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Use of biochar as an alternative material for the treatment of polluted wastewater

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Abstract: Biochar is the product of biomass decomposition, whose physicochemical characteristics are associated with its origin and the combustion method used. Among these properties, the surface area, the formation of macro and micropores, and the presence of functional groups stand out. Due to these characteristics, biochar becomes an alternative material with high adsorption capacity of toxic compounds present in contaminated wastewater. This work provides information on the generation mechanisms of biochar and how they interfere in its physicochemical characteristics. It also describes the parameters involved in the pollutant removal processes and mentions the treatments under which biochar can be subjected to improve its adsorption capacity. Finally, the possible uses or the appropriate final disposal of biochar in order to contribute to the circular economy strategy are indicated.

Keywords: adsorption; wastewater; surface area; biochar; biomass combustion; persistent pollutant; desorption; circular economy; functional group; feedstock; pH; porosity; removal; temperature

1. Introduction

Water is a resource that stands out for its importance in sustaining life on Earth as we know it today. Without it, agricultural, industrial and energy activities, as well as its use for human consumption, hygiene and health, would be seriously affected. In addition, population growth generates a high urban sprawl and an increase in the rates of both production and consumption, which in turn require a high demand for freshwater. It should be taken into account that water distribution, globally, is established as follows: of the 100% of available water, only 2.4% is fresh water; of this amount, 1.6% is found in glaciers and in the so-called perpetual snows; 0.7% is found in groundwater and in the atmosphere, and 0.007% is found in rivers, lakes and reservoirs [1].

Due to the varied uses of water to satisfy different human activities, an increasing number of polluting substances are being incorporated into aquatic ecosystems. In this sense, water quality is altered by the presence of a large number of components such as pesticides, pathogens, heavy metals, detergents, dyes, pharmaceuticals, and personal care and hygiene products, among others [2]. Of this group of substances, dyes, heavy metals and the so-called emerging pollutants, which are distinguished by their genotoxic (mutagenic and carcinogenic) potential, among other adverse effects, are particularly relevant, thus presenting a great risk to the health of both human beings in particular and the environment in general [3–6].

This fact, added to the scarcity of water resources and the high demand for it,

makes it necessary to implement treatment systems capable of eliminating the pollutant load. For this purpose, the so-called Wastewater Treatment Plants (WWTP) or Wastewater Treatment Plants (WWTP) have emerged. These plants operate by means of a set of conventional processes and operating units whose ultimate purpose is to improve the physical, chemical and biological characteristics of water; that is, to reduce or eliminate the concentration of certain substances or forms of energy that alter water quality, in order to subsequently comply with the established regulations [7,8].

However, given the properties of these pollutants, in most cases the efficiency of traditional treatment systems is limited [9–12]. Thus, the use of alternative technologies that are efficient and economically feasible is required, such as the use of adsorbent materials capable of removing both organic and inorganic pollutants from water, as is the case of biochar.

Biochar is the product from the decomposition of biomass through thermochemical processes with little or no oxygen (O), some of them known as pyrolysis, gasification, micro gasification and torrefaction [13–16]. The resulting biochar will have physicochemical variations depending on the thermochemical process and feedstock used.

Generally speaking, biochar is composed of particles of different sizes, which is directly associated with the origin and size of the biomass. In addition, it has a high porosity with a wide variety of pore shapes and sizes [17]. Macropores (internal diameter > 50 nm) come from the biomass own spaces and micropores (internal diameter <2 nm) are generated during the biochar production process. It should be noted that these pores are associated with the adsorption of liquid, solid and gaseous compounds [17,18]. Due to these and other additional characteristics, such as the surface area and functional groups present in biochar, it becomes a viable alternative material for use in the removal of pollutants from wastewater [15].

Due to its abundance, biodegradability and environmental friendliness, biochar is a potential source for a product with very good adsorption qualities. It should be noted that biochar has been used mainly for soil remediation and amendment; however, in recent decades, the number of scientific publications on the use of biochar for the removal of pollutants present in water has been increasing, largely due to its cost-effectiveness and sustainability [12].

In this order of ideas, the use of alternatives such as biochar for the treatment of contaminated wastewater can be part of a strategy that helps to end a production cycle, since biochar is a residue generated in previous processes of obtaining energy from the combustion of biomass, thus contributing to the establishment of the principles governing the circular economy. It should be noted that the circular economy is defined as an economic model that aims at the efficient use of resources by minimizing waste, reducing raw materials, closed production cycles, protecting the environment and obtaining economic benefits [19]. As a result, the use of biochar becomes even more relevant because it can not only act as an organic compound to remediate polluted water, but also play an important role in the development model framed within the circular economy.

Under this scenario, the main objective of this work is to carry out an exhaustive review of the state of the art regarding the application of biochar from

biomass combustion in water decontamination. Specifically, this work describes the basic concepts and intrinsic characteristics of biochar associated with its production process, as well as the most relevant factors involved in the removal of pollutants present in water. Likewise, the possible uses or ways of disposal of biochar after its application are also mentioned. Finally, reference is made to future perspectives and the most significant aspects related to the implementation of biochar as an alternative material for the treatment of contaminated water.

2. Concept and characteristics of biochar associated with the generation mechanism

Biochar is a waste produced from previous thermal processes that seek to generate renewable energy and, additionally, to reduce the volume of organic waste. However, its generation has aroused great interest in the scientific community to be used as a soil amender and as an adsorbent in the removal of different pollutants present in water due to its capacity to eliminate organic molecules and ions through processes such as physical absorption and ion exchange [20]. This fact allows providing this waste with an added value, since it can also be conceived from the perspective of providing a solution to the integral management of organic waste generated after the thermal processing of biomass.

In the literature reviewed in this study, it is evident that the technology implemented for the generation of biochar for which the largest number of scientific reports are available is pyrolysis. Pyrolysis is known as a process that uses temperatures between 200 and 900 °C with little or no O to decompose biomass [14], [21]. The biomass generally used to produce biochar (plant residues rich in cellulose, hemicellulose and lignin), decomposes gradually with increasing temperature, suffering a weight loss due to the evaporation of the water contained in it [22].

