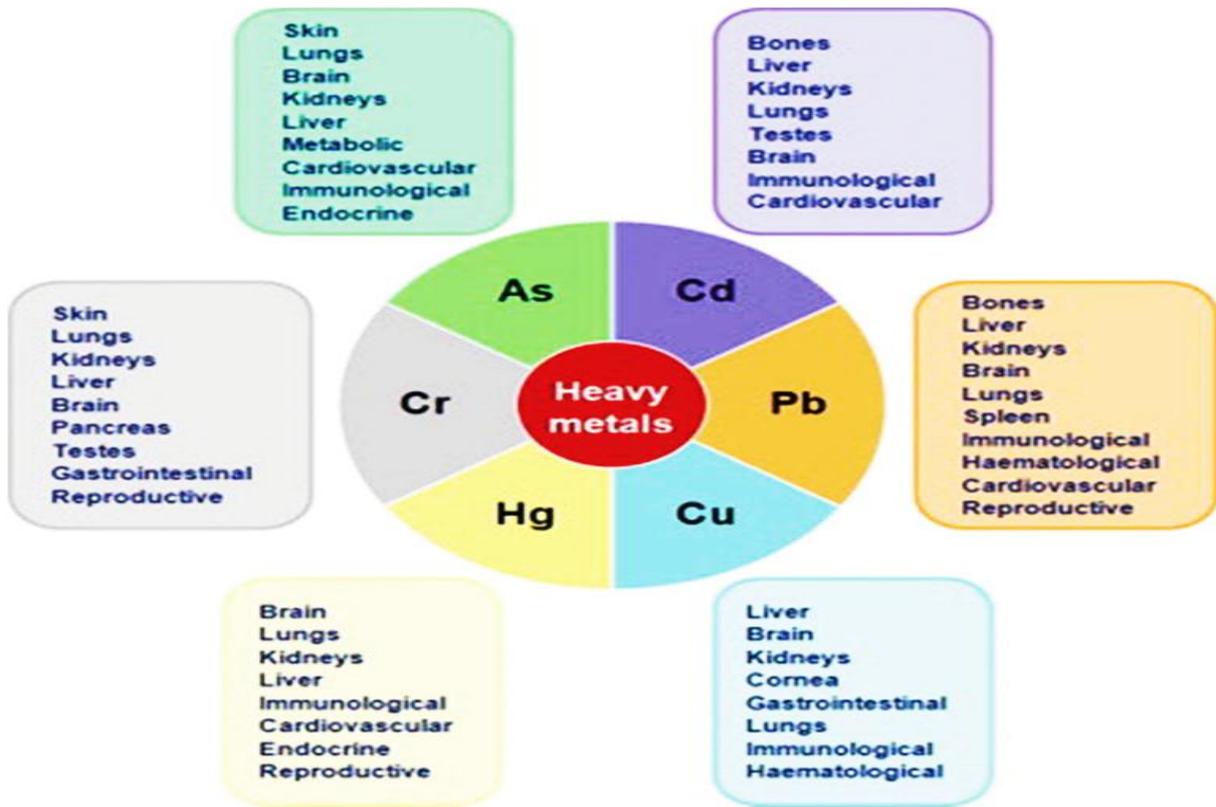


Figure 3: Influences of heavy metals on human being (Masindi&Muedi, 2018)

**Heavy Metal Remediation Mechanisms of Biochar**

Heavy metals remain in polluted soils' elongated periods because they are not decomposable. Elimination of heavy metals from contaminated soils is costly and lengthy (Cui and Zhang, 2004). Biochar can stabilize heavy metals, and develop contaminated soil quality. Biochar application effectively reduces the uptake of heavy metals by crops. So, the application of biochar can possibly be a remedy for heavy metal contaminated

soils. Biochar can include several potential processes as demonstrated in figure 4.

1. Heavy metals can be exchanged and co-precipitated with  $Ca^{2+}$ ,  $Mg^{2+}$ , and other cations on biochar surfaces.
2. The surface and inner-sphere complexation of them with different functional groups, free hydroxyl of mineral oxides
3. The stabilization of heavy metals by physical adsorption.

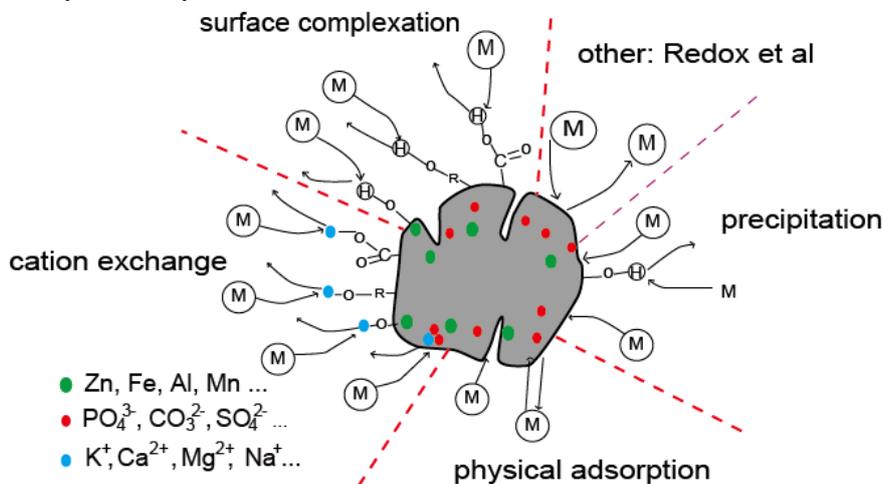


Figure 4. Heavy metals remediation processes by biochar (Wang et al., 2018)

**Heavy Metal Remediation Efficiency of Biochar**

Biochar can affect heavy metal movement and lead to their elimination from contaminated soil, which is illustrated in the table below.

