Journal of Medicinal Plants Studies
www.PlantsJournal.com

ISSN (E): 2320-3862
ISSN (P): 2394-0530
www.plantsjournal.com
JMPS 2024; 12(6): 11-18

Received: 13-09-2024
Accepted: 10-10-2024

Sajid M Mansoori
Shri Vile Parle Kelavni Mandal's, Mithibai College of Arts, Chauhan Institute of Science & Amrutben Jivanlal College of Commerce and Economics (Autonomous), Ville-Parle (West), Mumbai, Maharashtra, India

Shruti Tank
Shri Vile Parle Kelavni Mandal's, Mithibai College of Arts, Chauhan Institute of Science & Amrutben Jivanlal College of Commerce and Economics (Autonomous), Ville-Parle (West), Mumbai, Maharashtra, India

Corresponding Author:
Sajid M Mansoori
Shri Vile Parle Kelavni Mandal's, Mithibai College of Arts, Chauhan Institute of Science & Amrutben Jivanlal College of Commerce and Economics (Autonomous), Ville-Parle (West), Mumbai, Maharashtra, India

A review on recent advances in biochar and its applications

Sajid M Mansoori and Shruti Tank

Abstract
In the last few decades, there has been enormous research carried out on biochar for the removal of contaminants from wastewater or soil. e.g., organic and inorganic contaminants, metals." BIOCHAR" is defined by its physical and chemical properties. This review aims to highlight the applications of biochar's in wastewater and soil, including a quick view of the mechanism of sorption of the metals and modified biochar. Depending on the types of biochar metals are removed via various mechanisms like exchange of ions, complexation, physical sorption, precipitation, and electrostatic interactions. It also provides information about the potential of biochar in the remediation of soil and also summarizes the removal of dyes from the wastewater by recent advances such as adsorption and catalysis. Overall, further studies are required to reuse biochar.

Keywords: Biochar, sorption mechanisms, wastewater treatment, modification methods, remediation of soil

1. Introduction
Biochar is a substance that is derived from biomass i.e. pyrolysis it involves partial or lack of oxygen. These will change organic substances into valuable biochar and therefore the resultant application attracts the eye to biochar to remove contaminants from wastewater and improve soil quality (Sohi *et al*. 2012) [1]. Many processes have been demonstrated such as Torre faction, carbonization, and chemical processes for these by-products could be Biochar. Biochar surface has some chemical properties like porosity, surface area, behavior like acid and base, functional group, etc., achieved by the heating process, depending on temperatures (Ahmad *et al*, 2014) [2]. It's been shown that because of dehydration and deoxygenation biochar possess some functional group i.e. H and O at high temperature 600-700ºC but it showed aromatic nature and low ion exchange capabilities.(Uchimiya *et al*., 2011; Ahmad *et al*. 2014) [48, 2]. Opposite side, at low temperature 300-400ºC it showed various organic characters (Cao *et al*., 2009) [36]. To remove via sorption contaminants such as organic, inorganic and heavy metal biochar has some potency and quality. Water system needs to be contaminants free because it is worldwide accessible and as the population increases water demands also increase. (Sica *et al*. 2014) [18]. Almost all industrial effluent is discharged in water with no treatment resulting in decrease in water quality. Moreover, it will be harmful to any living being (Sohi,2012) [1]. Industries use an enormous quantity of artificial dyes because of its inexpensive, and therefore the easy chemicals to supply artificial dyes in a very sizable amount of colors that are accessible (Mahmood *et al*. 2016) [28]. To handle the imperative scenario of inadequacy of water and pollution, different attempts are abode to the result of enormously suitable substance.

1.1 Application of Biochar for wastewater treatment
A. Inorganic contaminants
Generally, these inorganic materials are not degradable and very harmful to living things at higher temperature that's why they are not suitable for the atmosphere. heavy metals are foremost virulent and toxic. (Uchimiya *et al*., 2011) [48]. but alternative inorganic pollutants like H_2S, NH_3, NH_4^+, NO_3^- are seen in wastewater. Biochar sometimes has enticing attributes for remedy of inorganic pollutants. mechanisms for heavy metal removal are discussed in this paper. Removal of NH_4^+ inorganic waste material was primarily achieved via exchange of ions, O_2 containing surface area at low pH and precipitation (Sica *et al*. 2014) [18].

B. Organic pollutant

There are important analysis efforts to look at the appliance to removal of organic contaminants from wastewater. Several organic contaminants that include pharmaceutical substance, dyes, organic compounds that is volatile in nature (Cao *et al*., 2009 [36]; Xu *et al*, 2011 [31]) some of them are mentioned further in this review.

Mechanism works for only those contaminants that will interact with biochar. For these contaminants chemisorption and physisorption are widely used. Other mechanism that can be use through microorganism that are present on surface of biochar or within that also called as biodegradation mechanism.(Cao *et al*. 2009) [36].

C. Miscellaneous pollutants

Biochar is additionally important to remove virulent material from effluent of assorted industrial processes. Miscellaneous pollutants include substances that are generated after treatment and various materials come from industrial areas.

D. Antibiotics

Materials in pharmaceutical effluent areas are tough to degrade within the atmosphere and thought to be rising surroundings pollutants (Carvalho & city,2016) [7]. Removal of pharmaceutical substances by biochar has become a hot pot. There are two most harmful antibiotics that transfer hazardous substances in water i.e. Tetracycline and sulfonamides (Yu *et al*., 2016) [61]. $ZnCl_2/FeCl_3$ doped wood biochar used to remove TCs by solutions consistently. This experiment showed that this type of biochar is used to remove TCs from wastewater (Zhou *et al*., 2017) [77]. Sorption mechanisms of SAs on biochar. SAs can be removed by micropores filling mechanism. Other antibiotics can be removed via coating of acid on magnetic biochars. The most sorption observed for ENR, NOR, and CIP. High FQs removal potency may well be because of hydrophobic electricity. Zhao *et al*. (2019) [76].