Pyrolysis can be divided into two groups according to the biomass residence time: fast pyrolysis and slow pyrolysis. Fast pyrolysis uses a residence time of seconds, while in slow pyrolysis the residence time is from hours to days [14]. Slow pyrolysis is probably more used to produce biochar because the percentage of biochar production is favored between 15 and 89% [15].

On the other hand, to the authors' knowledge, the number of studies reporting reviews, analyses and results concerning the use of processes such as hydrothermal carbonization, gasification, micro gasification and torrefaction for biochar generation are few. This may be largely due to the fact that the percentages of biochar production with these methods are lower and that the main objectives of these processes are not to obtain biochar, but energy from biomass [15,21].

It is important to mention that the physicochemical properties of biochar are associated with the biochar production method. Among these properties, of particular interest is its surface area and, consequently, the surface area of the biochar available for adsorption of the pollutant(s) under study.

Several studies report the fundamental role played by the production temperature on the adsorption and ion exchange properties of biochar. Thus, at high temperatures, biochar generated by pyrolytic processes shows a considerable increase in surface area and pH [15].

On the other hand, Campos et al. [23] conducted a study in which they used olive pits, rice husks and residues from olive pruning as biomass, which they pyrolyzed at a rate of 30 °C/min under an atmosphere of nitrogen gas (N2) to ensure the absence of O at temperatures of 350, 400, 500 and 600 °C with different residence times, which varied between 30 min and 4 h. These authors indicated that the biochar produced at 350 °C was strongly water repellent, a behavior that was attributed to the loss of aliphatic structures (organic compounds consisting of hydrogen (H) and carbon (C). This repellency tended to decrease with increasing temperature and residence time [23].

Likewise, Kim et al. [24] in their study on the removal of cadmium (Cd) from an aqueous solution by biochar produced from Miscanthus giganteus using slow pyrolysis at 300, 400, 500 and 600 °C, found that at temperatures > 500 °C, the biochar produced presented greater aromaticity and a lower number of polar functional groups, in addition to an increase in the surface area of the biochar, which resulted in an increase in the adsorption capacity of Cd. Electron microscopy images taken by the referred authors reflected morphological changes in the pore structure of the biochar obtained during pyrolysis at different temperatures (300, 400, 500 and 600 °C); so that at higher temperatures the pore size increased due to the volatilization of substances such as cellulose and hemicellulose. They also found that as the temperature increased, specifically in the range studied, the C content present in the biochar increased significantly between 68.48 and 90.71%, while the H and O contents decreased inversely proportional to the increase in temperature, resulting in a decrease in the H/C and O/C molar ratios. Similarly, the authors described that the nitrogen (N) content of biochar did not depend on the temperature used during biomass pyrolysis.

These findings suggest, therefore, that at higher temperatures more aromatic and less hydrophilic biochar can be produced. This fact can be attributed to the fact that as the biochar production temperature increases, the water content decreases; that is, dehydration reactions occur, while decarboxylation and dehydrogenation reactions take place, increasing the number of aromatic rings and, therefore, the aromatic character of the biochar. In fact, in a study by Nguyen et al. [25] it was shown that an increased amount of polycyclic aromatic hydrocarbons, especially of medium and high molecular weight, was produced due to the melting of the aromatic rings remaining after the aforementioned chemical reactions took place.

On the other hand, Campos et al. [23] noted that high lignin content promotes the amount of biochar produced. In addition, variations in proportions of cellulose, hemicellulose and lignin present in the feedstock influence the biochar yield.

On the other hand, Lee et al. [26], based on their study on the analysis of the characteristics of biochar production from the slow pyrolysis of Miscanthus giganteus using a packed bed reactor at laboratory scale under a temperature range of 300°C–700 °C with a heating rate of 10 °C/min, reported that the cellulose and hemicellulose from the species under study decomposed at 500 °C. Similarly, the authors evidenced that the biochar took the shape of a honeycomb with cylindrical holes (pores) of 5–40 µm in diameter. This fact was associated with the vascular cellular structure of the original biomass. In addition, the referred authors observed that the surface area of the generated biochar increased rapidly to 181 m^2/g [26].

3. Parameters involved in the removal of pollutants from waters

Due to the properties that biochar acquires when generated by biomass combustion, such as pore development and increased surface area, and the number of surface functional groups such as carboxyl (-COOH), phenols and hydroxyl (-OH) that it possesses, it becomes a great adsorbent of both organic and inorganic compounds present in water [14].

There are several parameters or factors that influence the adsorption properties of biochar, including the effect of the pH of the solution, which will be relevant in the interactions between the pollutant and the biochar; and the effect of the temperature of the solution, which will favor or limit the endothermic or exothermic reactions between the biochar and the pollutants. Likewise, the effect of the dose of biochar used should also be mentioned, which affects the adsorption capacity; and the effect of the constituents of the aqueous matrix, which are present in the water and may be direct competitors of the pollutants to be removed.

On the other hand, the effect of hydraulic retention time and biochar particle size, associated to the adsorption capacity due to its surface area, are factors to take into account since they affect the capacity of biochar to retain pollutants. Some of these parameters are related in the isothermal adsorption models proposed throughout history, being widely used the Langmuir, Freundlich and Temkin models, represented by Equations (1), (2) and (3), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \tag{1}$$

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{2}$$

$$q_e = A + B \log C_e \tag{3}$$

where C_e [mg/L] refers to the equilibrium concentration of the pollutant(s) under study, q_e [mg/g] refers to the amount of pollutant(s) adsorbed per gram of adsorbent used at equilibrium, q_m [mg/L] is the maximum adsorption capacity of the adsorbent material and b [L/mg] refers to the affinity constant between the adsorbent and the pollutant(s).

On the other hand, K indicates the approximate adsorption capacity and is expressed as [mg/g] [mg/L], $\frac{1}{n}$ refers to the adsorption intensity and A [mg/g] and B [L/mg] refer to the maximum adsorption capacity and adsorption energy, respectively [27].

