Review Paper:

Biochar for heavy metal removal from wastewater

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Abstract

Heavy metals are considered to be one of the major pollutants present in the environment and can cause toxic effects on humans and plants. Moreover, they can persist in the environment for a long period of time. Heavy metals can seep into the soil and pollute the groundwater aquifers. Hence, it is important to find out a way to remove heavy metals from water samples. Biochar, a carbonaceous product obtained by decomposition of organic biomass can act as an efficient adsorbent to remove heavy metals from aqueous solutions. Various technologies used to synthesize biochar have a significant impact on physicochemical features and commercial applications of biochar. Biochar can interact with metals by several mechanisms and has unique physicochemical properties that enable it to become an excellent adsorbent for metals.

In this review, processes used to prepare biochar and mechanisms involve removal of heavy metals. Biochar characterization techniques have been explained in detail. We can infer that biochar is an inexpensive, environment friendly and effective agent for the adsorption of heavy metals from aqueous solutions and it has a great potential as an upcoming wastewater treatment process.

Keywords: Heavy metals, wastewater, remediation, biochar, mechanism.

Introduction

Heavy metals present in the environment pose a high risk globally since they cause deleterious effects on the health of human beings, plants and animals. Heavy metals which are released into the water bodies directly or through the soil are toxic since they are non-biodegradable. Methods such as precipitation, membrane filtration, ion exchange resins etc. were used to remediate heavy metals from water samples earlier[79]. In order to remediate heavy metals from soil, techniques such as solidification/stabilization, physicochemical extraction, bioremediation and phytoremediation are widely used[34,66].

However, these methods are tedious, time consuming and expensive when applied at a large scale, Hence, in the recent years a great emphasis has been placed on the use of biochar for the heavy metal remediation from water bodies. Biochar is a carbon rich porous substance which is produced by the pyrolysis of organic biomass under low temperature conditions and in absence of oxygen. Biochar prepared from wood, popularly known as charcoal (or wood biochar) is most widely used. The use of other feedstocks such as agricultural waste, manure, sludge etc. are new and need more research. Biochar has a great capacity to resist degradation by chemicals and biological agents[1]. Generally, biochar has a basic nature and has high cation exchange capacity. Biochar can significantly improve the fertility and biological activity of soil since it acts as a great nitrogen and phosphorous source.

Biochar can effectively increase the sequestration of carbon in the soil since it is rich in carbon and also enhances the overall agricultural yield. Biochar has a great role in bringing about climate change[43], since it can act as a carbon sink to decrease the emission of greenhouse gases such as carbon dioxide produced from agricultural wastes. Biochar can act as an excellent adsorbent and hence has great potential to remediate organic and inorganic pollutants from soil and waste water[8]. The adsorption of heavy metals by biochar involves an electrostatic interaction among the cations of heavy metal and biochar surface (negatively charged).

There is also an ion exchange among the cations of metals and surface protons of biochar. There are various groups such as alkaline nitrogen groups, acidic oxygen groups (e.g. lactonic and carboxylic groups) and certain mineral impurities (e.g. metal and ash oxides) which help in enhancing the adsorption ability of biochar[50].

Preparation of biochar from different materials

Different kinds of feedstocks can be used for preparation of biochar. The most common feedstocks include agricultural and forest wastes, biomass of crops, sludge waste, industrial wastes, animal wastes, manure and other non-conventional wastes[89]. These waste products are generated on a large scale in the world, however they need to be managed well to be sustainable and eco-friendly.

Hence, using these wastes to prepare biochar is the best option. The forest and agricultural wastes are regarded as the most important feedstocks used in the production of biochar[31,36]. It has been anticipated that around 500 million tons of agricultural wastes generated per year globally can be utilized in the production of biochar[17].

A large portion of these wastes are direct by-products obtained from harvesting and processing of several crops. The crops included are: sugarcane bagasse[61], peanut shells[97], corn stalks[15], rice straw[48], wood waste from forests[81], wheat straw[49], cassava residue[28], coconut fiber[91], soybean and bamboo. The animal feedstock used to prepare biochar includes dead animal waste like poultry[25], dairy manure[52], manure obtained from pigs[78] and poultry litter (consists of spilled feed, bedding substances and feathers)[76]. A lot of scientists around the world are keen to explore the potential of industrial and municipal wastes and their by-products as biochar feedstocks[92].

Some of the research studies have demonstrated that wastes obtained from water/sewage treatment plants like sewage sludge[53] and bioenergy plants such as digested residues[44] can be used as biochar feedstocks. The potential of non-conventional substances as feedstocks for making biochar is still in the research phase. These substances include periwinkle shells[9], bioenergy residues[94], food wastes[72], plastics[21], diatoms and algae[96], waste tires[37] and bones[64]. It has been observed that different kinds of feedstocks can produce biochar having different physicochemical properties[77,80]. The amount of carbon present in biochar is a significant factor for deciding the effectiveness of biochar.

Various methods used to prepare biochar and the properties of biochar: Various techniques used for preparing biochar and its properties have been studied extensively[2, 37]. It was demonstrated by Tan et al[82] that slow pyrolysis is the most widely used technique to prepare biochar. This biochar can then be used in the treatment of contaminated water samples.

The preparation of biochar can be done via several thermochemical methods such as hydrothermal carbonization, gasification, flash carbonization, fast pyrolysis and slow pyrolysis[54,70].

Properties of biochar and biochar yield are dependent on the thermochemical method of preparation, feedstock used to prepare the biochar and operating conditions. It has been observed that biochar which is produced via slow pyrolysis technique at low temperature condition has highly acidic and polar surface. However, their aromaticity and hydrophobicity are low. The thermal breakdown of organic biomass takes place between 200^0 C- 500^0 C through a series of steps including partial lignin breakdown, partial and full hemicellulose breakdown and complete cellulose breakdown[73].

