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Heavy Metal Adsorption Using Biocarbón from Agricultural and Agro-Industrial Waste for Decontamination of Soils and Water Sources: a Review

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Currently, the presence of heavy metals in different ecosystems represents aserious threat to humanity and animals, since they are considered persistent, bioaccumulative and difficult to degrade, and for their removal, physicochemical methods such as adsorption have been widely studied. On the other hand, the accumulation of waste from the agricultural and agro-industrial sector has become an important environmental problem and a way has been sought to take advantageof these resources by producing an adsorbent material such as Biochar, which is organic carbon, used to decontamination of soils and aquatic habitats. Althoughthe removal efficiency of this material is lower than that of activated carbon, it is considered a low-cost and sustainable alternative, which has recently attracted alot of research attention due to its wide application prospects. Based on recent studies, the main characteristics of biochar were reviewed, factors that influence its behavior, as well as its application in decontamination through the removal of heavy metals in water and soil. In this review, high percentages of heavy metal removal efficiencies, modern adsorption methods were found, as well as the different properties and factors of the biosorbent such as surface area, pH, temperature, pressure, among others, that influence the performance of the material

1. Introduction

Biochar is a carbon-rich porous material produced from various biomass by pyrolysis at relatively low temperatures (<700 °C). It contains functional groups, such as carboxylic acid, phenols, hydroxyl, carbonyl, and quinine (Pal and Maiti., 2019). The organic carbon content of biochar can be up to 90%, depending on the biomass source. Biochar has generated great interest worldwide due to its use in multiple applications such as soil remediator, fuel, catalyst, adsorbent for pollutant removal and carbon sequestration (Toková et al., 2020; Agbede et al., 2020; Moradi et al., 2019; Bastos et al., 2020; Yang et al., 2019; Fidel et al.,2019; Jiang et al., 2020; Dejene and Tilahun, 2020). In addition to these applications, the production and use of biochar allows the recycling of organic wastes from agriculture such as sugar cane residues, corn straw or solid waste such as fruit husks and seeds, which are generally discarded and become a problem for the environment, threatening the quality of air, water and soil, additionally, the use of biochar allows solving problems related to livestock and wastewater (Baninajarian and Shirvani, 2020; Matheri et al., 2020; Salazar-López et al., 2021).
Considering the above, this review focuses on the different advances related to the decontamination of water and soil using adsorption as a removal method. Note that important factors influence the use of Biochar and its production, which will be discussed in this exhaustive research. Normally, pyrolysis is called this process, which will be described below.

2. Pyrolysis process

Pyrolysis is a thermal degradation process of biomass-derived feedstocks under oxygen-limited conditions (Hussain et al., 2017). The pyrolysis process generates three products: a liquid called bio-oil, syngas, and a solid or biochar (Lu et al., 2019; Zhou et al., 2020).

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Pyrolysis processes are classified into two main types, fast and slow, according to the rate at which the biomass is altered. Fast pyrolysis, with a biomass residence time of a few seconds, generates more bio-oil and less biochar than slow pyrolysis, for which biomass residence times can vary from hours to days (Woolf et al., 2016). Slow pyrolysis minimizes the risk of producing dioxins and polyaromatic hydrocarbons (Hansson et al., 2020). Depending on the type of pyrolysis and the conditions under which it is conducted, such as low or high temperature, low or high pressure, fast or slow speed, heating rate, particle size and biomass material, the yields of each phase change markedly (Lu et al., 2019).

Matamba et al. (2020) examined the influence of pressure on palm kernel hull pyrolysis. The experiments were conducted between 0.1 - 4.0 Mpa. The reactor pressure had a considerable influence on the pyrolysis yield. For palm kernel hull pyrolysis in a tubular reactor, 2 Mpa was the optimum pressure with respect to yield. Low temperature pyrolysis provides a material with more desirable soil improvement properties than charcoal or ash (Hansson et al., 2020; Fidel et al., 2019). In a conventional pyrolysis system, large particles are difficult to remove and process in the fluidized bed, as they tend to settle to the bottom of the bed where heat transfer and thermal processing rate is reduced (Wu et al., 2020). Generally, biochar is not a fully carbonized product because its production by pyrolysis is operated at low temperatures. Another characteristic that influences the yield of biochar is the inert and lignin content (Tomczyk et al., 2020).