Table 1 shows some of the studies reported in the literature that analyze the role played by the factors mentioned in the process of adsorption of pollutants present in water by biochar.

3.1. Effect of solution pH

The pH of the solution is a fundamental parameter for the adsorption process by biochar, which depends on its origin and the type of pollutant to be removed [28,29].

The presence of large amounts of hydronium ions could present a difficulty for the adsorption efficiency because they compete directly for a place in the biochar

with the pollutants to be removed in the water, in case they are in cationic form. Previous studies reported by Tan et al. [15] indicate that the adsorption capacity of biochar is directly proportional to the pH value of the aqueous solution or water to be treated. In the particular case of dyes, their adsorption has a high efficiency for pH values above 5. This fact is attributed to the electrostatic interaction between the positive and negative charges of the dyes and biochar, respectively.

However, it should be noted that the phenomenon of electrostatic repulsion can also occur. This phenomenon may be due to the interaction between cationic pollutants and biochar when the latter is positively charged [29]. But this fact is not completely negative in the treatment of polluted water, since the molecules of the pollutants that are in their anionic form would be electrostatically attracted by the positively charged biochar.

For this reason, it is essential to study in greater detail beforehand the type or types of contaminants to be removed, their behavior under certain pH conditions of the solution and the structure and characteristics of the biochar used, as well as its loading.

As indicated above, the functional groups and thus the pH of biochar depend on the biochar production process and the generation temperature. In a study conducted by Campos et al. [23], they reported that biochar produced by pyrolyzation at 350 °C for 30 min had low pH values compared to biomass that was not pyrolyzed.

One of the possible causes of acid pH results in biochar was also found to be that cellulose and hemicellulose at relatively low temperatures (108 °C–250 °C) are transformed into phenolic substances and organic acids [24,30].

Likewise, temperatures above 500 °C, in general, produce an increase in the pH of biochar, which is greater than 9. This increase is associated with an increase in ash, which is explained by the destruction of the -OH and -COOH groups, and the existence of alkaline elements present in the biomass [24].

3.2. Effect of solution temperature

The results reported in the literature indicate that the reactions carried out with different contaminants and at different temperatures are influenced by the temperature of the water to be treated [28,31].

In the study by Zhang et al. [28], the adsorption capacity of uranium (U) in aqueous solution was investigated. For this purpose, biochar produced by hydrothermal carbonization from pine needles at 180 °C in citric acid ($C_7H_8O_7$) solution at different temperatures (14.85; 24.85; 34.85; 44.85 and 54.85 °C) was used. In addition, the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$), represented in Equation (4) and Equation (5), were calculated to define the spontaneity of the reaction and whether it was endothermic or exothermic. In the spontaneity of the adsorption process it was evidenced that the increase in the value of $\Delta G°$, allowed inferring that at a higher temperature the adsorption process was favored.

Table 1. Application of biochar produced from different thermochemical processes and raw materials for the treatment of polluted water.

Raw materials	Treatment	Operating conditions	Contaminant(s)	Primary Purpose	Ref.
Agro-industrial wastes	Pyrolysis	400 to 800oC-1h	Malachite green (VM)	Optimization of VM dye adsorption.	[32]
Pine needles	Hydrothermal carbonization (CHT)	180oC-16h	U(VI)	Hydrothermal carbonization to improve the adsorption performance of U(VI) in aqueous solution	[28]
Maple wood	Pyrolysis	500°C-30min	Lead [Pb(II)].	Influence of oxidation on biochar to improve Pb(II) adsorption.	[33]
Pure glucose	CHT and Pyrolysis	190°C-24hy 600 to 900°C	Paracetamol (PRC)	Spherical biochar adsorption mechanisms for PRC removal	[34]
Grapefruit peels	Pyrolysis	600 to 900°C	PRC	Adsorption mechanisms of non-spherical biochar for the removal of PRCs.	[34]
Mangosteen shells	Pyrolysis	400°C-2h	Chromium [Cr(VI)].	Role of pyrolysis and its modification in the Cr(VI) adsorption process.	[35]
Wood chips and poultry waste	Pyrolysis	650°C-16min	Cd	Biothermal stability of biochar and its Cd adsorption capacity	[36]
Amur silver grass	Pyrolysis	300 to 600°C-1h	Cd	Biochar application for Cd removal from aqueous solution	[24]
Palm and eucalyptus bark	Torrefaction and pyrolysis	200°C and 400°C - 30min	Methylene blue (AM)	Evaluation of the adsorption potential of AM dye using biochar	[37]
Rice husk and manure	Pyrolysis	350°dh	Pb, Copper (Cu), Zinc (Zn) and Cd	Mineral components in biochar for the removal of heavy metals in aqueous solutions.	[30]
Date palm leaves	Pyrolysis	700°dh	AM	Functionalizing biochar with MgAl for enhanced MA adsorption	[31]

Source: own elaboration.

$$\text{LnKL} = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (4)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (5)$$

where T [K] refers to the absolute temperature of the solution, R is the universal ideal gas constant and is expressed as J/[mol k]. KL is a thermodynamic equilibrium constant.

An increase in temperature indicates an increase in the diffusion in the adsorbent molecules (biochar) both in its surface area and within its pores [38]. This fact is supported by the study carried out by Tan et al. [15], where it was reported that the increase in temperature values also indicated an increase in the adsorption capacity of the dye under study, AM, for this particular case. Probably the results obtained are supported by molecular diffusivity models such as the one established by Chapman-Enskog, represented by Equation (6), according to which diffusivity increases with temperature.

$$D_{AB}(cm^2/s) = 0{,}00188 \frac{\sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B}\right)}}{P\sigma_{AB}^2 \Omega_{AB}} \qquad (6)$$

where T *[K]* is the temperature, M_A and M_B [g/mol] refer to the harmonic mean molecular weight of substance *A* and *B*, respectively. Meanwhile, *P* refers to the pressure [bar], gab is the collision diameter [Â] and Ω_{AB} is the collision integral for diffusivity.