The ash content of biochar slowly increases with temperature during pyrolysis and has an effect on the immobilization of pollutants. For example, in one of the studies it was observed that biochar prepared from pine needle at 700^o C has almost 10 times higher ash content in comparison to its biomass. The reason behind this can be the increase in concentration of organic matter and basic minerals along with an increase in the pyrolysis temperature[3]. Moreover, elemental composition of biochar is dependent on the type of feedstock used for its preparation. Hence, different types of feedstocks have distinct element composition and show different properties.

Also, elemental composition of biochar varies with temperature conditions during pyrolysis. Hence, biochar obtained from a range of feedstock shows different performance. The carbon content of biochar generally increases with rise in the pyrolysis temperature whereas there is a decline in the hydrogen, sulphur, oxygen and nitrogen content involved in the formation of gaseous products[2,35]. Biochar which is obtained from animal manure and biosolids generally contains high level of sulphur, potassium, nitrogen and phosphorous[2,35,42].

Table 1
Various biochar production techniques along with common feedstocks used in the preparation[17,88]

Biochar Preparation Techniques	Conditions of preparation	Feedstocks used	Product(s) obtained
Slow pyrolysis	Temperature range: 350^0C-550^0C (Low) Oxygen free atmosphere	Agricultural wastes, rice husk, bioenergy by-products, tea wasted	Biochar and syngas
Slow pyrolysis	Temperature range: 600^0C-900^0C (Low) Oxygen free atmosphere	Hazelnut, rice straw, municipal solid wastes, peanut shells, saw dust	Syngas and Activated biochar
Fast pyrolysis	Anhydrous conditions	Wood pellets, rapessed oil, corn cereals, palm oil , agricultural wastes	Bio-oil, Biochar and syngas
Gasification	High temperature Presence of oxygen in the atmosphere	Chicken waste, sewage sludge, animal bones and manure, kitchen waste	Biochar, methane and combustible ethane
Carbonization	Black-380^0C Brown-300^0C	Animal bones and manure, woody wastes	Biochar

Biochar produced from plant manure and plant biomass also has a high concentration of sulphur, nitrogen, phosphorous and potassium in comparison to wood-based biochars. For example, wood-based biochar has a potassium content of 349 mg/kg and pH 8 whereas straw based biochar has comparatively greater pH (9.5) and potassium level (961mg/kg)[86]**.** It was demonstrated by Laird et al[42] that almost half of the sulphur and nitrogen amount can vanish when pyrolysis occurs and temperature rises from 350^0 to 600^0 C.

Physical properties such as surface area, adsorption capacity of biochar, pore distribution and structure depend upon the temperature conditions during pyrolysis and elemental composition of the feedstock used to prepare biochar[6,16]. Biochar feedstocks tend to lose the volatile components present in the matrix as they get evaporated due to the rising pyrolysis temperatures. Due to this, the functional groups and exchange sites present on biochar surface decrease and ash content and surface area of the biochar increase. The surface area, volume of pores and their distribution get enhanced with rise in pyrolysis temperatures since the aliphatic carbon groups are transformed into aromatic rings which have structure similar to graphene[2].

Biochar which has a large concentration of carbon in aromatic rings is likely to have less functional groups on the surface. The functional groups present on the surface of biochar have a significant effect on its adsorption capacity while the type and content of functional groups depend on the feedstock and the temperature at which pyrolysis occurs[40,83].

Biochar which is low in aromaticity is prepared at a low temperature which has more C-H and C=O functional groups that support the adsorption of pollutants. The hydrophilicity of biochar surface is estimated by the molar oxygen/carbon ratio. This can also be used to find out the surface functional groups which are polar[4]. The Oxygen/Carbon ratio is low at a high pyrolysis temperature which explains that the surface is having a low hydrophilicity and aromaticity since there is a decline in the number of polar functional groups and high carbonization[4].The (oxygen +nitrogen)/carbon ratio is also a measure of polarity and it reaches a small value with increase in temperature[4].

Apart from slow pyrolysis, hydrothermal carbonization is an effective thermochemical technique to prepare biochar having high carbon content. Hydrothermal carbonization has a high energy requirement in comparison to slow pyrolysis. Hydrothermal carbonization technique uses the atypical wet biomass as the source. However, the heat energy is dependent on the water/solid ratio and moisture content is required[51]. Biochar which is prepared through this process has high CEC and large number of functional groups having oxygen. This biochar has a high acidity as compared to biochar produced from slow pyrolysis[29,53].

Biochar produced via hydrothermal carbonization is biodegradable and is not capable for carbon sequestration. Therefore, biochar produced via slow pyrolysis has more stability and can sequester carbon in a better manner[36]. Studies have shown that hydrochars have low yield as compared to slow pyrolysis biochar[7].

Very limited information is available about the biochar which is prepared via torrefaction, gasification and flash carbonization techniques for the removal of contaminants present in wastewater since these techniques emphasize more on the preparation of solid fuel, synthetic gas or bio-oil. Another important technique to synthesize biochar is flash carbonization. This method can synthesize biochar by igniting a flash fire in a compact biomass bed at high pressure (around 1-2 MPa). Fast pyrolysis is also a technique which can use thermal energy to convert biomass into gas, bio-oil and then biochar[37].

The technique gasification is generally used in the release of gases such as carbon dioxide, carbon monoxide, nitrogen and hydrogen at the cost of biochar and oils. Torrefaction is a technique that is carried out at a temperature range of 225^0-300^0 C (relatively low as compared to other techniques). Using this technology, if pyrolysis of biomass is done for a long period of residence time (approximately 1 hour), then biochar is produced as a by-product[56,67].

