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Mechanisms of Trace Metal Elements Removal from Water using Low-Cost Biochar Adsorbents: A mini review

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ABSTRACT

Trace metal elements are toxic to the environment and human health and can be removed from water through adsorption. Development of low-cost adsorbents would always been a matter of achievement of every adsorption study as usually many adsorbents were found to be expensive in nature. In this regard, biochar adsorbents gained significant attention due to high adsorption capacity, low-cost and environmental sustainability. Pyrolysis is used to produce biochar adsorbents at varying temperature ranged from 300°C-700°C. The adsorption capacities of palm fiber biochar adsorbents are remarkable which was found around ~198 mg/g for cadmium removal. However, bamboo-based biochar had 868 mg/g of adsorption capacity for arsenate removal. This review aims to provide the current discusses the sources and impacts of trace metal elements in water along with properties of biochar including its composition, surface area, pore structure, and surface functional groups. Further, various types of biomasses have also been mentioned for producing biochar such as agricultural wastes, food wastes, forestry residues, etc. The paper also discusses the different types of mechanisms involved in the adsorption of heavy metal biochar adsorbents like electrostatic attraction, ion exchange, surface complexation etc.

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INTRODUCTION

The “phrase” heavy metals referred to metals having “atomic density” >5 g/cm^3 such as Sn, Cd, Cu, Hg Co, Pb, Mn, Ag, As, Al, Cr, Ni and Zn. All these metals are commonly believed to be the foremost detrimental contaminants which occurs in soil and water (Nadeem et al., 2006). The rapid increase in global population, economic activity, and improper management of industrial activities have all contributed to major heavy metal pollution. Hence, many rivers and groundwater bodies are having alarming levels of trace metal elements and it may dangerous for ecological systems. Furthermore, when trace metal elements enter the human body, they may considerably influence the health because of their reactive and non-biodegradable natures. However, all types of organisms require a variety of metals in small quantities for their growth. These metals are highly mobile in the ecosystems and bio-accumulative in the food chain when released without proper treatment. In order to protect public health and maintain a healthy environment, standards have been developed for acceptable discharge limits of the pollutants to control their levels in the discharging effluents of the industries (Kahlon et al., 2018; Martins et al., 2019; Dhiman et al., 2022). Pollution caused by heavy metal may be hazardous and can be cancer-causing agents which includes Cr, As, Hg, Cd, and Pb. Heavy metal contamination in

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agricultural and industrial wastewaters has led to toxicological manifestations in living things. In order to prevent heavy metal ions from entering the environment, it is crucial to remove them from wastewater effluents (Jaishankar et al. 2015; Ali et al., 2019; Shetty and Goyal, 2022). Consequently, heavy metal elimination from water has received a lot of attention. Currently, "ion exchange, chemical precipitation, electrodialysis, adsorption and membrane filtration" are the principal treatment techniques to eliminate the heavy metal from water (Demirbas et al., 2008). The various techniques for cleaning up heavy metal contamination from water are compared in which it shows that adsorption is currently the most effective way to reduce heavy metal pollution from water and it is also one of the widely recommended approaches for water purification due to of its benefits, including ease of use, high removal rate, broad applicability and affordable reusable adsorbents (Li et al., 2020).

The current global trends point to a greater requirement to improve ecological standards while utilizing the fewest resources possible for wastewater treatment. The selection of appropriate adsorbents is one of the prime factors in adsorption technology. The two most important considerations which are necessary while selecting effective adsorbents to eliminate the trace metal elements one is cost effectiveness and second selectivity. Greater surface area, rapid rate of adsorption, and quick equilibrium time are some qualities that make an excellent adsorbent (Cai et al., 2019). In this sense, biochar adsorbents are relatively more suitable because of high efficiency for the treatment of water owing to their lower-cost, abundance of raw ingredients, and minimal environmental negative impacts (Qiu et al., 2008). Therefore, in this mini review, advance information has been compiled to give an exposure to the researchers (especially nascent) working in similar disciplines.