However, different results from those referred to above are reported in the study by [34], in which they used two types of biochar from the pyrolysis of pure glucose at 900 °C (spherical biochar) and from grapefruit peel waste at 700 °C (non-spherical biochar) for the removal of CRPs in water. For both types of biochar, they found that the temperature of the water to be treated directly influenced the adsorption capacity of the two bio chars under study, as they observed that the adsorption of CRP decreased when the water temperature increased from 10 to 50 °C.

3.3. Effect of the dose of biochar used

The adsorption efficiency of biochar will be directly reflected with the dose of biochar used, as well as with other parameters such as contaminant concentration and contact times (hydraulic retention time), as well as those mentioned above. In the study conducted by Zubair et al. [31], in which they analyzed the removal of the AM dye, the removal efficiencies of all the experimental tests improved as the adsorbent doses increased, with the Langmuir adsorption model being the one that most closely approximated the experimental data obtained. This increase in adsorption capacity as the adsorbent dose increased can be attributed to the increase in the number of active adsorption sites.

However, depending on the type of pollutant to be removed and the origin of the biochar, the biochar dosage will have a different effect. In this sense, the case of an increase in the dose and in turn an increase in adsorption can occur, but the opposite effect can also take place; that is, although the adsorbent dose increases, the adsorption process is limited [15].

In agreement with the above, Lonappan et al. [39] in their research on the adsorption of diclofenac (DCF) with different types of biochar (biomasses from pine wood and pig manure) observed that for both types of biochar, increasing the adsorbent dose considerably improved the removal efficiency of the pollutant under study. The authors highlighted the great potential of biochar from swine manure, since its implementation resulted in a high removal of DCF (in 4 of the experimental trials the removal was 100%), compared to the results obtained with biochar produced from pine wood. However, it was observed that the adsorption capacity of biochar decreased when it was used in excess. This could be due to the fact that for the higher concentrations of biochar tested, the number of active sites decreased.

Studies such as the one developed by Gokulan et al. [40] investigate the remediation of remazol dyes through biochar derived from Caulerpa escalpelli for me, reporting results similar to those obtained by Lonappan et al. [39]. Using a biochar dosage of 1 to 10 g/L, constant pH values of 2.0 and temperature of 30 °C, as well as an initial dye concentration of 0.5 mmol/L, it was reported that the optimum biochar dosage was 2 g/L. Thus, it is evident that an increase in biochar concentration results in an increase in the number of biochar active sites that are available to receive contaminant molecules. However, when the amount of biochar is

in excess, particle agglomeration occurs, which leads to a decrease in its adsorption capacity. This fact makes it necessary that the dose of biochar used is a parameter to analyze and optimize when evaluating the efficiency of this adsorbent material in the treatment of contaminated water.

3.4. Effect of aqueous matrix constituents

Different industrial processes that discharge into water bodies contribute large amounts of organic and inorganic compounds to these waters. The biochar used for adsorption of a specific compound can also retain other coexisting compounds, so that its adsorption capacity could be altered [41]. Adsorption of organic compounds from water can occur by different processes such as H-bonding, fractionation, pore filling, electrostatic interactions, and aromatic interactions, which are directly related to reaction kinetics and, therefore, to adsorption isotherm models, including the Temkin, Langmuir, and Freundlich model [42].

In the study conducted by Lu et al. [41], regarding the removal of acenaphthene ($C_{12}H_{10}$) in the presence of coexisting heavy metals and phenanthrene, using biochar produced from rice bran and bamboo powder, no significant alterations in adsorption by the biochar used were evidenced due to the presence of Cr(VI). Likewise, it was identified that Cu(II) was directly bound to the O-containing functional groups of the biochar, and Cr(VI) was reduced to Cr(III), to subsequently bind to these functional groups. Both processes positively influenced the surface adsorption of acenaphthene in the presence of phenanthrene by biochar.

On the other hand, in the study carried out by Ni et al. [43] on the competitive adsorption of heavy metals in aqueous solution with biochar derived from anaerobically digested sludge, in which the adsorption potential of Pb(II) and Cd(II) was evaluated, and batch experiments were conducted in a single metal experimental system with an initial metal concentration ranging from 0.1 to 1.0 mmol/L, it could be observed that the adsorption capacity of biochar for each metal increased with increasing initial metal concentration. At a lower initial concentration, the heavy metals were adsorbed on the external surface of the biochar, whereas, when the concentration was increased, the heavy metals entered the internal structure of the biochar, resulting in higher pore occupancy in the biochar.

The biochar showed a higher adsorption capacity for Pb(II) compared to that of Cd(II). In the two-metal experimental system [coexistence of Cd(II) and Pb(II)], the adsorption capacity of Pb(II) at different initial concentrations (0.1–1.0 mmol/L) did not indicate significant changes compared to the experimental design carried out using a single metal. However, the adsorption of Cd(II) on biochar was significantly reduced when both metals were together. One explanation for this behavior was attributed to the existing differences in the characteristics of each metal and the resulting affinity for the adsorption sites of the biochar.

3.5. Effect of hydraulic retention time

Hydraulic retention time is also one of the important parameters affecting the adsorption process of biochar. Some studies indicate that 3 h is the adequate equilibrium time for proper adsorption of contaminants to take place. On the other

hand, it was found that the highest adsorption efficiency occurred in the first 30 min of the reaction [15,38].

The results of Idrees et al. [38] in their study in which biochar derived from animal manure produced by fast pyrolysis was used for the removal of Cu^{2+} from aqueous media indicated a high adsorption rate, which contributed significantly to the removal of this contaminant during the initial period of contact time, and then gradually slowed down. This rapid adsorption rate during the initial stage was probably due to the presence of a large number of active spaces in the adsorbent that were available to the target pollutant.

In Wang et al. [44], on the other hand, they found similar results in their study in which polyethylenimine (PEI)-modified biochar was used for the adsorption of U(VI) in aqueous solutions. These authors found that U(VI) adsorbed rapidly after several hours, gradually reaching adsorption equilibrium before reaching 8 h of contact.