The first step in torrefaction is the breakdown of hemicellulose present in biomass to release an unsaturated solid substance (70-88% weight) which has properties similar to biochar[38,84]. Hence, techniques such as torrefaction, flash carbonizastion, gasification and fast pyrolysis produce biochar as a side product. But this biochar cannot be used in the treatment of wastewater since they have unfavorable properties according to the nature of contaminants[19,56].

Heavy metal removal mechanisms: Biochar is an effective agent that can remediate heavy metals from water samples through various techniques. These techniques are based upon how heavy metals interact with biochar and they include: precipitation, chemisorption (electrostatic interaction), physical sorption, complexation and ion exchange[10]. Biochar has a high similarity with activated carbon, since they also display high absorption ability for metals due to their heterogeneous surface[38]. Moreover, it has been reported that biochar has large surface area along with an organized distribution of pores. The different types of pores are: macropores (pore size more than 50 nm), mesospores (pore size in the range of 2-50 nm) and micropores (pre size less than 2 nm)[60]. Heavy metal ions can be easily absorbed physically on the surface of biochar which has high pore volumes and more surface area. Hence, metals have a high affinity for this biochar and get deposited inside the pores[41]. Biochar whose surface is negatively charged can easily absorb heavy metal cations via electrostatic attractions.

Biochar also forms complexes with various metals through interaction by unique functional groups and ligands present on biochar surface[14, 63] or via mineral phase solid precipitates of biochar[10,64,65].

Physical sorption

Physical sorption is a technique which involves direct remediation of heavy metals through the surface. Metal ions directly diffuse into the pores of biochar without forming any chemical bond. Hence, this technique is also called surface absorption. Plant and animal derived biochar having high pore volume and high surface area can be prepared by raising the carbonization temperature (above 300° C).

For example, biochar prepared from plants such as pine wood at 700° C and switch grass at 300°C can remediate copper and uranium present in water samples efficiently through diffusive physical absorption[46,61]. Unique biochar obtained from animal bones was able to absorb metal ions like Zn (adsorption capacity of 33.03 mg/g), Cd (adsorption capacity of 53.6 mg/g) and Cu (adsorption capacity of 45.04 mg/g) inside pores[12].

Ion exchange

Another method which can be used for remediation of heavy metals is absorption of heavy metals by an exchange of heavy metal ions and cations/ionizable protons present on the surface of biochar. The absorption of heavy metal on the biochar depends on functional groups present on the char surface and size of the metal ions. Hence, these two factors help to decipher the efficiency of ion exchange method. This technique involves the substitution of metallic ions with specific cations present on the biochar surface. According to Goldschmidt's geochemical division, metals present in 1st to 3rd group (such as Be, Ca, K, Sc, Mg, Na and Li) in periodic table have a high probability of substitution with other metals of these groups on the basis of difference in the charge, types of bonds and similarities of ionic radius.

Various transition metals present in the periodic table also exhibit a strong affinity for these exchange sites. Cation exchange capacity (CEC) for plant biochars depends on the functional groups present on the biochar surface (i.e. surface chemistry). Plant biochar having high CEC is excellent to remediate heavy metals. Biochar obtained from grass and non-woody plants mostly has high amount of oxygen and its surface is acidic.

Hence, it has higher CEC than biochars obtained from woody plants which have less amount of oxygen[24]. Plant biochar which is prepared at 300^0-350^0 C and has more amount of carboxylic acids, hence, has the highest CEC whereas biochar produced at a high temperature (above 350° C) has low CEC values. For example, biochar produced from rice husk at 175^0-180^0 temperature was observed to have a high absorption of mercury (Hg) and zinc (Zn) by hydrogen ion de-protonation and simultaneous replacement of Hg^+ (mercury) and Zn^{2+} (zinc)[18]. Biochars obtained from animal bones also follow the ion exchange technique to absorb metals like cobalt from water samples.[63]

Electrostatic interactions

Another technique which can be used for immobilization of heavy metals is the electrostatic interaction among heavy metal ions and the charged biochar surface. Electrostatic interaction is based upon 2 important factors: biochar's PZC (point of zero charge) and aqueous solution's pH[14, 59]. Biochar which is prepared at high carbonization temperatures (above 400° C) favors the buildup of grapheme structures in it which supports sorption via electrostatic interaction[39]. For example, sorption of lead was observed in rice and wheat biochar[69] due to electrostatic interaction between negatively charge biochar and lead cation. Electrostatic interaction has also been observed between positively charged biochar and chromium anion (Cr VI) at an acidic pH (2)[14].

Complexation

Another important mechanism which can be used for remediation of heavy metals is complexation. This technique is based upon the build-up of complexes (multi-atom structures) which are formed via unique ligand-metal bonding. Certain metals, especially transition metals which have partly full d-orbitals have a high attraction towards ligands. Hence, this technique is extremely useful for these metals. Biochar prepared at a low temperature generally contains oxygen containing functional groups like lactonic, phenolic and carboxylic groups which can be observed to efficiently interact with metals[47,57]. The amount of oxygen present in biochar has been reported to increase along with time probably due to biochar surface oxidation and formation of carboxyl group[68].

This proves that the complexation technique can rise with time. It has been observed that plant-based biochar is more effective in forming complexes with metals in comparison to animal-based biochar and hence, plant-based biochar can efficiently interact with a lot of heavy metals including lead, nickel, copper and cadmium. This way, phenolic and carboxylic group-metal complexes can precipitate on char surface. Also, some biochar obtained from animal sources like dairy manure and chicken litter carbon has phosphate groups (obtained from feed rich in nutrients) which interacts with heavy metals such as lead to produce pyromorphite like metal complexes[22,66].