Biochar as low-cost sustainable adsorbents

A substance with a high content of carbon known as biochar is produced thermochemically converting biomass at temperatures <700 °C with a small amount (insignificant) of oxygen. Typically, crop stalks, wood chips, leaves, animal sludge, manure, and carcasses are employed as the raw material for biomass, which is used to make biochar (Tan et al., 2017). As a result of its capacity to fix carbon along with increasing the fertility of soil, biochar has drawn significant interests for their use in the generation of bioenergy and environmental clean-up (Laird et al., 2010). It has been remarked that biochar possesses beneficial characteristics such as distinctive pore volume, specific surface area, functional groups, and unique chemical characteristics (Xiao et al., 2020). Additionally, it has enormous potential for adsorbing heavy metal pollutants from water. Because of this, biochar has been employed frequently for the adsorption of "heavy metal" contaminants present in contaminated water. However, due to variation in the adsorption capabilities of produced biochar by employing various types of raw materials and manufacturing conditions, one biochar is unable to withdraw all kinds of trace metal elements from wastewater. The quantity of heavy metal might affect the adsorption efficiency of biochar. Therefore, different biochar adsorbents show varying adsorption capacities for different trace metal elements (Tan et al., 2015). Even though many biochar-based adsorbents have been shown poor adsorption capacity to extract trace metal elements from water (Ma et al., 2014). However, it can be improved after carrying out some modifications in the surface properties of the biochar adsorbents to increase the sorption capacity and selectivity towards heavy metal pollutants. Some studies demonstrated that the "presence of chemical species, pH, temperature, dose of biochar, adsorption period as well as concentration of adsorbates in polluted water," etc. may also affect the biochar's ability to adsorb contaminants. Additionally, prolonged contact to the environment may result into the alteration in the physical as well as chemical characteristics of biochar, which in turn decrease its ability to bind with trace metal elements. Therefore, it is advantageous to take corrective action to maximize the adsorption efficiency by examining the parameters that influence adsorption efficiency of biochar for trace metal elements (Chen et al., 2022). The most common method for producing bio-sorbents is through a straight forward carbonization of microorganisms like bacteria and algae as well as cheap and easily accessible biomass materials like bagasse, straw, and the shells of various foods including peanuts, egg shells, cottonwood, pinewood, clay, corn stalks, chestnut shells, and other agricultural wastes.

Biochar is one such bio-sorbent, and it is commonly made by pyrolyzing the different kind of feedstock as discussed above. Adsorbents produced from the biomass using a number of different additional carbonization processes (Panwar et al., 2019). Numerous techniques for improving the efficiency of the biochar-based sorbents, such as "chemical modification, mineral magnetic modification, steam activation, and sorbent impregnation" have been studied in depth (Rajapaksha et al., 2016; Park et al., 2016; Alam et al., 2018). Pine bark waste was used to extract heavy metal from metal industrial effluent (Reddy and Lee, 2014). Ahmad et al. (2018), made a compost from banana peels underwent heat treatment. It was discovered that the high productivity of biochar-based sorbents through the pyrolytic conversion of the biomass. Similar to this, adding nano-zero-valent iron to biochar-based sorbents improved their removal effectiveness. The presence of iron above the surface of biochar-based sorbents proceeded to an enhancement in the number of functional groups which contains oxygen and improved complexation. Adsorbents must exhibit great cyclic stability (regeneration possible) in order to be applied in any way to industry. In this regard, a study by Lata et al. (2015) demonstrates that desorption rates are high at lower acid concentrations, but at low pH values, the sorbents made of biochar are destroyed, lowering the biomass. However, adsorption and desorption are diametrically opposed processes. Therefore, the bigger the adsorption capacity and the more unfavorable desorption process will be, the more metal ions have an affinity for the adsorbent (Bogusz et al., 2015). Desorption is important for regenerating and recovering adsorbent and adsorbate molecules, which reduces secondary pollutants and process costs (Hassan et al., 2015). Many investigations on biochar-based sorbents have been successful in enhancing their adsorption capabilities. Researchers have recently developed sorbents based on biochar that are acceptable for industrial uses by magnetizing, impregnating nanoparticles, creating composites with other adsorbents, and making other modifications. Hence, it appears that biochar adsorbents and its associated products formed during pyrolysis can have industrial scope too (Godwin et al., 2019).

Formation of biochar adsorbents

In contemplation to achieve the necessary characteristics in the biochar adsorbent materials in terms of high metal removal efficiency, proper synthesis approaches must be followed. These processes should be economically viable along with least possible negative environmental effects. Moreover, their production should be in experimentally controlled methods. Biochar-based adsorbents have been created and modified using a variety of techniques. It has also been observed that the characteristics of bio-sorbents affected by the kind of biomass, the synthesis protocols as well as modifications processes carried out as shown in Figure 1. (Reguyal et al., 2017; Alizadeh et al., 2018; Dinari et al., 2018; Zhou et al., 2018).

To evaluate the efficiency of these approaches, a variety of parameters are taken into account, including mechanical strength, preparation costs, ease of synthesis, pore size, specific area, adsorption capacity, etc. Biochar was proofed as the efficient bio-sorbent for eliminating trace metal elements from aquatic environments in the regard of cost, environmental impact, and efficacy (Moreira et al., 2017; Wu et al., 2017). Its characteristics include high carbon content, huge surface area, higher porosity, and a strong attraction for trace metal elements (Qambrani et al., 2017). Gasification, combustion, and pyrolysis (quick pyrolysis, and slow pyrolysis) are the common thermo-chemical techniques that can be utilized to create efficient biochar adsorbents. Many different biomass wastes, including "paper mill waste, pine chips, peanut hulls, chicken litter, forest plant biomass, cotton seed hulls, manures, tyres, animal bones, agro-