Table 3. Heavy metal remediation efficiency of biochar.

Feedstock	Production temperature (°C)	Pollutant	Effects	References
Bamboo	Not available	Cadmium	The combined effect of electrokinetics, removed extractable Cd by 79.6 % within 12 days	Ma et al. (2007)
Hardwood	450	As, Cd, Cu, Zn	Reduction of Cd in soil pore water by 10-folds; 300- and 45-folds Zn concentrations reduction, respectively, in column leaching tests	Beesley et al. (2010); Beesley&Marmiroli, (2011)
Hardwood	450	As, Cd, Cu, Pb, Zn	Biochar surface mulch enhanced As and Cu mobility in soil profile; little effect on Pb and Cd	Beesley& Dickinson, (2011)
Wood	200 and 400	Cd, Zn	Reduction in Cd and Zn leaching loss up to >90%	Debela et al. (2012)

Biochar possesses the ability to ameliorate contaminated soils and can be developed as a viable technology. However, as an essential tool for contaminated cultivated soil remediation, many features still need to be established. Biochar sometimes may have some limitations in its ability to remediate highly contaminated soil. At present, the term modified biochar is becoming more popular than biochar in the case of nourishing contaminated soil.

**Heavy Metal Remediation Efficiency of Modified Biochar**

Different treatment processes can enhance biochar activities in terms of heavy metal remediation. Modified biochars have enhanced sorption capacity and enriched surface functional groups. Remediation of heavy metals with modified biochars application can involve several possible mechanisms as:

1. Acid and alkali treatment, coating and hydrogen peroxide treatment and digestion treatment increases heavy metal removal by:
  - a. Surface area extension, precipitation, and deposition
  - b. Complexation and  $\pi$ - $\pi$  interaction
  - c. Ion exchange
  - d. Pore volume extension

- e. Surface functional group activation like carboxyl, carbonyl groups, electrostatic interaction, etc.
2. Magnetic modification improves heavy metal remediation by:
  - a. Improving surface area
  - b. Chemical co-precipitation
  - c. Electrostatic interactions
  - d. Increasing cation exchange capacity
3. Steam/gas activation, ball mining, microwave modification processes remediate high heavy metal content by
  - a. Extension of biochar pore volume
  - b. Increasing surface area
  - c. Increasing O-containing surface functional group.

**Effectiveness of Modified Biochar Remediating Heavy Metal**

Biochar possesses the ability of heavy metal removal to a certain level. But in the case of modified biochar, the removal of heavy metals is at the highest level. Modified biochar possesses several times higher remediation efficacy than unmodified raw biochars. Modified biochar application for contaminant removal is still laboratory-based. We should apply it on a field basis for a broader outcome. Reduction of heavy metals by modified biochars in comparison with unmodified is given in the following table 4.

Table 4. Modified biochars contaminant removal efficiency compared to unmodified biochars.

Modification method	Biochar feedstock	Target sorbate	Enhancement	Reference
KOH modification	Municipal solid waste	As <sup>5+</sup>	>1.3 times adsorption than unmodified biochars	Jin et al. (2014)
Steam activation	Chicken litter, alfalfa stems, switch grass	Cu <sup>2+</sup>	–	Lima et al. (2010)
MnO <sub>x</sub> loaded biochar	Corn straw	Cu <sup>2+</sup>	Higher sorption capacity; maximum sorption capacity about 160 mgg <sup>-1</sup>	Song et al. (2014)
Magnetic biochars	Rice Hull	Pb <sup>2+</sup>	Significantly improved sorption capacity	Yan et al. (2015b)

Application of modified biochar may not be economically feasible but in the case of national-level production and application at a broader mandate will bring a better solution to control soil pollution with heavy metals.

### CONCLUSION

Biochar has the potential to ameliorate soils contaminated with various contaminants both inorganic and organic. Biochar application to soils can cause an increase in contaminant residues. It can have a strong implication as an environmental sorbent. Biochar from different sources and with diverse pyrolysis conditions demonstrates extremely diverse properties both physical and chemical, which may affect the capacity of heavy metal remediation. It can increase toxic metal mobility in soils. Therefore, the analysis of the biochar effectiveness on contaminant stabilization in multi-element polluted soils should be inspected. The fact that biochars stabilize pollutants in themselves is indicated by the strong adsorption and weak desorption of pollutants. However, with the aging process biochar's capacity to adsorb or sequester pollutants decreases. That's the reason for developing the term modified biochar.

Biochar modification is about to end in variations in its several surface properties, comprising surface area, surface charge, pore volume distribution, and functional groups. This technique results in a far better sorption capacity in contrast to raw unmodified biochar. Applying biochar and modified biochar for remediating contaminated soil will additionally become a way of carbon sequestration and climate change mitigation. Long-term trials on biochar and modified biochar

application to contaminated field soils are needed. As a potential technology for contaminants reduction from the soil, many aspects are still yet to be developed.

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