E. Microorganisms

Removal of microorganism primarily targets the treatment of urban storm water and then surface water. Removal of microorganism via biochar filters has gained a lot of attention. These filters are inexpensive for waste materials. To remove organism from water, the particle size of biochar matters the most. Biochar with additional pore size increase results and save time between organism and active site. Biochar sand filters are used to remove *E. coli*. (Kaetzl *et al*. 2019) [62].

F. Removal of organic contaminants from wastewater

Organic contaminants are removed by the heterogeneous surface of biochar via different mechanisms. None carbonized parts showed different activity. (Cao *et al*. 2009; Zheng *et al*. 2010) [36, 4]. Almond shells biochar at 650°C in Lyndberg chamber prolifically adsorbate dibromochloropropane (fumigant), and the best-earned surface assimilation capability (Klasson *et al*. 2013) [5]. Orange rind biochar at a higher temperature for surface assimilation of naphthalene and hydrocarbon. Partition and expense organized the surface assimilation of hydrocarbons, whereas surface assimilation of naphthalene. Organized via surface interaction (Chen 2009) [6]. Soybean plant biochar and peanut shell biochar at higher temperatures to remove trichloroethane (Chen 2009) [6]. Removal of phenol biochar gives a lovely choice (Zhang *et al*. (2018a) [78] according to sludge-derived biochar might take away phenol through ozonation. Different biochar was pyrolyzed at different temperatures. Rice husk and corn cobs biochar showed surface assimilation capability for phenol than other biochars (Liu *et al*. 2011) [51]. Wheat straw biochar showed adsorption of BPA, phenanthrene, and EE2. Biochar and organic contaminants are attached via functional groups present on biochar that will form surface assimilation of organic contaminants like BPA and EE2. Another way to remove BPA was biochar-derived sludge matter used as a substance to activate persulfate for change in reaction. For removal of phenanthrene through $\pi - \pi$ interaction mechanism for surface assimilation (Sun *et al*. 2011) [49]. Another mechanism used for surface assimilation is electrostatic interaction. Positively charged biochar attracts negatively charged organic substances or vice versa (Qiu *et al*. 2009; Xu *et al*. 2011) [32, 31], To form surface assimilation anionic organic substance attached to H bonding of biochar. Harwood biochar experimented for surface assimilation of sulfonamide. It's been reported that O, N, and S containing biochar showed more chemical degradation (Colmenares *et al*. 2016) [13].

G. Removal of inorganic contaminants

Water eutrophication may be an essential environmental drawback throughout the globe these days. For eutrophication of water, some inorganic compounds are liable, among them nitrogen and phosphate are the most common ones. The discharge of large domestic waste matter is affecting marine life. Nitrogen and phosphate discharge also affect the agricultural environment. Water ecosystem degrades due to water eutrophication and it gives rise to a variety of living things losses, protoctist bloom, large fish deaths, and economic losses (Smith 2003) [15]. Ammonia (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}) contain nitrogen and phosphorus inorganic nutrients. Many technologies and processes are managed to remove nitrogen and phosphate from waste effluent (Zhang *et al*. 2011) [16]. Nitrification processes to remove Nitrogen result in high value and high initial investment. Generally, this biological process microbic sensitivity is high towards the concentration of nitrogen (Sica *et al*. 2014) [18]. In contrast to NH_4^+, NO_3^- and PO_4^{3-} are oxyanions with contrastive behavior to every alternative. Each is negatively charged and so interested in positively charged surfaces, however, NO_3^- is way more mobile than PO_4^{3-}, which promptly binds to colloids in water. Biochar possesses physicochemical characteristics that came from sources, biomass, pretreatments, pyrolysis of biochar. Using this biochar is used as an adsorbent (Demirbas and Arin 2010) [19].

H. Removal of nitrogen and phosphate by biochar as an adsorbent

As mentioned above physiochemical characteristics suffered from varieties of sources, biomass, pretreatments, and pyrolysis. All these characteristics increase the capability to remove nitrogen and phosphate. Using this biochar is used as an adsorbent. (Demirbas and Arin 2010) [19]. Between pollutants and functional groups, some mechanism occurs that include ion exchange and adsorption. (Harvey *et al*. 2011) [21] Furthermore, some metal components in biochar generally came from two sources. The first source is to consume many minerals such as calcium, iron, magnesium, etc. The opposite supply is metal salts introduced by artificial means throughout the method of pretreatment. These multifunctional characteristics offer biochar an excellent potential to be used to efficiently absorb nitrogen and phosphate (NH_4^+, NO_3^-, PO_4^{3-}) removal from water. (Zhang *et al*.2012) [72].

I. Removal of pharmaceutical compounds from wastewater by Biochar

These contaminants are very harmful to every living being and this becomes a drawback worldwide (Yan and Song 2014) [55]. Due to increasing health awareness and better living consumption of pharmaceutical products has increased a lot in these years. That additionally acquired a lot of serious environmental problems because of the raised unharness of waste material that contains plenty of varied pollutants (Jain *et al*. 2018) [23]. Increasing antibiotics in water will lead to generating drug-resistant microorganisms, which might get killed by these antibiotics, so obtaining cornered in a very vicious circle (Bougnom and lamellibranch 2017) [25]. There are many ways such as the food chain through which these harmful components enter into human bodies and animals, resulting in life-threatening. That's why it is very important to get rid of these harmful components from effluents. Recently, biochar has been explored as a possible material for the adsorption of prescribed drugs from water.