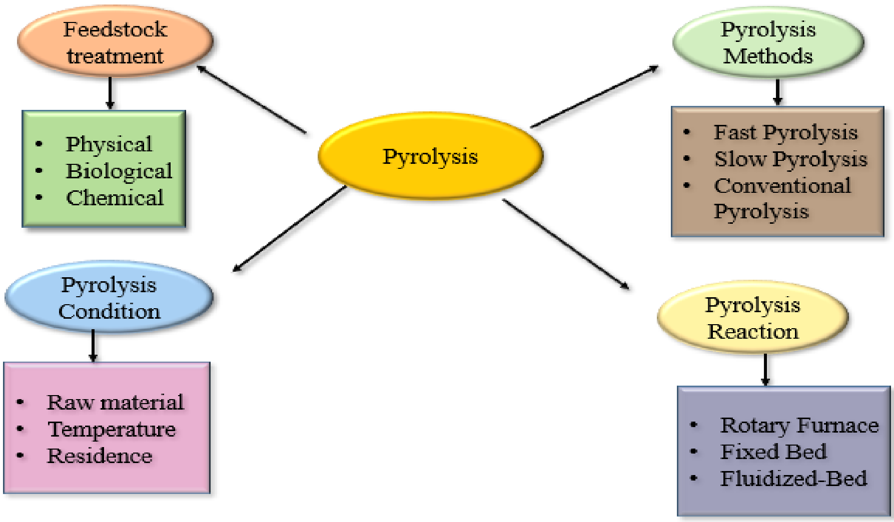

Fig. 1. Factors affecting the pyrolysis process for biochar production

industrial biomass, municipal solid waste, etc.", were observed to be employed in the synthesis of biochar. It was discovered that the kind of biomass material and conditions of pyrolysis induce a considerable effect on the characteristics of biochar. A larger lignin content in feedstock results in high yield of biochar, but, the large content of "cellulose or hemicellulose" resulting in easier thermal or chemical changes to the functional groups. Elongated residence durations, higher pressures, lower temperatures, and slow heating rate (at 0.01-2°C) are utilized in slow pyrolysis.

As a result, biochar with larger particles, more ash, and more lignin can be produced in greater amounts. Therefore, slow pyrolysis might be a reliable and affordable alternative for producing biochar on a modest scale. Fast pyrolysis, in comparison to slow pyrolysis, uses smaller residence durations. The drawback of this approach is that it yields 12% less biochar while creating 75% more bio-oil and 13% more non-condensable gases (Ghysels et al., 2019; Priharto et al., 2020; Gupta et al., 2020; Adeniyi et al., 2023). Additionally, it has been demonstrated that, in contrast to slow pyrolysis with extended residence durations, "quick pyrolysis" (lower temperature) produced partially pyrolyzed charcoal fractions. Gasification is another technique to make biochar which results in the conversion of biomass to vapour-phase (gases) such H_2 CO_2, CO and minimal quantity of CH_4 via heating the biomass at higher temperature (700–800 °C) in limited oxygen atmosphere. Only 10% biochar can be created with this method, and the remaining products include gases and tar (Yaashikaa et al., 2020; Gabhane et al., 2020; Liu et al., 2022).

Due to a number of drawbacks in pristine biochar and other bio-sorbents, modified bio-sorbents are now commonly used for enhanced metal removal from water even for low adsorbate concentrations, easy recovery, and reuse of adsorbents. The effectiveness of the bio-sorbents/biochar can be improved by including metals such as "zirconium, iron, nickel, chromium, copper, titanium, zinc, and alloys" in the form of their "salts, oxides", etc. in the matrix of the biochar adsorbents (Nistico et al., 2018). These materials were found to have greater adsorption capacity as well as improved pore size, surface area, crystalline nature, thermal stability, and surface functionality (Yin et al., 2017). From 4.28 emu/g at 400 °C to 36.8 emu/g at 650 °C, the degree of magnetization of biochar adsorbent was detected to be inversely related to pyrolysis temperatures (Gupta et al., 2020) as it has been reported that metal oxide ultrafine nanoparticles produced by a number of techniques, including "sol-gel, aqueous sol-gel, ball milling, hydrothermal and precipitation processes" have been successfully utilized as modifiers