Residence times in pyrolysis is a relevant factor when obtaining biochar or organic carbon, therefore, considering the above information, fast pyrolysis is not recommended in the case of increasing the production of biochar, since it is impossible to obtain biochar, by performing the process in a few seconds does not guarantee the formation of carbon and the total disappearance of other compounds present in the raw material to be transformed. However, uncontrolled accumulation of agricultural and agro-industrial wastes has led to evaluate the possible use and application of these wastes to produce biochar to contribute to decontamination and give added value by creating waste by products such as biochar.

3. Agricultural and agroindustrial wastes to produce biochar

There are many biomasses serve as feedstock to produce biochar, such as crop residues, wood biomass, animal litter, and solid waste. These residues have great potential to remove environmental pollutants due to its wide feedstock availability, low cost, and favorable physical/chemical surface characteristics, such as large specific surface area, microporous structure, active functional groups, and high pH (Huang et al., 2017). Residues such as sugarcane bagasse, corn, rice straw and stalks of different trees have been used to produce biochar. Biochar is produced from anaerobically digested sugarcane bagasse with the advantage of producing methane in the process; Additionally, biochar is produced from undigested sugarcane bagasse (Yang, 2016). The biochar produced from digested waste had more negative pH, surface area, cation exchange capacity, anion exchange capacity, hydrophobicity, and surface charge compared to biochar from undigested sugarcane bagasse. These characteristics of the biochar produced from anaerobically digested sugarcane bagasse can be efficiently used to improve soil quality, sequester carbon, or as a low-cost adsorbent to remove pollutants from wastewater (Saleh et al., 2020) The biochar produced from corn plants prepared at low carbonization temperatures (200-500 °C) by rapid pyrolysis and gasification. The results showed that biochar prepared in the temperature range of 200-500 ° C had a faster sorption rate and shorter sorption equilibrium time methods to produce biochar with desirable properties in relation to soil amendment compared to biochar produced at higher temperatures for fast pyrolysis. This indicates that it is important to monitor pyrolysis conditions and selection of appropriate and carbon sequestration (Zhang et al., 2019). Additionally, Zhao et al. (2020) investigated the ability of biochar produced from hardwood at 450 °C and corn straw at 600 °C to adsorb Cu (II) and Zn (II) in aqueous solutions.

However, at low metal concentrations there is low competition, with increasing concentrations of Cu(II) and Zn(II) the adsorption capacity of Zn(II) by the biochar decreased by approximately 75-85% in the presence of Cu(II) at concentrations above 1 mM. The results indicate that the biochar produced from agricultural wastes can act as an effective adsorbent surface, but caution should be exercised when using these adsorbents for treating mixed waste streams. Ghorbani et al. (2019) produced biochar from rice straw at a pyrolysis temperature of 500°C by varying soil physicochemical properties and nitrate leaching in two types of soil (sandy and clayey clay) under greenhouse and wet conditions. The benefits of biochar in the clay soil were greater than in the sandy clay soil, with improved soil aggregate stability and nitrate retention.

OK et al. (2018) studied the biochar produced from the pyrolysis of willow, pine and miscanthus biomass in their book and found that biochar amendments significantly influenced seed germination and plant growth. Recently, biochar was obtained from the slow pyrolysis of elephant grass as a feedstock in the gasification process using a mixture of steam and air in a cyclone furnace to produce a tar-free liquid fuel by evaluating the effects of surface area and inherent alkali and alkaline earth metal species on biochar reactivity (Ferreira et al., 2019).