Precipitation

The most common method used for heavy metal immobilization by biochar surface is precipitation. Precipitation refers to the production of solid/solids along with the sorption process. Precipitation can occur on a surface or in a solution. Rare earth elements and heavy metals having a medium ionization potential i.e. in between 2.5-9.5 (like Copper, Lead, Nickel and Zinc) have high chances to form precipitate[33] on the surface of biochar in comparison to the other elements.

Cellulose and hemicellulose present in plant biomass undergo thermal breakdown at high temperatures (above 300^0 C) and are likely to form basic biochar[76]. If these types of biochar are present in a solution, they can cause the precipitation of heavy metals. For example, in a study it was observed that biochar obtained from digested bagasse (having an alkaline pH= 10.93) had an ability to form a lead precipitate named Hydrocerrusite on biochar surface[65].

Apart from the alkaline nature of biochars, heavy metals can be precipitated due to the reaction of various minerals present in plant feedstock with metallic ions. High amounts of certain important minerals such as calcium, copper, iron, magnesium and silicon are present in those plant and animal biochars whose formation takes place at a high temperature. For example, the biochars produced from animal feedstocks like bone-based biochars and chicken litter-based biochars have 84% and 45% mineral content respectively[68]. Various mineral phases such as amorphous silica, hydroxyapatite, calcite, calcium anhydrite, quartz and slyvite are either internalized within biochar's carbon matrix or present freely.

It was suggested by Cao and Harris[11] that these mineral phases are present in a dissolved form in those biochars which are produced at a low temperature (less than 200^0 C). These mineral phases can have a direct interaction with heavy metals to produce precipitates like pyromorphite which are insoluble[66]. These mineral phases might also have less soluble forms which are present at relatively high temperatures (between 350 and 600^0 C). These forms have high chances to release while sorption takes place so that precipitates are produced on the biochar surface[32].

Characterization methods of biochar: Once the production of biochar is completed, the characterization of biochar is important in order to decipher the morphological structure and chemical constituents of biochar. The techniques used to analyze biochar involve XRD, NAI, TEM, SEM, XPS, NMR, EXAFS, EDS and NMR.

NAI or nitrogen adsorption isotherm is a technique which can measure biochar's surface area by calculating the adsorption capacity (multilayer) at a range of partial pressure of this gas (nitrogen). The calculation of surface area can be done on the basis of BET (Brunauer-Emmet-Teller) adsorption model (multilayer).

X-ray diffraction or XRD is used for analysis of carbon crystallites according to the intensity and angle of the diffracted beams. Carbon crystallites can be categorized into two groups. The result depends on the type of reflection pattern (RP). A broad RP denotes that it is non-graphitized carbon whereas sharp and narrow RP represents a graphitized carbon[95].

Fourier Transform Infrared Spectroscopy or FTIR technique can describe about the functional groups present on char surface on the basis of wave in light intensity's frequency domain with the help of the mathematical function (Fourier Transform). In this technique, we study the vibration occurring in the infrared spectrum at various positions which indicates diverse functional groups.

X-ray photoelectron spectroscopy or XPS is a technique that can calculate the valency of elements by finding out the photoelectron's energy diffusion.

Scanning Electron Microscopy or SEM estimates the morphological structure of biochar surface on the basis of reaction among samples and electron beams. Transmission Electron Microscopy or TEM is also used for the analysis of surface morphological structure with a higher resolution than SEM. TEM can also be used to estimate biochar's lattice constant.

X-ray spectroscopy or EDS is generally used along with an electron microscope so as to analyze the molar fraction of elements present on biochar surface according to the characteristic energy (X-ray photon based) for every element. If EDS is used along with TEM, it can analyze the molar fraction of chemical constituents available in biochar.

X-ray adsorption spectroscopy or EXAFS can be applied for characterization of biochar's poly-aromatic structure which is based upon the principle of scattering resonance that occurs multiple times.

Nuclear Magnetic Resonance or NMR can calculate the aromaticity of biochar carbon and can also find out the amount of non-protonated and protonated biochar carbon through the Zeeman splitting of nuclei (spin level) when placed in an external strong magnetic field.

Moreover, the pH, total nitrogen amount and total carbon concentration are the parameters applicable for characterization of biochar. The determination of pH can be done by mixing water and quantified biochar. The concentration of nitrogen and biochar can be done via the element analyzer[8].

Heavy metal removal from wastewater using biochar: Heavy metals can cause deleterious effects on the health of human beings even when they are present in a low concentration. Few heavy metals are extremely toxic and can get accumulated or stored in various organisms that are exposed to low concentrations of these metals for a long period of time.

Hence, the buildup of heavy metals inside the tissues of various organs can cause serious physiological effects. The heavy metals are one of the major contaminants of this century. Heavy metals released through industrial activities contribute towards the contamination of water bodies. The use of adsorption technique to remediate heavy metals from polluted water bodies is widely done[58]. Significant studies have been conducted on the adsorption of metal ions like nickel, arsenic, lead, mercury and cadmium via biochar and activated carbon since these are carbon rich, porous, cheap, easy to prepare and act as great heavy metal adsorbents[62].