Table 1. Summary of removal trace metal elements from water by biochar

Target heavy metal	Feedstock	Name of biochar	Pyrolysis temperature	Initial concentration (mg/L)	Adsorbent dose (g/L)	pH	Adsorption capacity (mg/g)	Reference
As(V)	Rice straw		600 °C	100	0.2	7	25.6	Mukherjee et al. (2021)
Hg(II)	Pine-tree needles	Sulfur-modified pine-needle biochar (BC700_S2)	700°C	100	-	8	48.2	Jeon et al. (2020)
Cr(III)	*Enteromorpha prolifera (E. prolifera)*	FMIB beads	500 °C	-	3	4	18.24	Qiao et al. (2020)
Cr(VI)				-		2	11.13	
Hg(II)	*Populus adenopoda*	FeCl$_3$- modified biochar	900°C	5	-	-	97%	Feng et al. (2020)
As(V)				5	-	-	42%	
As(III)				5	-	-	62.5%	
Cr(VI)				50	-	-	19.6%	
Pb(II)	Eucalyptus leaves	AHA/Fe3O4-γFe$_2$O$_3$@PBC	600 °C	50	0.01	5	99.82	Du et al. 2020
Cr(VI)	Corn straw	F1M3BC	400 °C	100	2	2	118.03	Zhu et al. (2020)
Cd(II)	Spent coffee	MBC	400 °C	40	0.1	7	10.42	Hussain et al. (2020)
Hg(II)	Sugarcane bagasse	CSB	550°C	1	0.0100	6	11.47	Giraldo et al. (2020)
Pb(II)	Grape pomace	GPL2700	700 °C	300	-	6.5	126	Jin et al. (2020)
As(V)	bamboo culms of Guadua chacoensis	BBCA-Fe)	-	10	0.05	7	868	Alchouron et al. (2019)
Pb(II)	Rice husk	RH700	700 °C	-	0.1	9.8	26.7	Shi et al. (2019)
Cd(II)	Corn straw	BC/FM	500 °C	100	125	5	127.83	Zhang et al. (2019)
Pb(II)	Corn straw		500 °C	100	125	5	154.94	
Cr(VI)	sugarcane bagasse	SMBC2	600 °C	100	1	4.6	71.04	Yi et al. (2019)
As(III)	Douglas fir	MBC's	900 °C	10	2	7	5.49	Navarathna et al. (2019)
Cd(II)	palm fiber	MBCO	400	200	1	6	197.96	Zhou et al. (2018)
Cd(II)	sycamore tree sawdust	TMBC (318)	550 °C	20	1.25	6	137.3	Li et al. (2018)

to improve the structural along with thermal stability of the adsorbents (Li et al., 2006). The formation of magnetic bio-sorbents includes a variety of changes, including pre-treatment, single-step modifications, post-treatment modifications, double-step modifications, alterations aided by microwaves, hydrothermal modifications, etc (Gupta et al., 2020). In the recent years, microwave aided synthesis of magnetic bio-sorbents has been carried out for quick adsorbent synthesis only it takes 5–10 min with high adsorption capacity, large surface area and huge pore size (Thines et al., 2017). This process can be a replacement of traditional pyrolysis method in the formation of magnetic biochar adsorbents. There are some studies on the use hydrothermal approach, which involves mixing of biomass feedstock with water at a temperature between 100 °C and 350 °C in order to limit greenhouse gas emissions because water can absorb the gas (Wiedner et al., 2013). Engineering biochar and magnetic bio-sorbents are still under investigation as a creative method that would allow the plant tissues to accumulate the metals or nanoparticles directly as bio-sorbents without requiring any complicated modification. They show better physico-chemical characteristics and adsorption capability, but this is still in the experimental stage and needs to be further investigated (Tang et al., 2017). The co-precipitation approach compels a solute to precipitate out of a solution through a carrier rather than dissolve in it, and which can also be used to create magnetic biochar adsorbents due to the phenomenon surface adsorption, inclusion, or occlusion mechanisms. In addition to the procedures discussed above, calcination is also used to forge magnetic adsorbents. This technique involves a heating of carbon material in a pressurized autoclave in the absence of fusion to dispel water, gases, and other volatile components, resulting in thermal breakdown (Williams and Misra 2011). The magnetic biochar produced with this approach with $FeCl_3.6H_2O$ had a larger surface area, varied morphology from macro-mesoporous structure high crystallinity, and easy to recover and reuse (Ma et al., 2014). Therefore, it is a critical need to create these innovative and successful approaches to increase the usability of biochar because biochar was not very effective at removing metals without the proper modification and functionalization.

Mechanisms involves in the elimination of trace metal elements from aqueous media by biochar

There are different mechanisms which can be used in the adsorption of the trace metal elements over the surface of the biochar from the aquatic environment like “physical adsorption, electrostatic interactions precipitation, ion-exchange, and complexation” as depicted in the Figure 2.

Physical adsorption

The main governing factors of physical adsorption are surface characteristics like specific surface area and pore structure. While mesopore growth might also encourage the diffusion of pollutants to speed up the adsorption kinetics, micropore growth and it will be an extra support to the physical adsorption (Yang et al., 2019). The physical adsorption is not involved in formation of any chemical bond as shown in Figure 2. The surface area as well as porosity increase if the feedstock derived from the organic waste pyrolyzed at higher temperature. For instance, it has been reported that Cu and U(V) may be removed from biochar made from switch grass and pine wood at temperatures of 300°C and 700 °C, respectively (Liu et al. 2010; Kumar et al. 2011). It was seen that the biochar made from the bones of animal is effectively employed for the removal of the Zn (33.03 mg/g), Cu (~45.04 mg/g), and Cd (53.6 mg/g), from the aquatic environment due to the greater porosity. The film pore diffusion model was employed to interpret the experimental data (Choy and McKay 2005).