BC shows effective potential to take away these contaminants from water. Oxidation of sulfonamide, sodium persulphate to activate this compound biochar is used, presence of biochar sulfonamide degraded and this processes analyzed by HPLC. Biochar might have degradation performance in water but because of that minor radical scavenger was observed (Kemmou *et al*. 2018) [26]. A similar study was also accomplished in that, to improve Nitrogen content in biochar, NH_4NO_3 was introduced to the treatment of biomass. Because of high N content, Biochar showed a large surface area. Due to doping of Nitrogen Biochar produced ample adsorption sites to bind the organic molecule and pharmaceutically active compounds to form the surface, which is in a metastable state, will be oxidized organic contaminants via direct electron transport.

2. Recent advances in dye removal technologies by biochar

Textiles industries, rubber industries, paper industries, and dye industries, etc., producing dyes are contaminants (Yagub *et al*. 2014) [27]. Dyes have certain characteristics such as they are soluble in water, chemically are stable, high in colours, due to these they are not decomposed easily. In aquatic systems, dyes are affecting the photosynthesis process and oxygenation process. Organic dyes are very dangerous to human bodies (Mahmood *et al*. 2016) [28]; therefore, the standard methods of treating water are unable to decolorize these contaminants with efficiency because of its complicated structure. To get rid of dyes successfully, several new methods, like separation of the membrane (Damodar *et al*. 2010) [29], sorption and advanced oxidation, precipitation, filtration, are used within the effluent. But two methods are used: adsorption and catalysis which are highly acceptable and effective to remove dyes from wastewater (Adeyemo *et al*. 2015) [30]. Compared to activated charcoal, biochar contains a wide selection of sources, as well as industrial waste, agricultural by-products, placental mammal manure, sludge, etc Biochar itself has the benefits of enormous pores, high surface area, and rich surface functional groups, Rich surface functional groups are significantly a lot of necessary than high porousness within the adsorption method.

Biochar has a porous structure and the presence of functional groups on the surface. Because of this biochar can be used as an adsorbent to take away dye from wastewater. Methyl violet dye adsorbed by different biochar likewise canola straw, peanut straw, soybean plant, rice husk among this canola straw showed high adsorption capacity, and the least was seen in rice husk biochar adsorbed a lots of rhodamines Bowing to a massive extent and huge micropores. Because of the micropores structure of biochar molecules of dyes will be moved aside. Rice straw biochar sufficiently takes up mineral inexperience. At 200–700, °C was discovered. Biochar created from waste bamboo at higher temperatures is used to take away certain dyes like methylene blue, acid yellow 117, and acid blue. For the adsorption of dyes, two mechanisms are suitable for electrostatic interaction and intermolecular hydrogen bonding (Qiu *et al*. 2009; Xu *et al*. 2011) [32, 31].

Additionally, to surface assimilation, chemical action degradation has conjointly been widely accepted as an economical approach for the coloring waste material treatment. Catalyst is used for photocatalysis of dyes. There are some more catalysts also used to remove dye contaminants. one of them is TiO_2. (Khan *et al*. 2014) [33]. Biochar is taken into account to be a good support catalyst due to its various properties. Catalytic degradation additionally provides the proper result to get rid of dye from effluent. In general, the hybridization of biochar is classified into two major types:

- Chemical properties such as more surface functional groups and higher porosity.
- To introduce catalysts like TiO_2. These will increase the removal percentage of contaminants. (Zhang and Lu 2018) [78].

Potential of biochar for the remediation of heavy metal contaminated soil

Contamination of soil has become a major problem nowadays (Cao 2010) [67]. Heavy metals create serious health threats even at low concentrations. Pollutants in soils are not only harmful to ecosystems and agricultural production but are also a significant threat to human well-being. In contrast to organic contaminants, metals are non-biodegradable and their bioavailability makes them extremely harmful to living organisms. Heavy metals are harmful and stay within the atmosphere because of they cannot be diminished (Cao 2010) [67]. Through the food chain, heavy metal enters human bodies and it's very harmful to human health and it also decreases the quality of the soil. Through the food chain, transfer of heavy metal could be possible from soil to plant and eventually its effect on human health (Khan 2010) [69]. Bio-fertilizers and inorganic components increase the pollution of heavy metals in soil. It is important to get rid of the inaccessibility of heavy metals to plant for the restoration of production of healthy and safe food. Remediation techniques are emphasized in numerous studies of heavy metals. Researchers investigated the utilization of biochar as in-place soil change, it was effective to increase the quality of soil by taking away heavy metals.

Because of some reasons, biochar was found to be effective for removing heavy metals from soil: It's found to be effective towards adsorbing heavy metals and also reduce some toxin stress into plants and microbes that are present in soil. Generally, biochars are a source of organic components and some minerals for microorganisms. Microbes that are beneficial to remediation and protect them from predators' biochar promote such kinds of microbes. Fertility of soil and growth of plants improves by biochar and also accelerates properties of soils including physical and chemical properties. (Fang 2015) [70].

Application of biochar will probably offer a brand new resolution for remediation of the soils contaminated by heavy

metals. Generally, heavy metals are found in soil like Cu, Ni, As, Pb, Zn, Si, Cd, etc. which are injurious to human health and plants also. These metals are non-biodegradable so that heavy metals will continue to impure soils for an extended time (Zhang 2013) [65]. There's a necessity to get rid of heavy metals, therefore the best method used to remediate soil is Biochar. Taking Pb^{2+} as an example, the most declension of transferable lead achieved at 10% by sugarcane biochar. Biochar is rich in nutrients such as calcium, magnesium, phosphorus, and many more. As temperature increases the concentration of nitrogen and carbon decreases, but other nutrients like magnesium, calcium, and phosphorus concentration increase as temperature increases (Cao 2010) [67]. 93% of you look after lead was absorbed by biochar at a hundred, but at a higher temperature like 200 and 300° C lead was taken off completely off from soil (Cao 2010) [67]. If soil is acidic, pH is the main parameter that will remove these metals. Adsorption of Pb(II) will increase by the application of biochar. Increased pH will develop a negative charge on the surface and attract positive charge molecules within the soil (Wu *et al*. 2012) [68]. Increased pH is good for heavy metals in bulk soil. Similarly, remediation of different heavy metals, different mechanisms are applied to various types of biochars within the soil.