Similarly, Liu et al. [45] conducted comparative studies of the adsorption properties of biochar from Enteromorpha prolifera species modified with zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and potassium permanganate ($KMnO_4$) for the removal of Cd from an aqueous solution. The referred authors found that the adsorption rate of Cd(II) increased with time for all the adsorbents studied as the contact time was prolonged, especially during the first treatment times, until it reached the stability level.

Additionally, Khan et al. [46], in their work on hydrothermal liquefaction of rice husk and cow dung for the generation of biochar to remove the dye Congo Red at a concentration of 100 mg/L and with a contact time of 0–96 h, they found that the maximum removal efficiencies of the dye of interest were 91.5%–96.9% and 81.3%–98.8% with a contact time of 72–84 h using biochar obtained by combustion of rice husk and cow dung, respectively. In addition, it was observed that when the contact time increased, the removal efficiency of the target dye also increased significantly.

It should be noted that the kinetics that take place in these processes can be particularly related to the isothermal models of adsorption referred to above, which in turn describe the effect that the concentration of the pollutant in solution has after chemical equilibrium and subsequent adsorption on the adsorbent material has been achieved.

3.6. Effect of biochar particle size

It is important to highlight that a large surface area contributes to enhance the adsorption process of the pollutant [20]. In fact, the chemical adsorption of the adsorbate that occurs on the -COOH and -OH functional groups present on the biochar surface, and the electrostatic attraction that occurs between the pollutants in their ionic form and the biochar, are benefited by the increase in the surface area of the adsorbent material, which is a consequence of the decrease in the particle size of the adsorbent [20]. In the study of adsorption of biochar derived from peanut shells to remove Cr(VI) from an aqueous solution, Han et al. [47] reported that the adsorption of biochar differed significantly with particle size, obtaining that smaller biochar particles had a larger surface area.

As shown in section 2, the physicochemical properties of biochar are closely linked to the origin of the biomass and its production method. Thus, the particle size and related biochar characteristics, such as surface area, will positively or negatively influence the adsorption of contaminants present in water [48].

4. Biochar handling after treatment

The main disadvantage of using biochar as an adsorbent is that it does not destroy or degrade the pollutant, but retains it. It should be considered that the biochar used is generally loaded with toxic pollutants (dyes, heavy metals, pharmaceuticals, etc.), which can cause other environmental problems such as soil contamination, fauna and flora, and even surface and subsurface water bodies could be affected by leaching [49]. Thus, these toxic compounds would be reincorporated into the different environmental compartments if the biochar obtained after the water treatment process is not adequately treated [49].

In this context, the post-treatment handling of biochar is of vital importance for the application of biochar as an alternative material in the treatment of contaminated water to become a profitable and sustainable practice. Thus, desorption operations must be carried out in order to separate the pollutants adsorbed on the biochar and to be able to reuse it again in the treatment of polluted water until its regenerative capacity is exhausted. In this sense, the study carried out by [50] stands out, in which a solvent such as methanol (CH_3OH) was used to separate the emerging pollutants IBU and salicylic acid (AS). After using methanol, 88% and 93% of IBU and AS were recovered, respectively [50].

On the other hand, Essandoh et al. [51] used biochar from Pinus kesiya for the removal of the anionic dye alizarin red (AR) from water. For desorption of the dye under study, they used a sodium hydroxide (NaOH) solution, which was kept with the contaminated biochar under stirring for 3 h. Subsequently, the biochar was washed and dried for further use [51]. As a result, a regenerated biochar was obtained whose AR removal efficiency was 90.13%. Using this desorption technique, the biochar could be recycled for up to 3 cycles [51].

Once the biochar has completed its cycle, it must be put to its proper use. Currently, the main alternatives for handling biochar after it has been used in the treatment of contaminated water consist of disposal in a sanitary landfill, safe storage or encapsulation, and reuse of biochar. Among the options aimed at biochar reuse, the study conducted by Bădescu et al. [52] stands out. They propose that residual biochar could be used as a fertilizer to improve soil quality, provided that this biochar is loaded with macro and micronutrients beneficial to the soil (such as Cu, Ni, Zn, etc.). However, it is important to mention that, if the recovered biochar has the presence of toxic organic and inorganic contaminants, its application to the soil would contribute to soil degradation [52].

Another possible use of biochar used in wastewater treatment is mentioned by Choudhary et al. [12] in their study where biochar is generated from Opuntia ficus-indica, which is used for the adsorption of the VM dye, Cu^{+2} and nickel (Ni^{+2}) present in the aqueous medium. The referred authors propose to use the residual biochar as an energy source. For this purpose, they based this on the measurement of

the calorific value (CP) of the biochar used during their research, which was 20.37 MJ/kg, and compared it with the CP required for the incineration of solid waste (7 MJ/kg). This meant a considerable difference in favor of post-treatment biochar, which is why the referred authors propose as a viable option the use of biochar as an energy source in cement and iron and steel plants, among other industries [12].

However, despite the options proposed and reported in the literature, further studies are required in order to analyze other possible alternatives for the desorption and reuse of biochar used during the treatment of pollutants present in water.

5. Future prospects

It is important to mention that the adsorption capacity of biochar can be improved by modification techniques, such as treatment of biochar with acids, bases, metal oxides and clay minerals, among others [20].

As an example, the study carried out by Truong et al. [53], in which biochar was modified with PEI in order to improve the removal of natural organic matter present in water, stands out. These authors prepared biochar by mixing it with a concentrated (5 M) alkaline potassium hydroxide (KOH) solution at a mass ratio of 1:4. The mixture was kept stirred for 4 h at room temperature and was subsequently carbonized at 475 °C for 3 h to ensure the formation of porous structures and functional groups with the presence of O. This biochar exhibited a porous structure with a volume of 0.31 cm^3/g of mesopores (diameter > 2 nm) and a surface area of 230 m^2/g. After activation, the surface area of the biochar increased to 745 m^2/g. On the other hand, the high O content of the PEI-modified biochar indicated that activation increased not only its surface area but also its functional groups with the presence of O. These results demonstrated an increase in the adsorption capacity of the biochar.