Biochar for removal of nickel: Known to have carcinogenic properties, Nickel is a metal that has also reached prevalence when it comes to widespread soil toxicity. Hence, WHO (World Health Organization) has decided that permissible limit of nickel will be 0.02 mg/L. Nickel carries mutagenic properties and functions as an endocrine disruptor when inside the human body. Upon contact with dermal tissues, they may bring about allergic skin reactions such as itching, hair loss. Higher concentrations of it may also cause infertility due to its genotoxic, neurotoxic and immunotoxic properties. Upon growing accumulation in plants, it may cause browning of root tips reducing all other activities such as seed germination, photosynthesis, nutrient uptake, eventually leading to death of the plant. Major sources of nickel contamination in the soil include paints and pigments, plastic stabilizers and incineration of cadmium containing plastics and phosphate fertilizer[75].

In a study, a comparison between biochar produced from two digested feedstocks- whole sugar beet (DWSBB) and dairy waste (DDWB) was done for the remediation of four different heavy metals from water samples[31]. It was observed that DWSBB is more effective to remove nickel as compared to DDWB. It can remove upto 97% Ni^+ from aqueous solutions whereas DDWB has a very low efficiency of removal for Ni^+ i.e. 26%. The analysis of biochar was done using FTIR, SEM-EDS and XRD.

Gazi et al[20] reported that a MB (Magnetic Biochar) based on palm seed was used for nickel removal from water. The efficiency of this MB was checked at various pH, temperature values and different concentrations of nickel ion. It was observed that adsorption increases with temperature and concentration until an optimum value was reached. The effect of competing ions on the uptake of nickel was also observed. The efficiency of nickel removal by MB was found to be 28 mg/g or 87%. The maximum adsorption happened at an acidic pH (pH 3). The adsorption efficiency of MB declined when competing ions and salt were added into the solution.

It was found to be in the range of 15 to 24 mg/g (i.e. 45-75%). The MB had micro-mesopores on the surface and had a high magnetization value (65.8 $Am^2\ kg^{-1}$). Shen et al did a comparative study on the adsorption of nickel from four biochar obtained from rise husk (RH) and pellets of wheat straw (WSP) at two different temperatures- 550^0 C and 700^0 C i.e. RH550, RH700, WSP550. Kinetic studies were done to determine the adsorption equilibrium.

Also, the influence of solid/liquid ratio, pH and physiochemical properties of biochar on the nickel adsorption capacity was studied. The results of kinetic studies revealed that nickel (Ni^{2+}) adsorption on biochar obtained equilibrium before five minutes. It was observed that rise in the solid/liquid ratio led to an increase in the removal efficiency of nickel but decline in the amount of adsorbed nickel per unit gram of biochar. pH played an important role in the removal efficiency of nickel. The removal efficiency of nickel increased when the solution's pH was acidic (2-4), was constant around pH 4-8 and suddenly rose upto more than 98% at pH 9 and then remained same at more alkaline pH range (9-10).

WSP700 was observed to be the best adsorbent for nickel having the maximum adsorption capacity (0.427 millimole/gram) followed by WSP550 (0.215mmol/g), RH700 (0.173mmol/g) and RH550 (0.117 mmol/g). Biochar's pH and CEC can be factors for identifying the maximum removal efficiency for nickel ion and display an exponential and positively linear relationship respectively.

Vilvanathan and Shanthakumar[87] used *Chrysanthemum indicum* for removal of nickel ions via biosorption from a water sample. This experiment specifically involves the use of a fixed bed column (FBC). Here, a comparison between the raw form of the *Chrysanthemum indicum* flower (CI-R) and the biochar obtained by pyrolysis from the waste of this flower (CI-BC) was done to find out the more efficient biosorbent for Ni^{2+}. This study was based on multiple factors including the flow rate and bed height of the FBC and the initial nickel ion amount. The range of the flow rate was 1-5 mL/minute, bed height was 1-3 cm and the initial Ni^{2+} concentration was 25-75 mg/L.

This study indicated that these three factors are interdependent on each other and have a significant effect on the dynamic adsorption (DA) of Ni^{2+}. The equilibrium biosorption capacity of nickel was found to be 29.44 for CI-BC and 14.02 for CI-R at an initial Ni^{2+} concentration of 50 mg/L. The bed height was 1 cm and flow rate of column was 1mL/minute. In addition, desorption of nickel from the column was done using HCl as an eluent. Hence, it was proved that CI-BC is a better biosorbent for nickel and both CI-BC and CI-R are eco-friendly and effective feedstocks for both absorption and desorption of nickel ions.

Yang et al[93] prepared biochar from sewage sludge (SSB) and its modified form used for adsorption of nickel from aqueous solutions. It was observed that SSB had an adsorption capacity of 20.38 mg/g but when it was modified by loading α-FeOOH and α-Fe_2O_3 on SSB, then the modified SSB (MSSB) displayed a better adsorption capacity i.e. 35.50 mg/g with 0.01g of MSSB in an aqueous solution where nickel is present at a concentration of 100ppm. The most suited pH for adsorprtion to take place was 7 (neutral). Four major mechanisms were observed to be involved in adsorption of nickel onto MSSB. These were ion-exchange, co-precipitation, complexation and electrostatic interaction. Hence, sewage sludge is a great option for remediation of nickel and also a means to recycle the sludge.

Biochar for removal of copper: Copper is one of the most commonly available heavy metals mostly found in fertilizers and pesticides. Hence, WHO has kept the limit for copper to be 2mg/L in water. It can be highly poisonous to human beings and can cause severe damage to kidney and brain. It can also cause cirrhosis in liver, chronic anemia, irritation in stomach and intestine and Wilson's disease. In case of extremely high concentrations, copper can also be lethal for humans[75].