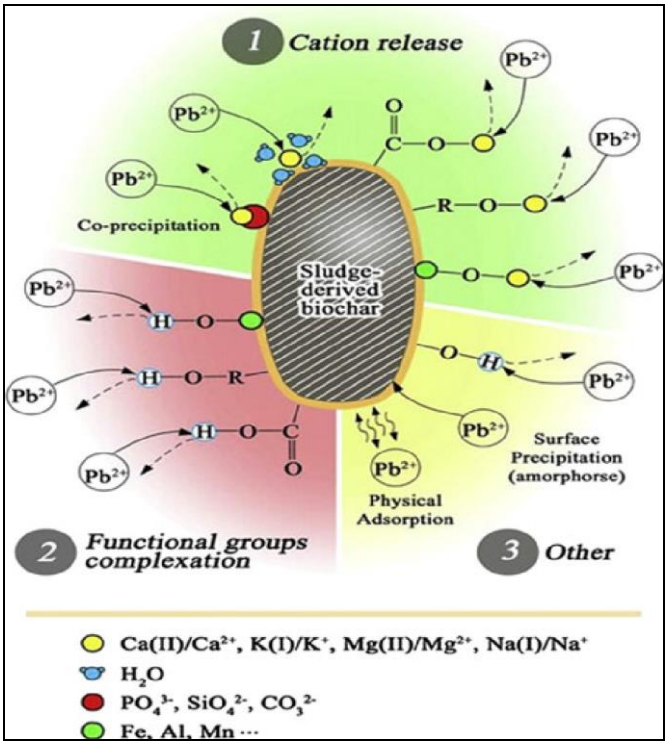


Fig 1: Mechanism various types of biochars within the soil.

Mechanism to remove Pb^{2+} from the soil

The efficiency of biochar in the removal of pesticides from watershed system

Pesticides to regulate pests (insects, weeds, and diseases) represent crop management in trendy agriculture that may assist with the provision of stable, top-quality, and inexpensive food. Pesticides can be harmful to the environment if they are used erroneously and needlessly. Pesticides residues have been seen in environment matrix-like water, soil, and microorganism bodies or air. Protecting the environment from these pesticides is necessary nowadays. For the removal of pesticides, biochar is applied (Dai *et al*., 2019). Zhang *et al*. (2018) [37, 78] made biochar from maize straw at different temperatures such as 300, 500, and 700°C to review the sorption of thiacloprid. They studied that various mechanisms are involved to remove pesticides such as pore filling, π-π interaction, hydrophobic interaction. Swine manure biochar made by pyrolysis at high temperature was used to take away imidacloprid. The pore-filling mechanism is probably going to be more dominant for the sorption process compared to other mechanisms (Jin *et al*. 2016) [24]. Biochar made from the almond shell by pyrolysis with the treatment of steam has shown a bigger area of surface and more capability of sorption for dibromochloropropane, a roundworm pesticide. (Uchimiya *et al*. 2010) [73] introduced biochar made from broiler litter by pyrolysis at 350 and 700°C to get rid of desisopropyl atrazine and atrazine from water. At higher temperatures like 700°C biochar shows large micropores and larger aromaticity, so that contaminants can easily be removed, whereas at low temperatures like 500°C shows low efficiency to remove pesticides.

3. Mechanism of metal sorption by biochar

Metals are omnipresent within the surroundings, adversely affecting human health. As we all know the definition of biochar, has a porous structure and is rich in carbon material. Biochar is made up of biomass by thermal decomposition in absence of O_2 or limited O_2 at a temperature <900 °C (Lehmann *et al*., 2006) [35]. Biochar gained a lot of recognition, because of its structure and properties, it shows excellent results in the removal of metals (Cao *et al*., 2009) [67]. Biochars are made from numerous feed stocks at totally different pyrolysis conditions to absorb metals from water or soil.

There are five main mechanisms by which metals can be removed from wastewater (Ahmad *et al*., 2014) [2]. (1) Interaction between the surface of biochar and metals by electrostatic interaction ;(2) Exchange of ions between the surface of biochar and metals; (3) By complexation domain will form on biochar with help of functional groups and π electron; (4) Precipitation will form insoluble material; and (5) Physical sorption to remove heavy metal by the movement of metal ion without forming chemical bonds. These mechanisms will differ on basis of biochar properties and contaminants. Metals have different valence states at different pH.

This review paper discussed the mechanism to remove metals from wastewater by biochar. This review paper furnishes biochar properties and its capability to remove metals.

3.1 Electrostatic interaction

To immobilize metal, surface charge biochar and target metals interact electrostatically. This mechanism mainly relies on two conditions 1. pH and 2. PZC (point zero charges) (Dong, *et al*. 2011) [38]. Wheat and rice-derived biochar showed excellent results for lead. Electrostatic interaction between charged surface biochar and charged Chromium (VI) reported at low pH i.e. two (Dong, *et al*. 2011) [38].