On the other hand, Zhang et al. [54] modified rice-derived biochar by nitration and nitroreduction to improve the adsorption of Cd(II) ions present in water. For this purpose, 50 mL of nitric acid (HNO_3) and 50 mL of sulfuric acid (H_2SO_4) were added and placed in a salt and ice bath. Subsequently, 5 g of biochar was added to the solution for a time of 2 h, in order to introduce a considerable amount of functional groups with the presence of nitrogen ($-NH_2$) on the surface of the biochar. The results allowed the identification of a large amount of particles in the improved biochar. These particles could be Cd chelates formed after adsorption by the biochar, and could indicate that the $-NH_2$ groups on the surface of the modified biochar would have the ability to complex with Cd(II). This process would be responsible for the increase of just over 72% of the adsorption capacity of the biochar [54].

Another example is the modification with magnesium oxide (MgO) of biochar produced from wood residues for phosphorus (P) adsorption. For this, 55. Oginni et al. [55] premodified the biochar samples by immersing them in a solution with 1.43 kg magnesium chloride ($MgCl_2$) and 6 L of water for 24 h. They then heated the oven to 500 °C for 24 h. The samples were then heated in a furnace at 500 °C. Then, they heated the furnace at 500 °C under a N2 flow of 2 L/min for 30 min. The results of this procedure evidenced that the impregnation of $MgCl_2$ into the modified biochar resulted in a significant improvement of the specific surface area, cation

exchange capacity and pore diameter compared to the unmodified biochar. The P adsorption capacities of natural and modified biochar were 1.88–2.78 mg/g and 28.20–29.22 mg/g, respectively. Which indicates that the modified biochar showed about 11 times higher P adsorption potential than that of natural biochar.

The techniques mentioned above, capable of increasing the adsorption and retention capacity of pollutants present in water by biochar, are only a few examples of the large number of studies reported in the literature related to this field of knowledge [45,56–58]. However, it is important to mention that some of these may be technically or economically unfeasible in terms of scaling up the treatment systems studied in the laboratory. In this context, further research is needed.

As can be seen from all the information provided in this work, studies on how to obtain biochar according to different thermochemical treatments, the improvements that can be made to it to increase its adsorption performance and its use for the removal of pollutants present in water are increasingly arousing greater interest among the scientific community, so that over the years the number of research studies in the literature has increased, as can be seen in **Figure 1**.
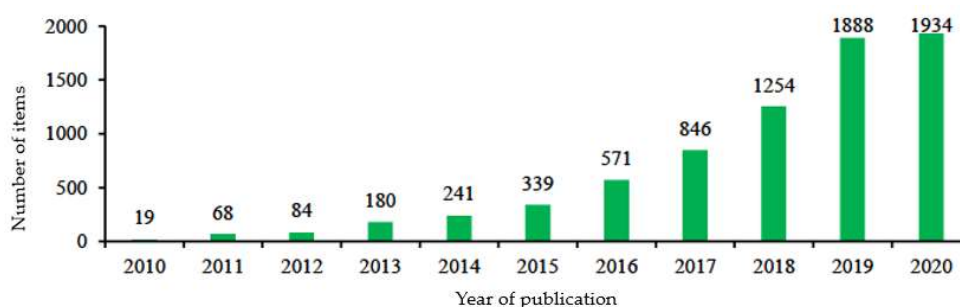

Figure 1. Review and research articles published in the ScienceDirect database with the keywords "biochar" and "sorption". Source: own elaboration.

This fact leads us to consider the possibility of using this type of alternative for the treatment of contaminated water, given its advantages from the point of view of ease of operation and maintenance of the system, as well as its profitability due to the low economic costs and high associated efficiencies.

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References

1. Spain: Ministry of Defense. Spanish Institute for Strategic Studies, Cuadernos de Estrategia 186 Water: source of conflict or cooperation? Spain: Ministry of Defense; 2017.
2. Espigares García M, Pérez López JA. Wastewater: The wasted resource (Spanish). Universidad de Granada; 1990.
3. Preston RJ, Skare JA, Aardema MJ. A review of biomonitoring studies measuring genotoxicity in humans exposed to hair dyes. Mutagenesis. 2010; 2(1): 17-23. doi: 10.1093/mutage/gep044

4. Klaunig JE, Kamendulis LM, Hocevar BA. Oxidative stress and oxidative damage in carcinogenesis. Toxicologic Pathology. 2010; 38(1): 96-109. doi: 10.1177/0192623309356453

5. Javaid R, Qazi UY. Catalytic Oxidation Process for the Degradation of Synthetic Dyes: An Overview. International Journal of Environmental Research and Public Health. 2019; 16(11): 2066. doi: 10.3390/ijerph16112066

6. Pagalan Jr E, Sebron M, Gomez S, et al. Activated carbon from spent coffee grounds as an adsorbent for treatment of water contaminated by aniline yellow dye. Industrial Crops and Products. 2020; 145: 111953. doi: 10.1016/j.indcrop.2019.111953

7. De la peña ME, Ducci J, Zamora V. Wastewater treatment in Mexico. Inter-American Development Bank, Mexico; 2013.

8. Valdez EC, Vásquez AB. Engineering of wastewater treatment and disposal systems (Spanish). Mexico: Fundación ICA; 2003.

9. Anjaneyulu Y, Sreedhara Chary N, Samuel Suman Raj D. Decolourization of Industrial Effluents—Available Methods and Emerging Technologies—A Review. Reviews in Environmental Science and Bio/Technology. 2005; 4(4): 245-273. doi: 10.1007/s11157-005-1246-z

10. Cortazar Martínez A, González Ramírez CA, Coronel Olivares C, et al. Biotechnology applied to the degradation of textile industry dyes. Biotechnology applied to the degradation of textile industry dyes. Universidad y Ciencia. 2012; 28(2): 187-199.