In an experiment, switchgrass was used as the feedstock for preparation of biochar by the HTC hydrothermal carbonization process and efficiency of biochar for the adsorption of cadmium and copper present in an aqueous solution was evaluated[85]. The HTC biochar was activated at room temperature by using an alkali (Potassium Hydroxide or KOH) in order to increase the adsorption capacity and porous structure of HTC biochar. In this study, a comparison between, HTC biochar (HTCB), activated HTC biochar (AHTCB) and a commercially available PAC (Powdered Activated Carbon) was done to find out the most efficient adsorbent of cadmium and copper.

The adsorption was dependent on factors such as dose of biochar, contact time and pH of aqueous solution. The characterization of biochar revealed that there was only a minute difference in the functional groups present on HTCB and AHTCB surface and that aromatic carbon was one of most the observed functional groups. PAC had a low adsorption of copper despite having greater surface area due to the surface structure. PAC lacked functional groups containing oxygen whereas AHTCB and HTCB had an abundance of these groups.

Hence, PAC was a weak adsorbent in comparison to both the biochars. AHTCB was the best adsorbent for copper. When carried out at pH 5, initial copper ion concentration of 40mg/L and a 24-hour contact time, it was seen that AHTCB at 2g/L had almost 100% removal efficiency whereas HTCB had 16% and PAC had 4%. The maximum adsorption capacity of AHTCB for removal of copper was 31mg/g (0.503 mmol g^{-1}) followed by HTCB (4mg/g) and PAC (1.8mg/g).

In a study, removal of copper by feedstocks such as orange waste, olive pomace, rice husks and compost, has been observed[65]. The preparation of biochar was done by the pyrolysis (temperature between 300^0C- 600^0C) and hydrothermal carbonization (temperature 300°C) technique. It was observed that adsorption of copper depends on several factors such as initial Cu^{2+} ion concentration, dose of the adsorbent, contact time and pH of the solution. For all the biochars, the optimum adsorption of Cu^{2+} occurred at a pH of 5-6, reaction time of 2-4 hours and an adsorbent dose of 5-12g/L.

In the comparison between various biochars, it was observed that olive pomace and rice husk biochars had the maximum copper adsorption efficiency by pyrolysis at 300^0C whereas for the compost and orange waste, maximum removal of copper was achieved by hydrothermal carbonization and pyrolysis at 300^0C methods. When pyrolysis was conducted at 600°C, low adsorption capacity of copper was observed for all the biochars.

Hadjittofi et al[23] conducted a study to evaluate the removal of copper by biochar synthesized from the fibers of cactus (*Opuntia ficus indica*). The impact of several factors like ionic strength, pH, temperature, ICC and contact time on adsorption of Cu^{2+} has been evaluated. The activation was done by oxidation via nitric oxide. The adsorption capacity of cactus biochar was reported as 3.5 mol/kg. Physiochemical parameters study indicates that outer-sphere complexes are formed at low pH and inner-sphere complexes are formed around an almost neutral pH (7). Overall, activated cactus fiber biochar is an efficient copper adsorbent and can be used in wastewater treatment.

Amin et al[5] reported that biochar produced from banana peel can be used for the adsorption of copper and lead from aqueous solutions. For obtaining the maximum adsorption, the influencing factors such as initial Cu^{2+} concentration, contact time, dose of the adsorbent and pH of the solution were evaluated. There were minimal changes in the adsorption capacity after 30 minutes and the adsorption equilibrium was obtained after 90 minutes. The adsorption efficiency of copper increased by around 40% -50 % when pH went from acidic (3) to slightly basic (9). Since the banana peel biochar had a greater surface area and extra adsorption sites, when the biochar dose increased from 0.2-0.5 g, a linear increase occurred in the copper ion adsorption. 1.5 g was the optimal biochar dose.

A decline of 50-70 % in the removal efficiency was observed when initial copper concentration went up from 50 mg/L to 300 mg/L. Although biochar was observed to be a better adsorbent of lead, decent amount of copper could also be removed by the banana peel biochar. Chemisorption was the most probable mechanism for adsorption of copper. Hence, the banana peel which is a waste product has a great potential for treatment of wastewater after a required modification and pretreatment that can enhance its response.

Liatsou et al[45] reported that activated biochar produced from the fibers of *Luffa cylindrical* can be used for the adsorption of copper from water samples. The influence of several factors such as mass of the adsorbent, temperature, pH, initial concentration of copper ions (ICC), contact time and ionic strength haven been well explained by the batch adsorption studies.

It was observed that even at an acidic pH (pH 3), the activated biochar had a removal efficiency of more than 85% and the adsorption capacity is Q_{max}= 248 g/kg. In addition, the mechanism of adsorption was the inner-sphere complexation between carboxylic moieties of surface and *Luffa cylindrical* biochar.

Hoslett et al[27] focused on the use of biochar obtained from the mix of municipal discarded materials (MMDM) for the adsorption of Cu^{2+} from aqueous solutions. The MMDM biochar was prepared by pyrolysis in a unique pyrolysis reactor based on a heat pipe. The effect of copper concentration (range of 50-250 mg/L) and pH of the solution (acidic range of 3-6) on the removal of copper from aqueous solution was evaluated. It was seen that the adsorption of copper was highly dependent on the solution pH and declined below pH 4.5 whereas copper concentration did not have any significant effect on the copper removal, especially at high concentrations (more than 100 mg/L). MMDM biochar prepared at a low temperature (about 300^0C) was observed to be an effective copper adsorbent having an adsorption capacity of 4-5 mg/g at pH 4.5 and initial copper amount between 50-100 mg/L.

The correlation with isothermal and kinetic models was altered due to the difference in the concentration of paper, plastic and organic biochars in MMDM, since all these materials have different properties. Plastic char was shown to have a high interaction between positive ions at the copper and biochar surface. On the other hand, organic and paper chars have less localized copper concentration. Hence, mechanism of adsorption of copper is different for the organic, plastic and paper biochar. Before using this biochar for decontamination of drinking water, it should be successful in the removal of other heavy metals and organic pollutants.