Ion-exchange

A second possible mechanism for the elimination trace metal elements from water through adsorption is ion exchange. It involves the interchange of positively charged heavy metal ions in an aqueous environment by the positively charged ions on the biochar surface, as depicted in Figure 2 (Zhao et al. 2017). According to Qian et al. (2016), a rise in temperature (between 100 and 400 °C) can significantly enhance the capacity of charcoal adsorbents to extract Cr(III). The sorption of Cr(III) by cations like Ca and Mg over the biochar surface suggests that cation exchange is considered to be the primary mechanism for the sorption of heavy metal. Because of the high amounts of Ca and Mg that the biochar discharged into the water as CaO and MgO, respectively, during the sorption of Cr(III), there was a minor pH rise that may have contributed to this. The efficiency of biochar adsorbents obtained from agricultural wastes in immobilising Cd was examined by Trakal et al. (2014). They discovered that the “cation exchange” process was the prime mechanism for the sorption of Cd and that grape stalk biochar had greater cation exchange capacity as compared to plum stone biochar. At pH 2–5, Ca and Mg were the primary contributors to the sorption of Pb (40–52%), although Na and K only contributed 4.8–8.5% via the “cation exchange” process. Through cation exchange procedure, lead was adsorbed on biosolid biochar (Lu et al. 2012). Additionally, Pb sorption on oak biochar revealed that cation exchange was the chief mechanism for adsorption of Pb (Mohan et al. 2007).

According to Zhang et al. (2015d), the quantity of released cations from water hyacinth biochar would be same as the amount of Cd sorbed, proposing that the sorption of Cd on biochar occurred through cation exchange. The pH less than 8.0, cadmium has a low propensity to hydrolyse, however pH greater than 11.0, entire cadmium is present as a hydroxo-complex.

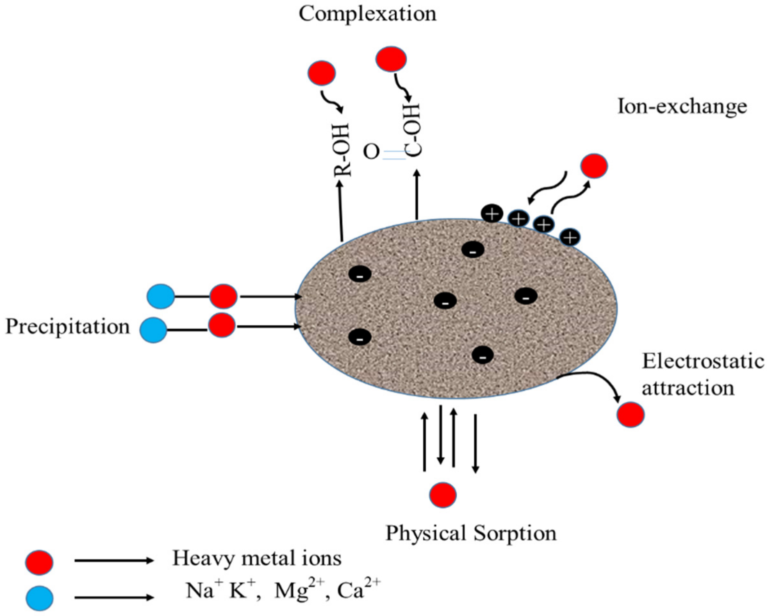

Fig. 2. Possible mechanisms for the adsorption of heavy metal ions from wastewater

Cd(II) is the dominating species in an aquatic natural solution. Harvey et al. (2011) shed light on the mechanism which involves in the sorption of Cd via honey mesquite, cordgrass, and loblolly pine biochars from an aqueous solution. The ability of these plant biochars to exchange cations was used to divide them into 2 categories: low or/and high. The principal method for Cd sorption for high-capacity group would have been cation exchange. It was seen that using a flow calorimetry experiment on how K and Cd might behave in place of Na-saturated biochar. The form and intensity of the heat signals for the Cd exchange for Na and the K exchange for Na have been similar, suggesting that cation exchange is the primary mechanism, according to flow calorimetry.