3.2 Exchange of Ions

Metals sorption by ion-exchange mechanism i.e. exchange of cations and protons that are present on the surface of biochar with targeted metals, which are in dissolve form. The efficiency of this mechanism to keep metals on biochar surface purely depends on the metal size and functional groups of biochar surface. Exchange of ions of metal contaminants happens by replacing positive ions on the surface of biochar with metal contaminants. Most metal species inside groups one to three (e.g., Na, K, Ca, Li, Mg,

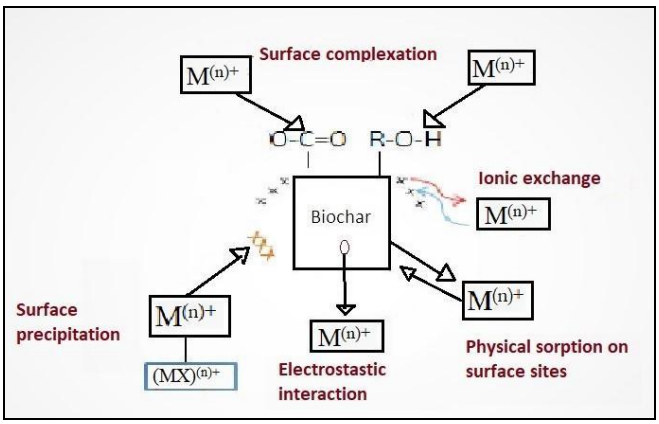
Be, and Sc) on the periodic table are a lot of possibilities to be changed with alternative elements like metallic inside this group supported the similarities of their ionic radii, charge variations. Consequently, biochar derived from rice husk made at low temperatures showed robust natural processes of Hg and Zn principally via de-protonation of H^+ and ulterior interchange of Zn^{2+} and Hg^+. Biochar produced from bone has a large number of ions and can remove metals such as Co easily from wastewater via the exchange of ions (Pan, *et al*. 2009) [40].

3.3 Complexation

Complexation mainly formed multi-atom structures that also include the inner and outer sphere of biochar i.e. its form metal-ligand complexes. Complexation is probably vital because it has partly filled d-orbitals with transition metals and ligands have high affinity. Biochar binds effectively to metals in the presence of functional groups like carboxylic and phenol groups (Mohan, *et al*. 2007) [41]. Biochar contents O_2 have additionally shown to extend in recent years, possibly because of oxidation on the surface of biochar, therefore it will form carboxylic groups. Overtime use of this mechanism may increase. Biochar made from plants binds easily to some metals such as Cu, Ni, Cd, and Pb and precipitates on the surface of biochar in the form of phenolic complex and carboxylic complex. Biochar produced from animals can also bind to metals such as lead with ligand and create metallic complexes. (Cao, *et al*. 2009) [36].

3.4 Precipitation

In this mechanism, solid will form on the surface of biochar or in solution while the sorption process is carried out. This mechanism is one of the best mechanisms to immobilize heavy metals. Metals having intermediate ionization potentials of about 2.5 or 9.5 are likely to be precipitated on the surface of biochar compared to some other metals. (Krauskopf 1967) [39] Biochar's derived from animals and plants at high temperatures are rich in minerals such as iron, calcium, silicon these mineral phases as well as calcium carbonate, silicon dioxide, calcium sulfate, potassium chloride all of these are present in free form or inside biochar's matrix. These phases in the soluble form are present at a lower temperature and form insoluble solid by directly interacting with metals (Cao, *et al*. 2009) [36]. Those mineral phases present at higher temperatures is less soluble in nature and possible to be discharged throughout the process of sorption and form insoluble solid on the surface of biochar (Inyang, *et al*. 2011b) [42].



3.5 Physisorption

Without forming a chemical bond there is the movement of metal ions in pores of sorbent to take away heavy metals from effluents described as surface or physical sorption. Higher temperatures of carbonization will increase the surface area of biochar and also increase the size of pores in biochar, for animals and plants derived from biochar. E.g., switch grass biochar and pinewood biochar, will each successfully take away Cu through diffusing surface adsorption method. Biochar produced by animals were to retain Cd, Cu, and Zn in pores, and the sorption process was described using film pore, diffusion model. (Choy and McKay 2005) [44].

4. Mechanism of removal of contaminants by modified biochar

Once the biomass is heated at a higher temperature with a very small amount of O_2 or absence of O2, biochar behaves as a stable carbon substance that is obtained by a thermal process. To activate biochar further in their properties such as volume of the pore, area of surface, functional groups known as modified biochar. Untreated biochar are restricted in the ability to by selection take up contaminants of high concentrations (Kwiatkowski, 2008) [60]. Modified BCs are often utilized as successful sorbents for taking away all types of contaminants from effluent (Tan *et al*., 2015). Functional groups were liable to gather contaminants from wastewater. The highlight of this paper is to study modified biochar for taking away heavy metals and some other contaminants from an aqueous solution (Ahmed *et al*., 2015) [59].

Modification strategies

Biochar's modification of the surface will be completed in numerous methods that are covered in the following sections.

4.1 Modification by chemical

This modification can be done by one-step process and two-step process. In a one-step process within the presence of an activating chemical agent, carbonization and activation steps are carried out at the same time throughout this process. Whereas in a two-step process the first step involves carbonization of feedstock and then activation, a process carried out of the product, which is carbonized by the chemical agent or pretreated precursors. (Azargohar and Dalai, 2008; Qian *et al*.,2015) [45, 46].

4.2 Treatment by acids and base

All treatments produce further prices, however are helpful within the end because of increased properties. Chemical modification treatments are usually administered by the addition of acids and bases. To modify functional groups of surfaces, an oxidizing agent is used like peroxide (H_2O_2), potassium permanganate ($KMnO_4$), ozone, and ammonium persulfate [$(NH_4)_2S_2O_8$], and many more. (Cho *et al*., 2010; Uchimiya *et al*., 2011) [47, 48]. Phosphoric acid is normally used as an oxidizing agent for modification chemically and it is also non-polluting compared to other hazardous reagents like $ZnCl_2$. (Sun *et al*., 2011) [49]. On carbonized surface material, functional groups like paraffin and carboxyl groups were seen because of strong acid treatment. Exchange of cation and complexation with active sites enrich the affinity of metal activity and capability.

Sodium hydroxide and potassium hydroxide are used to increase the O_2 level and basicity of the surface for activation of biochar. Biochar treated with KOH or NaOH has a larger area of the surface (Fan *et al*., 2010) [50].