In another study, Tomczyk et al. (2020) compared the characteristics of biochar produced by slow pyrolysis at 600°C for agricultural residues: sunflower leaves, a mixture of sunflower leaves and rapeseed pomace, and wood waste. In this study, the biochar from the mixture of sunflower leaves and rapeseed pomace showed the highest specific surface area, surface charge value and functional group content of the three biochar. The carbon content of the biochar ranged from 84 wt% to 89 wt%.

3.1. Use of biochar for heavy metal adsorption

Biochar has excellent adsorption capacity due to its large surface area, which is suitable for use as a low-cost chemical adsorbent (Alam et al., 2020), including some of the most common environmental pollutants such as heavy metals. Figure 1 shows the surface area of biochar produced from Miscanthus (Ok et al., 2018), rice straw, broiler litter (Song and Guo, 2012), corn and Zacate stubble (Jaganathan and Varunkumar, 2020), pine leaf wood chips (Choudhary et al., 2020), poultry litter (Pariyar et al., 2020), *Lemna minor* (Reyes-Ledezma et al., 2020), safflower seeds (Zhou et al., 2020), swine manure (Meng et al., 2018), hemp (Wallace et al., 2019), walnut wood, bagasse and bamboo (Sun et al., 2014).It is notable that the surface area increases with high pyrolysis temperature in each type of biomass.

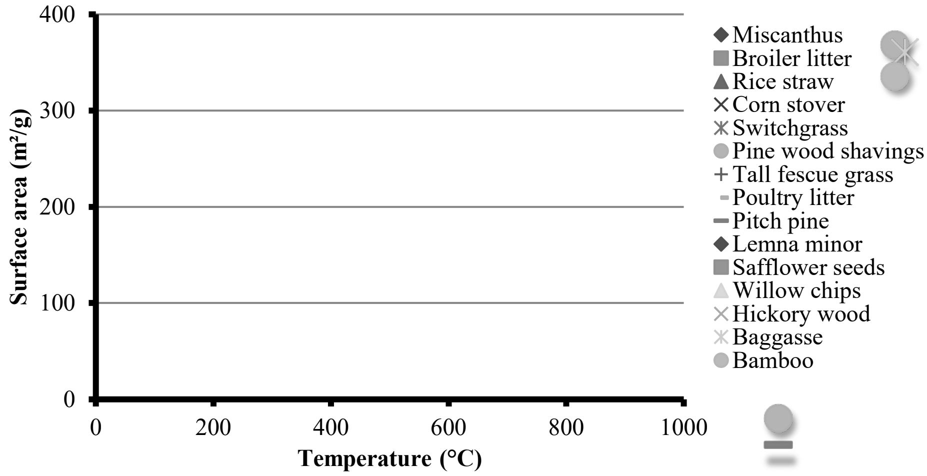

Figure 1. Surface area of biochar. An increase in temperature pyrolysis results in an increase in surface area.

Additionally, it was identified as a "super-adsorbent" of neutral organic compounds. This component removes dyes from aqueous solutions, and due to its large surface area and micropore structure, it is an effective adsorbent of cationic and anionic dyes (Qiu et al., 2020). However, considering the use of biochar in soils, some properties attributed to it that positively affect these were studied. In a forage oat crop, it was concluded that the application of biochar (BC) to the crop soil is an alternative to improve the yield of this crop, where BC had a beneficial influence on plant height and oat biomass production.