Biochar for the removal of lead: Historically used for plumbing purposes, the use of lead in industries has shrunk due to its notorious reputation for being toxic even at low concentrations. Hence, WHO has set the permissible limit of lead in drinking water as 0.01 mg/L. However, it still sees applications in battery manufacturing, herbicides, insecticides and the byproduct of aerial emissions from combustion of leaded petrol. Long term, excessive exposure of lead in children is known to cause impaired development, short term memory loss, reduced intelligence, coordination problems and disabilities in learning. In adults, extended exposure may lead to increased risk of cardiovascular disease, foot drop/wrist drop palsy and nephropathy[75].

Ding et al[13] focused on evaluation of properties of biochar synthesized from sugarcane bagasse (SBB) at four different temperatures (250^0C, 400^0C, 500^0C, 600^0C). The mechanisms involved in the adsorption of Pb^{2+} from aqueous solutions were also studied. It was observed that all the biochars proved to be efficient adsorbents of lead. There was a sharp decline in the maximum adsorption capacity of SBB from 21 mg/g to 6.1mg/g.

The removal of lead was rapid in the initial stages and was under the influence of complexation and cation exchange mechanisms. However, it became slow in the later stages which can be due to the intraparticle diffusion method. High sorption of lead occurred on the SBB produced at low temperatures (250^0C and 400^0C) since functional groups containing oxygen were present on the char surface.

The high temperature SBB (500^0C and 600^0C) had a lower lead removal efficiency. A decline in the amount of phosphorous (P) revealed that precipitation induced by P is also one of the methods involved in the adsorption of lead. The desorption of lead was done by HCl which denotes a reversible reaction. Hence, we can infer that temperature conditions during pyrolysis have a major impact on the properties and amount of metal adsorbed by the biochar. Baggase biochar can be effectively used for decontamination of lead containing solutions.

Ifthikar et al[30] reported the efficiency of magnetic sewage sludge biochar (MSSB) as an adsorbent of lead. It was observed that MSSB can be produced at a low cost with a feasible technique. It can enable recycling of sewage sludge which is a waste. It has excellent adsorption capacity. It can regenerate itself quickly and shows equal performance in a range of pH conditions. Moreover, due to its high magnetization, it can be easily separated via a magnetic field. The results explained that adsorption equilibrium of MSSB occurred under 1 hour and 2g/L of MSSB had an adsorption capacity of 249 mg/g, when the concentration of lead was 200 ppm. The mechanisms of adsorption were observed to be ion exchange and electrostatic interaction initially and steps of rate of adsorption were dependent on the inner sphere complexation and co-precipitation mechanism. The presence of pores, active sites and large surface area make MSSB an excellent lead adsorbent which can be commercially used for lead removal from wastewater.

In a study, the physicochemical characteristics of biochar obtained from anaerobic digestion sludge (ADS) and waste activated sludge (WAS) prepared by pyrolysis at 19 different temperatures (between 400^0C- 800^0C) were examined[26]. The adsorption capacity of the sludge-based biochars for various heavy metals was also evaluated. The adsorption of lead from aqueous solutions was studied in detail. It was observed that biochar produced from ADS at 600^oC (ADSB600) had a high thermal stability, excellent arrangement of pores and unique chemical groups on the char surface. Moreover, it was an efficient adsorbent for lead ions with an adsorption capacity of 51.2 mg/g.

Ion exchange and precipitation are the major possible mechanisms for removal of lead followed by surface complexation and electrostatic interaction. Hence, we can conclude that ADS is an effective adsorbent for heavy metals and can be successfully used in decontamination of wastewater along with effective recycling of the waste sludge.

Mireles et al[55] reported the use of nine biochars obtained from three distinct types of biomass at variable temperatures for the removal of lead from aqueous solutions. This biomass includes pistachio shell (PS), corn stover (CS) and organic peel (OP). These are pyrolyzed at 3 different temperatures (300 °C, 450 °C and 600 °C). The adsorption of lead was evaluated on the basis of physicochemical characteristics of the biochar and batch adsorption studies. It was observed that CS biochar produced at 600 °C and OP biochar produced at 300 °C were the best adsorbents for lead with removal efficiency (RE) more than 94%. PS biochar had a low lead RE (just around 20%-35%). The RE of Pb^{2+} increased with the pH (range 2-6). The highest removal occurred at pH 6. Langmuir model best co-related the experimental adsorption results with the calculated results.

Hence, monolayer adsorption occurred and it was seen that CS biochar prepared at 600 °C (CS600) was the best adsorbent of lead out of all the biochars since its S_{MAX} was 2-10 folds more than PS and OP biochars The adsorption capacity of lead was 25,000 mg /kg for CS600 followed by 11,111 mg/kg for OP300 and 2500 mg kg^{-1} for PS600. Functional groups having oxygen and char surface area are the two factors that have a major impact on the adsorption of lead. This experiment proves that corn stover is an effective adsorbent for lead and pH and temperature of pyrolysis are significant for causing changes in the RE of lead.

Biochar for removal of arsenic: Arsenic is an element that belongs in the metalloid category. Usually found along with sulfur and other metals, arsenic also occurs naturally in crystalline forms. WHO has decided the limit for arsenic to be 0.01 mg/L.The main source from which arsenic leeches into the soil content usually comes from pesticides and wood preservatives. Once they enter the human cell, they cause serious effects to essential cellular processes such as oxidative phosphorylation and ATP synthesis. The accumulation of too much arsenic in the human body causes a condition known as arsenic poisoning. It has many short terms symptoms such as encephalopathy and watery and bloody diarrhea. If too much arsenic is accumulated in plants, they may end up disrupting the crucial phosphate dependent metabolism present in plants[75].