Chemically modified biochar increases the ability to remove contaminants via ample sorption sites on an area of surface,

this will help with mechanisms like complexation and precipitation. As an example, oxidation by H_2O_2 will give a cation exchange site to the surface of biochar by increasing the carboxylic group for Pb^{2+} and Hg (Tan *et al*., 2011) [51]. KOH modified biochar showed more sorption activity for As^{5+} due to enlargement of pore volume and area of surface and functional groups (Jin *et al*., 2014) [53].

With the help of π-π EDA (electron donor-acceptor) interaction that happens between organic aromatic rings and biochar, organic contaminants become easy to remove (Fan *et al*., 2010) [50]. Biochar that is modified by KOH solution showed more sorption for tetracycline. Whereas biochar modified with NaOH solution showed more sorption than unmodified biochar for chloramphenicol (Fan *et al*., 2010) [50].

4.3 Modification of functional groups

Functional groups that present on the surface of biochar and their hydrophilicity will be modified chemically to suit the particular necessities to protect the environment by taking away contaminants from effluent (Li *et al*., 2014c). Using modification agent chitosan, a heavy metal such as lead, copper, and cadmium can be removed easily by introducing an amino group on the surface of biochar. Because of the amine group of chitosan-modified biochar, a strong chemical bond will form between heavy metal and biochar, and uptake of heavy metal will be easy (Yong *et al*., 2013) [56]. Biochar derived from peanut hulls that are modified by H_2O_2 have more amount carboxylic functional groups which will increase sorption capability for heavy metals like Cd^{2+}, $Ni^{2+,}$ and Pb^{2+} (Xue *et al*., 2012) [57].

4.4 Modification by organic solvents

Using esterification and carbodiimide modification of the carboxylic group can be done with the help of acidic methyl alcohol. Development of electron-donor-acceptor (EDA) interaction between the surface of biochars and this contaminant can be accelerated by treatment biochars with methyl alcohol, In methyl alcohol modification, the chemical reactions concerned are esterification and then direct reaction between methyl alcohol and carboxylic groups of biochar (Jing *et al*., 2014) [53].

4.5 Biochar coating

Biochar has been coating with metal oxide recently to improve the capability of sorption and biochar properties.

A. Coating with Metal Oxides

To take away contaminants like heavy metals from effluent, bamboo biochar coated with cobalt and Fe metal oxide (Wang *et al*., 2012) [72]. Studies have shown that the capacity of sorption of biochar coated with MgO is more than the uncoated biochar for anionic dyes Zhang *et al*. (2014b) [55]. Bamboo biochar coated with Cobalt oxide has shown a significant increase in Cr^{6+} oxyanion activity compared to uncoated or unmodified biochar. Cobalt-coated biochar showed a high area of surface and increased in pore size contrast to not coated biochar which will increase the sorption of capability.

B. Carbon Nanotubes coating

To get rid of contaminants carbon nanotubes (CNTs) are extremely essential because it has more area of surface and nanostructure, but due to the overpriced and inconvenient application of engineering, it restricted their use. Biochar might function as a microporous or mesoporous carrier of carbon nanotubes to grow new reusable sorbents for effluent. Nonetheless, biochar synthesis for CNTs is cheap and easy. As a result, this carbon nanotubes coating biochar are cheap and easy to remove various contaminants such as organic and inorganic, dyes, etc. from wastewater (Zhang *et al*. 2009) [75].

5. Conclusion

This review gives a broad application of biochar in wastewater treatment and soil to remove various contaminants such as inorganic, organic and heavy metals, etc. In addition, it includes mechanisms to remove metals. Various modification methods are also explained to improve the performance of biochar. Hence Biochar can be used in agriculture for better growth of crops and pulses. Overall, further studies are required to reuse biochar.

Conflict of interest

Authors declare no conflict of interest.

Funding: None

6. References

1. Sohi SP. Carbon storage with benefits. Science. 2012;338(6110):1034-5.
2. Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere. 2014;99:19-33.
3. Cao X, Ma L, Gao B, Harris W. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ Sci Technol. 2009;43:3285-91.
4. Zheng W, Guo M, Chow T, Bennett DN, Rajagopalan N. Sorption properties of green waste biochar for two triazine pesticides. J Hazard Mater. 2010;181:121-6.
5. Klasson KT, Ledbetter CA, Uchimiya M, Lima IM. Activated biochar removes 100% dibromochloropropane from field well water. Environ Chem Lett. 2013;11:271-5.
6. Chen B, Chen Z. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere. 2009;76:127-133.
7. Carvalho IT, Santos L. Antibiotics in aquatic environments: a review of the European scenario. Environ Int. 2016;94:736-57.
8. Liu WJ, Zeng FX, Jiang H, Zhang XS. Preparation of high adsorption capacity biochars from waste biomass. Bioresour Technol. 2011;102:8247-8252.
9. Huang BC, Jiang J, Huang GX, Yu HQ. Sludge biochar-based catalysts for improved pollutant degradation by activating peroxymonosulfate. J Mater Chem A. 2018;6:8978-8985.
10. Sun K, Keiluweit M, Kleber M, Pan Z, Xing B. A sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. Bioresour Technol. 2011;102:9897-9903.
11. Qiu Y, Zheng Z, Zhou Z, Sheng GD. Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresour Technol. 2009;100:5348-5351.
12. Xu R, Xiao S, Yuan J, Zhao A. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresour Technol. 2011;102:10293-10298.
13. Colmenares JC, Varma RS, Lisowski P. Sustainable hybrid photocatalysts: Titania immobilized on carbon materials derived from renewable and biodegradable