11. Barrios-Ziolo LF, Gaviria-Restrepo LF, Agudelo EA, et alTechnologies for the Removal of Dyes and Pigments from Wastewater (Spanish). DYNA. 2015; 82(191): 118-126. doi: 10.15446/dyna.v82n191.42924

12. Choudhary M, Kumar R, Neogi S. Activated biochar derived from Opuntia ficus-indica for the efficient adsorption of malachite green dye, Cu+2 and Ni+2 from water. Journal of Hazardous Materials. 2020; 392: 122441. doi: 10.1016/j.jhazmat.2020.122441

13. Mašek O, Budarin V, Gronnow M, et al. Microwave and slow pyrolysis biochar—Comparison of physical and functional properties. Journal of Analytical and Applied Pyrolysis. 2013; 100: 41-48. doi: 10.1016/j.jaap.2012.11.015

14. Ahmad M, Rajapaksha AU, Lim JE, et al. Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere. 2014; 99: 19-33. doi: 10.1016/j.chemosphere.2013.10.071

15. Tan X, Liu Y, Zeng G, et al. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere. 2015; 125: 70-85. doi: 10.1016/j.chemosphere.2014.12.058

16. Manyà JJ, Azuara M, Manso JA. Biochar production through slow pyrolysis of different biomass materials: Seeking the best operating conditions. Biomass and Bioenergy. 2018; 117: 115-123. doi: 10.1016/j.biombioe.2018.07.019

17. Escalante A, Pérez G, Hidalgo C, et al. Biocarbon (biochar) I: Nature, history, manufacture and use in soil Biocarbon (biochar) I: Nature, history, manufacture and use in soil. Terra Latinoamericana. 2016; 34(3): 367-382.

18. Lehmann J. Bio-Energy in the Black. Frontiers in Ecology and the Environment. 2007; 5: 381-387. doi: 10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

19. Morseletto P. Targets for a circular economy. Resources, Conservation and Recycling. 2020; 153: 104553. doi: 10.1016/j.resconrec.2019.104553

20. Sizmur T, Fresno T, Akgül G, et al. Biochar modification to enhance sorption of inorganics from water. Bioresource Technology. 2017; 246: 34-47. doi: 10.1016/j.biortech.2017.07.082

21. Inyang M, Dickenson E. The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: A review. Chemosphere. 2015; 134: 232-240. doi: 10.1016/j.chemosphere.2015.03.072

22. He J, Strezov V, Kan T, et al. Slow pyrolysis of metal(loid)-rich biomass from phytoextraction: characterisation of biomass, biochar and bio-oil. Energy Procedia. 2019; 160: 178-185. doi: 10.1016/j.egypro.2019.02.134

23. Campos P, Miller AZ, Knicker H, et al. Chemical, physical and morphological properties of biochars produced from agricultural residues: Implications for their use as soil amendment. Waste Management. 2020; 105: 256-267. doi: 10.1016/j.wasman.2020.02.013

24. Kim WK, Shim T, Kim YS, et al. Characterization of cadmium removal from aqueous solution by biochar produced from a giant Miscanthus at different pyrolytic temperatures. Bioresource Technology. 2013; 138: 266-270. doi: 10.1016/j.biortech.2013.03.186

25. Nguyen VT, Nguyen TB, Chen CW, et al. Influence of pyrolysis temperature on polycyclic aromatic hydrocarbons production and tetracycline adsorption behavior of biochar derived from spent coffee ground. Bioresource Technology. 2019; 284: 197-203. doi: 10.1016/j.biortech.2019.03.096

26. Lee Y, Eum PRB, Ryu C, et al. Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1. Bioresource Technology. 2013; 130: 345-350. doi: 10.1016/j.biortech.2012.12.012

27. Arroyave-Manco JC, Arboleda-Echavarria JC, Hoyos-Ayala DA, et al. ZLTA and FAU eolites obtained from fly ash and their application in chromium removal (Spanish). DYNA. 2018; 85(204): 150-160. doi: 10.15446/dyna.v85n204.67096

28. Zhang ZB, Cao XH, Liang P, et al. Adsorption of uranium from aqueous solution using biochar produced by hydrothermal carbonization. Journal of Radioanalytical and Nuclear Chemistry. 2013; 295(2): 1201-1208. doi: 10.1007/s10967-012-2017-2

29. Abdel-Fattah TM, Mahmoud ME, Ahmed SB, et al. Biochar from woody biomass for removing metal contaminants and carbon sequestration. Journal of Industrial and Engineering Chemistry. 2015; 22: 103-109. doi: 10.1016/j.jiec.2014.06.030

30. Xu X, Cao X, Zhao L. Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars. Chemosphere. 2013; 92(8): 955-961. doi: 10.1016/j.chemosphere.2013.03.009

31. Zubair M, Manzar MS, Mu'azu ND, et al. Functionalized MgAl-layered hydroxide intercalated date-palm biochar for Enhanced Uptake of Cationic dye: Kinetics, isotherm and thermodynamic studies. Applied Clay Science. 2020; 190: 105587. doi: 10.1016/j.clay.2020.105587

32. Vyavahare GD, Gurav RG, Jadhav PP, et al. Response surface methodology optimization for sorption of malachite green dye on sugarcane bagasse biochar and evaluating the residual dye for phyto and cytogenotoxicity. Chemosphere. 2018; 194: 306-315. doi: 10.1016/j.chemosphere.2017.11.180

33. Wang Q, Wang B, Lee X, et al. Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH. Science of The Total Environment. 2018; 634: 188-194. doi: 10.1016/j.scitotenv.2018.03.189

34. Tran HN, Tomul F, Thi Hoang Ha N, et al. Innovative spherical biochar for pharmaceutical removal from water: Insight into adsorption mechanism. Journal of Hazardous Materials. 2020; 394: 122255. doi: 10.1016/j.jhazmat.2020.122255

35. Shan R, Shi Y, Gu J, et al. Aqueous Cr(VI) removal by biochar derived from waste mangosteen shells: Role of pyrolysis and modification on its absorption process. Journal of Environmental Chemical Engineering. 2020; 8(4): 103885. doi: 10.1016/j.jece.2020.103885

36. Qi F, Yan Y, Lamb D, et al. Thermal stability of biochar and its effects on cadmium sorption capacity. Bioresource Technology. 2017; 246: 48-56. doi: 10.1016/j.biortech.2017.07.033