3.2 Removal of heavy metals for water decontamination

Heavy metals can be found in wastewater discharges from many companies in the mining, metal smelting, material manufacturing and oil industries, contributing to the toxic load of lakes, rivers and seas. Note that heavy metals are recognized as extremely dangerous environmental pollutants, due to their high toxicity, carcinogenicity and potential for bioaccumulation and persistence, even at low concentrations. Among the metals found in surface waters are Chromium (Cr), Lead (Pb), arsenic (As), mercury (Hg), copper (Cu), cadmium (Cd), among others. Studies demonstrate the potential of biochar to immobilize and remove these elements from aquatic environments. Deng et al., 2020 obtained biochar from sawdust waste modified with silicate and magnesium salts to remove Cu (II) and Zn (II) in aqueous solution, considering properties such as surface area, pore volume and adsorption kinetics of the material. The results indicated a high percentage of metal removal (99%) when reaching the adsorption equilibrium with a Cu and Zn concentration of 10 mg/L in one day. Tomczyk et al., (2020) has been studied in the effective removal of Ag and Cu from aqueous media by using a biochar obtained from sunflower husks, a mixture of sunflower husks and rapeseed pomace and wood residues at pH 5 and adsorption temperature of 21°C, where efficiencies of 83.6 for Cu and 99.8 for Ag were found in only 50 min of operation, demonstrating the high percentage of removal of the above-mentioned biomasses. Biochar was six times more effective in adsorbing Pb than commercial activated carbon (Alam et al., 2020). Biochar from tea waste has been used to remove Cr (VI) from aqueous solutions as a function of pH, contact time and

biochar mass. The maximum adsorption capacity for Cr (VI) was 123 mg/g in acidic medium and equilibrium was reached in 16 h (Khalil et al., 2020).
In another case, biochar from tea waste was used to immobilize Cd as a function of size, pyrolysis temperature and time using sediment-water meso-microcosms with 14 days of incubation. Liu et al, (2009) showed that the contact time for 95% lead removal with biochar was less than 5 h. Mohan et al, (2007) also found that a 40-70% reduction of total lead using wood as biomass occurred within 1 h.

Table 1. Biomass source, heavy metals, operating conditions, and adsorption capacity.

Bioadsorbent	Solute	Operating conditions		Adsorption capacity (mg/g)	References
		Ph	Temperature (°C)		
Sawdust waste	Cu (II)	4	-	214.7	Deng et al., 2020
	Zn (II)			227.3	
Pineapple wate	Cd (II)	6	25	92.7	Teng et al., 2020
Sludge	Cr (III)	4	25	28.89	Qui et al., 2020
Sunflower husk and pomace rapeseed mixture	Cu (II)	5	21	12.9	Tomczyk et al., 2020
	Ag			136.2	
Rice straw	Pb (II)	5.5	25	127.57	Liu et al., 2020
Modified peanut shell	Cd (II)	6	40	21.2	Ho et al., 2017
	Pb (II)			47.0	
	Ni (II)			22.5	
	Zn (II)			18.1	
	Cr (II)			8.3	
Water hyacinth	Cd (II)	5	30	41.05	Ding et al., 2016
	Pb (II)			43.2	
Prosopis africana husk	Cd (II)	4	22	29.9	Elaigwu et al., 2014
	Pb (II)			31.3	
Kans Grass Straw	As(III)	7	40	2.0	Baig et al., 2014

Qiu et al., 2020 biomass being studied as sludge from agro-industrial processes for the removal of Cr(III) and Cr(VI) from wastewater. The biochar preparation was given considering different pH, pyrolysis temperature of 600 °C and ambient adsorption temperature. The results show the importance of pH in the adsorption processes, where the best removal efficiency occurred at pH 4, obtaining efficiencies of 28.89 and 64.12%, respectively. These results shows an average potential of this type of biomass for water decontamination. Kans Grass straw was pyrolyzed at 500 °C for 2 and 4 h to evaluate the adsorption efficiency of As (III, V) under different operating conditions. The results showed better adsorption efficiency at pH 7 and 40 °C with a contact time of 3.4 h, achieving 70 and 88% for As (III) and As (V) respectively (Baig et al., 2014).
Considering the above, it can be deduced that the adsorption time influences the efficiency, observing that after 1 h of execution a high percentage of removal is achieved. However, the pH shows that when it is between 4 - 6, the adsorption capacity and adherence of heavy metals to the biochar surface increases. Another relevant factor is the operating temperature, where it can be observed that the higher the temperature, the higher the removal or immobilization of contaminants. Table 1., shows operating conditions, efficiencies, biomasses used and the solute to be treated for water decontamination. It is evident that sawdust and rice straw have a higher adsorption capacity, due to the composition of the biochar obtained from them, as well as the surface area they can present.