Complexation

Complexation is the process in which the "metals" and "ligands" on the surface of the biochar forms an inner- or outer-sphere multi-atom complexes (Figure 2). Since transition metal with partially fulfilled d-orbitals have substantial attraction to the ligand this form of sorption is crucial. Due to the significant attraction that transition metals with half-filled d-orbitals have to the ligands, this form of sorption is necessary (Crabtree 2009). It has been shown that, oxygenated functional groups, like "hydroxyl, carboxyl, and phenolic groups," retained at biochar prepared at lower temperature, effectively bind and fasten trace metal elements from water (Liu et al. 2010). The percentage of oxygenated functional groups on biochar multiplied with time due to oxidation processes that result in the production of additional carboxyl groups on the material's surface, which strengthened ligand-metal interactions in aquatic environments (Harvey et al. 2011). The major trace metal elements, like Cd, Ni, Cu, and Pb are readily drawn and bound to the plant-based biochar to form the complexes of "carboxylic" and "phenolic-metal" on the biochar surface. Phosphate ligands from nutrient-rich diets are also present in some animal-based biochar adsorbents like chicken litter, and dairy manure. They also manufacture metallic compounds (pyromorphite) and that would be bind to the trace metal elements, particularly Pb (Cao et al. 2009). The Cd-carboxyl group's complexation process can also be involved in Cd sorption. FITR spectra before and after the adsorption of Cd via biochar showed a slight change in the spectral regions of carboxyl groups responsible for the sorption of Cd (Trakal et al. 2014). However, Cd removal from aqueous solutions was mostly accomplished through formation of complex of Cd with the surface of biochar bearing a negative charge for example biochar having graphene-like structures derived from loblolly pine, cord-grass, honey and mosquito (Harvey et al. 2011). Dong et al. (2013) manifested that the "carboxylic, hydroxyl, and phenolic" functional groups of "Brazilian pepper" biochar have an important role in producing Hg complexes. The scientists also discovered that when pyrolysis temperature increased (from 300°C to 600 °C), the sorption of Hg dropped from 24.2 mg/g to 15.1 mg/g (pH 7). In addition to this, biochar formed at 300°C and 450 °C indicating that carboxylic, phenolic, and hydroxyl groups were connected in the sorption of Hg from 23% to 31% and 77% to 69%, respectively. However, only 9% of the Hg was adsorbed by the process of complexation with hydroxyl and phenolic functional groups, while 91% of the Hg sorption was recorded on biochar adsorbents produced at 600 °C. According to Xu et al. (2016), complexation was the predominant mechanism in the sorption of Hg from water by biochar adsorbents developed from hickory chips and bagasse. Hg complexes were primarily observed in the XPS spectra after adsorption of Hg by bagasse biochar. According to Qian et al. (2016), biochar colloids showed a significantly higher rate of Cr removal than residue-based biochar, which was assigned to the colloids' higher concentrations of surface functional groups rich in oxygen. This finding suggests that complexation is a common process during the removal of Cr(III) from water.

Studies on Cr(III) are uncommon, while a majority of those is on Cr(VI). They mainly focus on removing Cr using biochar (Wnetrzak et al., 2013; Yang et al., 2013; Pan et al., 2013). According to the scant literature, the three mechanisms for Cr(III) sorption by biochar are electrostatic attraction occurs between positively charged Cr(III) ions and negatively charged biochar, cation exchange, and complexation of oxygenated functional groups. Rice, followed by peanut, soybean, canola, and biochar generated from crop straws, exhibited the highest sorption capacity (0.48, 0.33, 0.28, and 0.27 mmol kg^{-1}), which is commensurated with the quantities of oxygenated functional groups (1.34, 1.13, 0.80, 0.63 $mmol^{-1}$). According to a research, functional group complexation likely contributes significantly to the sorption of Cr(III) via biochar.(Pan et al. 2013). The FTIR spectra of biochar after Cr(III) sorption demonstrated, peak shifting of functional groups compatible to phenolic OH region stretching, aromatic C=C ring stretching, and aliphatic C-H stretching (Pan et al., 2013). According to Qian et al. (2016), colloids of rice straw biochar (2 mm) have a substantially higher capacity for sorbing Cr(III) than residues, which is consistent with the fact that biochar colloids contain more oxygen functional groups and shows that complexation may be involved in Cr(III) sorption.

Electrostatic attraction

The literature also reports a different way to confine trace metal elements through electrostatic interactions between the trace metal elements and charged surfaces of biochar (Figure 2). To assess the appropriateness of this mechanism in the adsorption of trace metal elements by biochar, the pH of the water and the point of zero charge of the biochar adsorbents can be used (Dong et al. 2011; Mukherjee et al. 2011). Due to the structure of biochar, like that of graphene structures, is what causes heavy metal adsorption to happen, it is more favourable when higher temperatures are employed in the biochar synthesis process (Keiluweit and Kleber 2009). The exceptional Pb adsorption effectiveness on rice and wheat straw biochar is caused by the potent electrostatic interactions between the negatively charged biochar surface and the positively charged Pb ions (Qiu et al. 2008). Furthermore, Dong et al. (2011) also reported that the electrostatic interaction is responsible for the elimination of Cr(VI) from water (Dong et al., 2011). Wang et al. (2015) employed pinewood biochar produced at 600°C (pH_{PZC} >7) with a maximum As(V) sorption of 0.3 mg/g to sorb As(V) from water at pH 7. At a solution pH of 7, As(V) predominantly existed as $HAsO_4^{2-}$, whereas the biochar surface beared positive charge and some of the functional groups were protonated. As(V) oxyanions interrelate to the positively charged functional groups via electrostatic attraction. Biochars are more positively charged and have huge levels of protonation of functional groups at lower solution pHs than at higher solution pHs, making them able to electrostatically attract As(V) oxyanions. According to Wang et al. (2016b), pinewood biochars with pH_{PZC} >10 improved As(V) sorption as solution pH was decreased from 9 to 2. Ni/Mn oxide-modified pinewood biochars showed similar pH influences on As(V) sorption (Wang et al., 2016a).