Van Vinh et al[85] reported the use of biochar derived from raw pine cone (PC) and the modified form (loaded with zinc) for the adsorption of As (III) (arsenite) from aqueous medium. The results explained that the As^{3+} removal was almost constant (66.08 ± 3.94% for raw PC biochar and 87.62 ± 3.88% for zinc loaded PC biochar) when pH increased from 2-4 (acidic) and declined when there was an increase in the pH from 4-12. The reason behind this can be the high affinity between positive char surface and arsenic species. It was found out that the PC biochar loaded with zinc had a relatively high adsorption capacity (7.0 ug/g) in comparison to raw PC biochar (5.7 ug/g).

Hence, surface modification enhanced the adsorption of arsenic. Although the process of adsorption of arsenic on the zinc modified PC biochar is a spontaneous and exothermic process, the zinc loaded PC biochar is a cost-effective efficient adsorbent of arsenic from groundwater or polluted surface water. Wang et al[90] reported the use of magnetic biochar (MB) obtained from hematite for the adsorption of arsenic from water samples. In this study, MB was produced by the direct pyrolysis of mixture of pinewood biomass and natural hematite mineral. The heat treatment of hematite produced a composite substance based on biochar and converted hematite into gamma Fe_2O_3 particles. The biochar modified by hematite had better adsorption capacity for arsenic since the gamma Fe_2O_3 particles on char surface acted as adsorbents for arsenic from aqueous solution via electrostatic attractions. MB has a high magnetization and can be easily removed via external magnets. Hence, MB is an inexpensive agent that can be used in various environmental applications to remediate arsenic.

In a study, the adsorption of arsenate and arsenite by the biochar derived from pyrolysis of perilla leaf at two different temperatures (300^{o}C and 700^o C) has been studied[60]. It was observed that the biochar prepared at 700^o C (B700) was the best adsorbent for arsenic and had the highest RE for As^{3+} followed by B700 (As^{5+}), B300 (As^{3+}) and B300 (As^{5+}). (Adsorption capacity in the range of 3.85-11.01 mg/g). It was seen that there was a decline in the arsenic removal (from 76% - 60%) when the pH increased from neutral (7) to basic (10), only with the exception of B700 (As^{3+}) for which the removal of arsenic was directly proportional with the increase in pH i.e. 88% - 90% from pH range 7-9. The adsorption data and characterization of biochar revealed that precipitation/ surface complexation and pore filling were the most important mechanisms for removal of arsenic, especially by B700.

B700 was a better arsenic adsorbent compared to B300 because it had a greater surface area and high aromaticity. Both B700 and B300 were effective in the removal of arsenic from the groundwater naturally contaminated by As, when arsenic concentration was in the range of 23-190 ug/L despite the presence of competing anions in groundwater like carbonate, phosphate and sulphate and cations in well water. The highest RE for As was 97%-100% by B700.

It can be concluded that biochars obtained from perilla leaf, especially B700 can effectively remediate the groundwater containing arsenic. The effect of pyrolysis temperature on arsenic removal needs to be studied in detail. The advanced spectroscopic techniques give us a basic idea about redox conversion of As^{3+}/ As^{5+} with biochar and how biochar interacts with arsenic in an aquatic atmosphere.

Sattar et al[74] did a comparison between the removal efficiency (RE) of arsenite (As^{3+}) and arsenate (As^{5+}) by peanut shell (PS) and biochar produced from peanut shell (PSB) from aqueous solutions. The effect of various factors such as pH, dose of the adsorbent and initial concentration of arsenic on removal of arsenic was also studied. It was observed that the RE of PSB was relatively higher than RE of PS. PSB successfully remediated 95% of As^{3+} (Adsorption capacity= 4.75 mg/g) at 7.2 pH and 99% of As^{5+}

(Adsorption capacity= 5.01 mg/g) at 6.2 pH. The dose of adsorbent was 0.6 g/L, equilibrium time of 2 hours and initial arsenic concentration was 5 mg/L.

Surface complexation between arsenic and functional groups on char surface was the main possible removal mechanism. The characterization of biochar revealed the presence of aromatic and hydroxyl functional groups on biochar surface which contributed towards the adsorption of arsenic by electrostatic attraction and surface complexation.

Hence, it was proved that PSB is an eco-friendly effective biosorbent for arsenic and can be utilized for the decontamination of arsenic rich water samples (especially arsenate rich) and can provide effective means for the recycling of peanut shell waste.

Conclusion

This review has focused on the removal of heavy metals from aqueous solutions by biochar. The production of biochar can be done by a wide variety of biomass materials used as feedstocks and are pyrolyzed by different processes at various temperatures. This biochar can then be used to reduce water pollution. The analysis of interaction mechanisms reveals that different kinds of interactions including chemical bonding, chemical interaction, physical adsorption, ion-exchange and electrostatic attraction are predominantly responsible for binding of heavy metals on biochar surface.

A lot of studies have reported that biochar is a eco-friendly and cost-effective biosorbent for the removal of various heavy metals from an aqueous solution. This is because of certain physicochemical characteristics of biochar such as excellent adsorption ability, high surface area, charged surface and presence of unique functional groups. Biochar has a great potential to adsorb heavy metal contaminants. Addition of biochar decreases the leachability, bioavailability, toxicity and mobility of organic and inorganic pollutants and is beneficial for the immobilization of contaminants present at high concentrations. Hence, biochar can be seen as an extremely important agent for remediation of heavy metals from waste water in the coming years.

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