37. Sun L, Wan S, Luo W. Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: Characterization, equilibrium, and kinetic studies. Bioresource Technology. 2013; 140: 406-413. doi: 10.1016/j.biortech.2013.04.116

38. Idrees M, Batool S, Kalsoom T, et al. Animal manure-derived biochars produced via fast pyrolysis for the removal of divalent copper from aqueous media. Journal of Environmental Management. 2018; 213: 109-118. doi: 10.1016/j.jenvman.2018.02.003

39. Lonappan L, Rouissi T, Brar SK, et al. Adsorption of diclofenac onto different biochar microparticles: Dataset — Characterization and dosage of biochar. Data in Brief. 2018; 16: 460-465. doi: 10.1016/j.dib.2017.10.041

40. Gokulan R, Avinash A, Prabhu GG, et al. Remediation of remazol dyes by biochar derived from Caulerpa scalpelliformis— An eco-friendly approach. Journal of Environmental Chemical Engineering. 2019; 7(5): 103297. doi: 10.1016/j.jece.2019.103297

41. Lu L, Lin Y, Chai Q, et al. Removal of acenaphthene by biochar and raw biomass with coexisting heavy metal and phenanthrene. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2018; 558: 103-109. doi: 10.1016/j.colsurfa.2018.08.057

42. Deng Y, Huang S, Dong C, et al. Competitive adsorption behaviour and mechanisms of cadmium, nickel and ammonium from aqueous solution by fresh and ageing rice straw biochars. Bioresource Technology. 2020; 303: 122853. doi: 10.1016/j.biortech.2020.122853

43. Ni BJ, Huang QS, Wang C, et al. Competitive adsorption of heavy metals in aqueous solution onto biochar derived from anaerobically digested sludge. Chemosphere. 2019; 219: 351-357. doi: 10.1016/j.chemosphere.2018.12.053

44. Wang S, Ai S, Nzediegwu C, et al. Carboxyl and hydroxyl groups enhance ammonium adsorption capacity of iron (III) chloride and hydrochloric acid modified biochars. Bioresource Technology. 2020; 309: 123390. doi: 10.1016/j.biortech.2020.123390

45. Liu J, Huang Z, Chen Z, et al. Resource utilization of swine sludge to prepare modified biochar adsorbent for the efficient removal of Pb(II) from water. Journal of Cleaner Production. 2020; 257: 120322. doi: 10.1016/j.jclepro.2020.120322

46. Khan N, Chowdhary P, Ahmad A, et al. Hydrothermal liquefaction of rice husk and cow dung in Mixed-Bed-Rotating Pyrolyzer and application of biochar for dye removal. Bioresource Technology. 2020; 309: 123294. doi: 10.1016/j.biortech.2020.123294

47. Han Y, Cao X, Ouyang X, et al. Adsorption kinetics of magnetic biochar derived from peanut hull on removal of Cr (VI) from aqueous solution: Effects of production conditions and particle size. Chemosphere. 2016; 145: 336-341. doi: 10.1016/j.chemosphere.2015.11.050

48. Veiga PA da S, Schultz J, Matos TT da S, et al. Production of high-performance biochar using a simple and low-cost method: Optimization of pyrolysis parameters and evaluation for water treatment. Journal of Analytical and Applied Pyrolysis. 2020; 148: 104823. doi: 10.1016/j.jaap.2020.104823

49. Harikishore Kumar Reddy D, Vijayaraghavan K, Kim JA, et al. Valorisation of post-sorption materials: Opportunities, strategies, and challenges. Advances in Colloid and Interface Science. 2017; 242: 35-58. doi: 10.1016/j.cis.2016.12.002

50. Bhomick PC, Supong A, Baruah M, et al. Pine Cone biomass as an efficient precursor for the synthesis of activated biocarbon for adsorption of anionic dye from aqueous solution: Isotherm, kinetic, thermodynamic and regeneration studies. Sustainable Chemistry and Pharmacy. 2018; 10: 41-49. doi: 10.1016/j.scp.2018.09.001

51. Essandoh M, Kunwar B, Pittman CU, et al. Sorptive removal of salicylic acid and ibuprofen from aqueous solutions using pine wood fast pyrolysis biochar. Chemical Engineering Journal. 2015; 265: 219-227. doi: 10.1016/j.cej.2014.12.006

52. Bădescu IS, Bulgariu D, Ahmad I, et al. Valorisation possibilities of exhausted biosorbents loaded with metal ions—A review. Journal of Environmental Management. 2018; 224: 288-297. doi: 10.1016/j.jenvman.2018.07.066

53. Truong HB, Ike IA, Ok YS, et al. Polyethyleneimine modification of activated fly ash and biochar for enhanced removal of natural organic matter from water via adsorption. Chemosphere. 2020; 243: 125454. doi: 10.1016/j.chemosphere.2019.125454

54. Zhang Y, Yue X, Xu W, et al. Amino modification of rice straw-derived biochar for enhancing its cadmium (II) ions adsorption from water. Journal of Hazardous Materials. 2019; 379: 120783. doi: 10.1016/j.jhazmat.2019.120783

55. Oginni O, Yakaboylu GA, Singh K, et al. Phosphorus adsorption behaviors of MgO modified biochars derived from waste woody biomass resources. Journal of Environmental Chemical Engineering. 2020; 8(2): 103723. doi: 10.1016/j.jece.2020.103723

56. Li H, Dong X, da Silva EB, et al. Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere. 2017; 178: 466-478. doi: 10.1016/j.chemosphere.2017.03.072

57. Zhou X, Zhou J, Liu Y, et al. Preparation of iminodiacetic acid-modified magnetic biochar by carbonization, magnetization and functional modification for Cd(II) removal in water. Fuel. 2018; 233: 469-479. doi: 10.1016/j.fuel.2018.06.075

58. Feng Y, Liu P, Wang Y, et al. Mechanistic investigation of mercury removal by unmodified and Fe-modified biochars based on synchrotron-based methods. Science of The Total Environment. 2020; 719: 137435. doi: 10.1016/j.scitotenv.2020.137435