resources. Green Chem. 2016;18:5736-5750.
14. Paerl HW. Controlling eutrophication along the freshwater–marine continuum: dual nutrient (N and P) reductions are essential. Estuar Coasts. 2009;32:593-5601.
15. Smith VH. Eutrophication of freshwater and coastal marine ecosystems is a global problem. Environ Sci Pollut Res. 2003;10:126-139.
16. Zhang T, Li Q, Ding L, Ren H, Xu K, Wu Y, Sheng D. Modeling assessment for ammonium nitrogen recovery from wastewater by chemical precipitation. J Environ Sci. 2011;23:881-890.
17. Zhang M, Gao B, Yao Y, Xue YW, Inyang M. Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. Chem Eng J. 2012;210:26-32.
18. Sica M, Duta A, Teodosiu C, Draghici C. Thermodynamic and kinetic study on ammonium removal from a synthetic water solution using ion exchange resin. Clean Techn Environ Policy. 2014;16:351-359.
19. Demirbas A, Arin G. An overview of biomass pyrolysis. Energy Sources. 2010;24:471-482.
20. Cao X, Ro KS, Libra JA, Kammann CI, Lima I, Berge N, *et al*. Effects of biomass types and carbonization conditions on the chemical characteristics of hydrochars. J Agric Food Chem. 2013;61:9401-9411.
21. Harvey OR, Herbert BE, Rhue RD, Kuo LJ. Metal interactions at the biochar-water interface: energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry. Environ Sci Technol. 2011;45:5550-5556.
22. Yan S, Song W. Photo-transformation of pharmaceutically active compounds in the aqueous environment: A review. Environ Sci Process Impacts. 2014;16:697-720.
23. Jain K, Sharma P, Jayalakshmi M. A comparative study of consumption behavior of pharmaceutical drugs. In: International conference on recent developments in science, engineering, and technology. 2018;799:27-33.
24. Jin J, Kang M, Sun K, Pan Z, Wu F, Xing B. Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine. Sci Total Environ. 2016;550:504-513.
25. Bougnom BP, Piddock LJV. Wastewater for urban agriculture: A significant factor in dissemination of antibiotic resistance. Environ Sci Technol. 2017;51:5863-4.
26. Kemmou L, Frontistis Z, Vakros J, Manariotis ID, Mantzavinos D. Degradation of antibiotic sulfamethoxazole by biochar activated persulfate: factors affecting the activation and degradation processes. Catal Today. 2018;313:128-133.
27. Yagub MT, Sen TK, Afroze S, Ang HM. Dye and its removal from aqueous solution by adsorption: A review. Adv Colloid Interface Sci. 2014;209:172-184.
28. Mahmood S, Khalid A, Arshad M, Mahmood T, Crowley DE. Detoxification of azo dyes by bacterial oxidoreductase enzymes. Crit Rev Biotechnol. 2016;36:639-651.
29. Damodar RA, You SJ, Ou SH. Coupling of membrane separation with photocatalytic slurry reactor for advanced dye wastewater treatment. Sep Purif Technol. 2010;76:64-71.
30. Adeyemo AA, Adeoye IO, Bello OS. Adsorption of dyes using different types of clay: A review. Appl Water Sci. 2015;7:543-568.
31. Xu R, Xiao S, Yuan J, Zhao A. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresour Technol. 2011;102:10293-10298.
32. Qiu Y, Zheng Z, Zhou Z, Sheng GD. Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresour Technol. 2009;100:5348-5351.
33. Khan MM, Lee J, Cho MH. Au@TiO2 nanocomposites for the catalytic degradation of methyl orange and methylene blue: An electron relay effect. J Ind Eng Chem. 2014;20:1584-1590.
34. Zhang S, Lu X. Treatment of wastewater containing Reactive Brilliant Blue KN-R using TiO2/BC composite as heterogeneous photocatalyst and adsorbent. Chemosphere. 2018;206:777-783.
35. Lehmann J, Gaunt J, Rondon M. Bio-char sequestration in terrestrial ecosystems: A review. Mitig Adapt Strateg Glob Change. 2006;11:395-419.
36. Cao XD, Ma LQ, Gao B, Harris W. Dairy-manure-derived biochar effectively sorbs lead and atrazine. Environ Sci Technol. 2009;43:3285-3291.
37. Dai Y, Zhang N, Xing C, Cui Q, Sun Q. The adsorption, regeneration and engineering applications of biochar for removal of organic pollutants: A review. Chemosphere. 2019;223:12-27.
38. Dong XL, Ma LNQ, Li YC. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. J Hazard Mater. 2011;190:909-915.
39. Krauskopf BK. Introduction to geochemistry. New York: McGraw Hill Book Company; c1967.
40. Pan X, Wang J, Zhang D. Sorption of cobalt to bone char: Kinetics, competitive sorption and mechanism. Desalination. 2009;249:609-614.
41. Mohan D, Pittman Jr CU, Bricka M, Smith F, Yancey B, Mohammad J, Steele PH, Alexandre-Franco MF, Gomez-Serrano V, Gong H. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J Colloid Interface Sci. 2007;310:57-73.
42. Inyang M, Gao B, Ding W, Pullammanappallil P, Zimmerman AR, Cao X. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. Sep Sci Technol. 2011;46:1950-1956.
43. Liu Z, Zhang FS, Wu J. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. Fuel. 2010;89:510-514.
44. Choy KKH, McKay G. Sorption of cadmium, copper, and zinc ions onto bone char using Crank diffusion model. Chemosphere. 2005;60:1141-1150.
45. Azargohar R, Dalai AK. Steam and KOH activation of biochar: experimental and modeling studies. Microporous Mesoporous Mater. 2008;110:413-421.
46. Qian K, Kumar A, Zhang H, Bellmer D, Huhnke R. Recent advances in the utilization of biochar. Renew Sustain Energy Rev. 2015;42:1055-1064.
47. Cho HH, Wepasnick K, Smith BA, Bangash FK, Fairbrother DH, Ball WP. Sorption of aqueous Zn(II) and Cd(II) by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon. Langmuir. 2010;26:967-981.
48. Uchimiya M, Chang S, Klasson KT. Screening biochar for heavy metal retention in soil: Role of oxygen