3.3 Heavy metal removal for soil decontamination

Due to the presence of metals in all environments, it has become necessary to evidence and demonstrate their presence in soils. There are indications that it influences the decrease of microorganisms in the soil, damage to fauna and health problems in terrestrial animals.
The addition of biochar to soil has become a solution to soil erosion and nutrient leaching problems, as it improves soil fertility, promote plant growth, increase crop yields and reduce contaminations. The main properties of biochar are as follows: high surface area with many functional groups, high nutrient content and slow release fertilizer. Given the high total porosity of biochar, which increases water holding capacity in its small pores and helps it infiltrate from the soil surface to the topsoil, the use of biochar can increase the available water capacity by more than 22%, thereby increasing the stability of soil aggregates and crop production.

It is proposed that biochar can be used to provide nutrients and increase soil fertility, and the potential of biochar, as well as the number of nutrients depends on the biomass and pyrolysis temperature; it can improve the physical, chemical and biological properties of the soil, including microbial activity and structure (Ding et al., 2016). However, biochar has become a solution to remove, immobilize and remediate soils contaminated by heavy metals due to its high resistance to chemical and biological decomposition favoring that carbon remains longer in the soil, reducing CO_2 emissions. Additionally, the benefits of its application include increased crop production and reduced nutrient losses by leaching due to its high retention capacity. Liu et al., (2020) evaluated the effect and action mechanisms of lychee biochar in the remediation of Pb, Cd, As and Zn from soil using sunflower (Helianthus annuus) finding a 5% growth in sunflowers. However, the concentrations of the metals studied in the leaves and receptacles of sunflower plants did not vary, but their concentration in roots, stems and seeds decreased significantly by 10 - 37% compared to the control ($P < 0.05$).

Abbas et al., (2017) evaluated the effect of biochar obtained from rice straw on soil Cd immobilization and uptake of other metals by wheat. The results showed an increase in soil pH and silicon content. Additionally, from plant morphology they observed an increase in plant height, ear length and grain and root production compared to the control. the presence of biochar in soils significantly decreased Cd. In contrast, in wheat shoots, roots, grains, Zn and Mn concentrations increased and Cd and Ni increased. In conclusion, the use of biochar is effective in the immobilization of metal in the soil and reduce its absorption and possible effect on crops.

4. Conclusions

In this review, different raw materials from agricultural and agroindustrial wastes were evaluated to know their potential as biochar in the decontamination of heavy metals in aquatic and terrestrial environments. It was found that some factors that directly influence their adsorption are surface area, pyrolysis temperature and pH, the latter pH the most relevant. The pH range in which a good performance of the biochar is considered is between 4 - 6 because it is observed that at these points the surface properties of the adsorbent showed the best operating conditions. Regarding the pyrolysis temperature, it was found that the higher the pyrolysis temperature, the higher the surface area of the biochar, which generates a better adsorption capacity of the metal ions present in the samples. Alternatively, the adsorption of metals such as Pb, Zn, Ni, Cr and Cu was significant in terrestrial environments, contributing even more to this thanks to its remediation power and its contribution of nutrients to the soil, thus generating relevant changes in these and in the plants.

In this review, biochar was obtained from a wide variety of biomass materials as raw material and pyrolyzed using different processes to reduce the contamination present in aquatic and terrestrial ecosystems. In future, the biochar is considered a novel and feasible adsorbent, due to the excellent adsorption capacity, low cost, and contribution to the improvement of the environment.

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