Precipitation

The formation of solids over the surface of biochar adsorbents is a common indicator of the process of heavy metal precipitation during the adsorption from aqueous solution (Figure 2). In general, precipitation is regarded as a crucial method to remove trace metal elements using biochar adsorbents. In comparison to other elements, precious metals with intermediate ionisation potentials, like Ni, Pb Cu, and Zn, produce more precipitates on biochar (Krauskopf and Bird 1967). The biochar (alkaline) is obtained from plant (waste) by pyrolyzing “cellulose” and “hemicellulose” at a higher temperature (>300 °C), when applied to adsorb metallic ions from water and it may result in the generation of metal ion precipitates (Cao and Harris 2010).

Precipitation was proposed as the primary Cd sorption mechanism because dairy dung biochar contains comparatively large quantities of dissolved “carbonate and phosphate” (Xu et al., 2013). The rise in Cd sorption capacity with temperature expands from 200 to 350°C is majorly due to a rise in minerals, particularly soluble CO_3^{2-} in biochar (2.52 vs. 2.94%), (31.9 to 51.4 mg/g). When dairy manure biochar was created at 350°C using visual MINTEQ modelling and an FTIR experiment, it was found that 88% of the Cd sorption was ascribed to the “precipitation” of “metal-phosphate and carbonate”, while 12% of the Cd sorption was from Cd^{2+} bonding (Xu et al., 2013). Due to the restricted amount of soluble P in biochar formed at 350°C, metal phosphate precipitation made about 3% of the total precipitation, but carbonate precipitates were responsible for up to 98% of the Cd. Due to the comparatively high concentration of soluble P in the biochar generated at 200°C, phosphate precipitates accounted for 22% of the total Cd sorption, whereas carbonate precipitates accounted for 78% (Xu et al., 2013). X-ray diffraction experiments following Cd sorption proved that water hyacinth biochar produced Cd carbonate and phosphate minerals (Zhang et al., 2015d). Additionally, Trakal et al. (2014) showed by FTIR spectra that the CO_3^{2-} peaks in biochar containing greater degree of ash from grape stalks and husks migrated subsequent Cd sorption, most likely as a result of surface precipitation of Cd carbonates. According to Xu et al. (2014), the organic fraction’s Pb sorption capacity was only 1 mg/g, compared to the inorganic fraction’s >300 mg/g, suggesting that Pb complexation with functional groups contributed little in elimination of Pb and precipitation was the main mechanism. In the case of manure biochar, phosphate precipitation led to higher Pb sorption than carbonate precipitation (68 vs. 32%), but straw biochar showed the opposite trend (36 vs. 64%).

Challenges and future scope

Apart from economic advantages, biochar adsorbents have been found very effective adsorbents in the removal multiple types of water contaminants such as dyes, trace metal elements, etc. Moreover, such types of adsorbents can be developed by using waste biomass so it would a bit helpful in managing biomass wastes too. However, a number of obstacles and restrictions may also exist during the production and use of biochar adsorbents in water treatment. In order to avail full advantages, these hurdles must be reduced/removed to achieve better results during water treatment. Hence, a number of topics need to be addressed prior to the production as well as application of biochar adsorbents such as:

a) The evidence revealed that standardising of biochar production processes depends not only on the intended use but also on the types of feedstocks used. For example, to create high-quality biochar adsorbents, the post-optimization and synthesis processes should work together. To lessen the negative effects on the environment, very less quantity of the chemicals can be used during the preparation process. Further, exploration of doping agents and green activators can also be an extra advantage.

b) Selection of appropriate feedstock as well as figuring out the best pyrolysis temperature are also determining the quality of biochar produced. Additionally, polycyclic aromatic hydrocarbons produced during biochar pyrolysis may be released into the environment which can deteriorates the quality of human as well as wildlife, thus, their alternative options or remedy should also be addressed carefully.

c) Therefore, to ascertain the connection between the biochar's structural features and its characteristics, substantial research is needed. Due to the appearance of several types of functional groups, free radicals and few unwanted impurities on the surface, it is crucial to maintain the quality of biochar adsorbents in specific circumstances. Moreover, it is also important to ensure the availability of desired functional groups (beneficial for adsorption) throughout the process of converting biomass into biochar and developing its porous structure.

d) It is important to indicate the structure of biochar at both the macroscopic and microscopic levels in order to describe its properties. Additionally, it is feasible to search the effects of various types of treatment methods on the surface functional groups and sorption performance of the biochar adsorbents produced, which can be helpful in reducing the levels of alkaline, acid and loading materials.