functional groups. J Hazard Mater. 2011;190:432-441.
49. Sun K, Jian-chun J, Dan-dan C. Preparation of activated carbon with highly developed mesoporous structure from Camellia oleifera shell through water vapor gasification and phosphoric acid modification. Biomass Bioenergy. 2011;35:3643-3647.
50. Fan Y, Wang B, Yuan S, Wu X, Chen J, Wang L. Adsorptive removal of chloramphenicol from wastewater by NaOH modified bamboo charcoal. Bioresour Technol. 2010;101:7661-7664.
51. Tan Z, Qiu J, Zeng H, Liu H, Xiang J. Removal of elemental mercury by bamboo charcoal impregnated with H2O2. Fuel. 2011;90:1471-1475.
52. Jin H, Capareda S, Chang Z, Gao J, Xu Y, Zhang J. Biochar pyrolytically produced from municipal solid wastes for aqueous As(V) removal: Adsorption property and its improvement with KOH activation. Bioresour Technol. 2014;169:622-629.
53. Jing XR, Wang YY, Liu WJ, Wang YK, Jiang H. Enhanced adsorption performance of tetracycline in aqueous solutions by methanol-modified biochar. Chem Eng J. 2014;248:168-173.
54. Zhang XN, Mao GY, Jiao YB, Shang Y, Han RP. Adsorption of anionic dye on magnesium hydroxide-coated pyrolytic biochar and reuse by microwave irradiation. Int J Environ Sci Technol. 2014;11:1439-1448.
55. Li JH, Lv GH, Bai WB, Liu Q, Zhang YC, Song JQ. Modification and use of biochar from wheat straw (*Triticum aestivum* L.) for nitrate and phosphate removal from water. Desalin Water Treat. 2014;1-13.
56. Yong S, Bolan NS, Lombi E, Skinner W. Synthesis and characterization of thiolated chitosan beads for removal of Cu(II) and Cd(II) from wastewater. Water Air Soil Pollut. 2013;224:1-12.
57. Xue Y, Gao B, Yao Y, Inyang M, Zhang M, Zimmerman AR, Ro KS. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests. Chem Eng J. 2012;200-202:673-680.
58. Wang Y, Wang XJ, Liu M, Wang X, Wu Z, Yang LZ, *et al*. Cr(VI) removal from water using cobalt-coated bamboo charcoal prepared with microwave heating. Ind Crops Prod. 2012;39:81-88.
59. Ahmed MB, Zhou JL, Ngo HH, Guo W. Adsorptive removal of antibiotics from water and wastewater: progress and challenges. Sci Total Environ. 2015;532:112-126.
60. Kwiatkowski M. Application of fast multi-variant identification technique of adsorption systems to analyze influence of production process conditions on obtained microporous structure parameters of carbonaceous adsorbents. Microporous Mesoporous Mater. 2008;115(3):314-331.
61. Yu F, Li Y, Han S, Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere. 2016;153:365-385.
62. Kaetzl K, Lübken M, Uzun G, Gehring T, Nettmann E, Stenchly K, *et al*. On-farm wastewater treatment using biochar from local agro residues reduces pathogens from irrigation water for safer food production in developing countries. Sci Total Environ. 2019;682:601-610.
63. Li Y, Shao J, Wang X, Deng Y, Yang H, Chen H. Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. Energy Fuels. 2014;28(8):5119-5127.
64. Gunathilake SK. Methods of removing heavy metals from industrial wastewater. J Multidisc Eng Sci Studies. 2015;1(1):12-18.
65. Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, *et al*. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ Sci Pollut Res. 2013;20:8472-8483.
66. Abdel Hafez AA, Li J, Abbas MHH. Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil. Chemosphere. 2014;117:66-71.
67. Cao X, Harris W. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour Technol. 2010;101:5222-5228.
68. Wu W, Yang M, Feng Q, McGrouther K, Wang H, Lu H, *et al*. Chemical characterization of rice straw-derived biochar for soil amendment. Biom Bioenergy. 2012;47:268-276.
69. Khan S, Rehman S, Khan AZ, Khan MA, Shah MT. Soil and vegetable enrichment with heavy metals from geological sources in Gilgit, northern Pakistan. Ecotoxicol Environ Saf. 2010;73:1820-1827.
70. Fang Y, Singh B, Singh BP. Effect of temperature on biochar priming effects and its stability in soils. Soil Biol Biochem. 2015;80:136-145.
71. Al-Wabel MI, Usman ARA, El-Naggar AH, Aly AA, Ibrahim HM, Elmaghraby S, *et al*. Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. Saudi J Biol Sci. 2014;22:503-511.
72. Lu H, Zhang YY, Huang X, Wang S, Qiu R. Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar. Water Res. 2012;46:854-862.
73. Uchimiya M, Wartelle LH, Lima IM, Klasson KT. Sorption of de-isopropyl atrazine on broiler litter biochars. J Agric Food Chem. 2010;58:12350-12356.
74. Zhang P, Sun H, Min L, Ren C. Biochars change the sorption and degradation of thiacloprid in soil: insights into chemical and biological mechanisms. Environ Pollut. 2018;236:158-167.
75. Zhang J, Huang ZH, Lv R, Yang QH, Kang F. Effect of growing CNTs onto bamboo charcoal on adsorption of copper ions in aqueous solution. Langmuir. 2009;25:269-274.
76. Zhao J, Liang G, Zhang X, Cai X, Li R, Xie X, *et al*. Coating magnetic biochar with humic acid for high efficient removal of fluoroquinolone antibiotics in water. Sci Total Environ. 2019;688:1205-1215.
77. Zhou Y, Liu X, Xiang Y, Wang P, Zhang J, Zhang F, *et al*. Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: adsorption mechanism and modeling. Bioresour Technol. 2017;245:266-273.
78. Zhang F, Wu K, Zhou H, Hu Y, Sergei P, Wu H, *et al*. Ozonation of aqueous phenol catalyzed by biochar produced from sludge obtained in the treatment of coking wastewater. J Environ Manag. 2018;224:376-386.