e) Moreover, production process can also be altered little bit and feedstock needs to be pre-treated in order to produce clean biochar materials which will be fully free from toxic chemicals/derivatives. It is obvious that a thorough examination of the process of converting biomass into biochar should be conducted with the aim of maximising the composition along with enhancing adsorptive characteristics of biochar.

f) Development of novel and environmentally friendly biochar matrix composites with large surface areas and specific surface properties can also be explored for better results. Since biochar is an interesting research topic, however, still there are many gaps and uncertainties have been observed during its commercialization and its use at ground application which demands for more investigation.

g) Importantly, methods of recycling and renewing biochar, the raw materials used to produce biochar, are among the critical factors for efficient biochar utilisation. It is interesting to note that improvements in synthetic and microbiological chemicals are probably connected to changes in the valorisation of lignocellulosic biomass. To further decrease solid waste on a large scale and enhance resource efficiency, fresh solid wastes should be used as feedstocks for the production of biochar for removing heavy metal from water.

h) The direction of future research could comprise carrying out pilot-scale experiments, making field applications, and researching more efficient and environmentally friendly methods for designing biochar adsorbents to remove trace metal elements.

i) Additionally, it is also important to devise appropriate methods for safely handling biochar materials during the adsorption of trace metal elements at large scale to avoid the aggregation of competing materials found naturally in water. Pilot-scale research may also be employed to contrast with commercial sorbents in order to thoroughly assess the improved biochar life cycle, which includes biochar's stability and reusability cycles.

j) Long-term stability demands additional research because it is a persistent problem in restoration science. Furthermore, more in-field study is required to demonstrate the durability and metal-binding capacity of biochar.

k) Additionally, it is important to address a number of issues, such as how to prevent following chain impacts and the ageing process as well as pore clogging due to presence of biotic or abiotic materials.

l) Prior to their commercial deployment, these bio-adsorbents must be examined for the presence of any kind of possible environmental hazardous materials. In order to assess the practicality of these bio-adsorbents in real water treatment processes, additional research is essential on the hazardous effects of already employed bio-adsorbents and it can be further helpful in protecting both the environment and human health.

m) Currently, heavy metal removal uses innovative adsorbents made from biowaste are very common. Therefore, it is important to investigate using industrial bio-waste materials to create bio-adsorbents. This would ensure the manufacturing of affordable bio-adsorbents using wastes and decrease the negative effects on the environment.

n) Even though the mechanism of heavy metal adsorption onto bio-adsorbents has been studied in a variety of ways, the majority of the findings published are based on short-term experimental investigations and provide little information on the long-term consequences. Therefore, it is crucial to investigate the long-term adsorption impacts of bio-adsorbents in order to enhance the practical uses for the treatment of trace metal elements-polluted water. To optimise the adsorption mechanism and equipment design, further research on the mechanism of heavy metal adsorption onto bio-adsorbents is therefore still needed.

o) It is necessary to choose and select a suitable agricultural waste as an adsorbent which might give effective affinity for the adsorbate in order to obtain maximal adsorption capacities and selectivity.

p) Adsorption investigations typically use a single adsorbent; few studies have taken into account several adsorbents. Therefore, in order to investigate the potential of hybrid bio-adsorbents which would successfully increase adsorption capabilities, extensive research is required.

q) Further, maintenance expenses, high energy requirements, decreased efficiency, and the regenerating of bio-adsorbents are also hot topics for future studies during heavy metal removal from water.

Apart from above limitations of requirements, biochar adsorbents have been considered to be as an alternative potential treatment due to its many advantages over typical carbonaceous materials. The mean energy requirement to produce biochar is found to be much lower than that required to generate activated carbon. Most importantly, biochar has gained attraction among new sequestration techniques as it is believed to have sufficient economic values along with replacing conventional carbon compounds. Additionally, developing biochar with enhanced catalytic and adsorptive features have been reported recently. Due to their high affinities for metal ions, the adsorbent obtained from the bio-wastes have become environment friendly and economically advantageous for the treatment of water that has been contaminated by trace metal elements over the years.

CONCLUSION

Biochar adsorbents are low-cost adsorbents and can be developed through various types of raw materials like agricultural wastes, fruit peel, etc. It will also be helpful to manage these wastes somehow. Pristine biochar adsorbents are having less adsorption efficiency for water pollutants removal. Surface of biochar adsorbents can be changed using many types of metallic ligands and their efficiency will be enhanced as observed in previous studies. Slow pyrolysis is one the approach which could produce the best quality biochar adsorbents. Mechanisms of trace metal elements removal may include physical adsorption, chemisorption or else. Regeneration of such materials is also possible so that they can be used in several cycles. Hence, it can be considered as sustainable adsorbents for heavy metal removal from water. Moreover, it will also be helpful in providing safe water to the low-income communities as per the objectives of sustainable development goals ("SDG 6: CLEAN WATER AND SANITATION") as suggested by the United Nations in year 2015.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

In addition, no life science threat was practiced in this research.

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