

Review

# Removal of Antibiotics by Biochars: A Critical Review

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**Abstract:** Antibiotics are pharmaceuticals that are used to treat bacterial infections in humans and animals, and they are also used as growth promoters in livestock production. These activities lead to an alarming accumulation of antibiotics in aquatic environments, resulting in selection pressure for antibiotic resistance. Given that it is impractical to completely avoid the use of antibiotics, addressing the removal of antibiotics from the environment has become an important challenge. Adsorption methods and adsorbents have received particular attention because adsorption is highly efficient in the removal of low-concentration chemicals. Among the different adsorbents, biochars have shown promise for antibiotic removal, owing to their low cost and efficiency as well as their potential for modification to further increase their adsorption capacity. This review attempts to analyze the surface properties and ash contents of different biochars and to critically discuss the knowledge gaps in antibiotic adsorption. A total of 184 articles on antibiotic properties, adsorption of antibiotics, and biochar properties were reviewed, with a focus on the last 12 years. Antibiotic adsorption by pristine biochars and modified biochars was critically reviewed. Recommendations are provided for the adsorption of different antibiotic classes by biochars.

**Keywords:** antibiotics; biochar; tetracycline; surface area; ash content



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## 1. Introduction

Antibiotics are traditionally defined as natural or synthetic pharmaceuticals that inhibit or eliminate bacterial infections (i.e., bacteriostatic or bactericidal agents) [1,2]. Sometimes, the definition of antibiotics is extended to include antiviral, antifungal, and antitumor compounds [3]. More than 250 antibiotics of about 38 different classes are currently being used in human and animal medicine [4,5]. Interestingly, antibiotics are not only used for therapeutic purposes, but also frequently used as growth enhancers in the production of livestock such as cattle, chickens, pigs, etc. [6,7]. In fact, this is now the most frequent use of antibiotics, accounting for approximately 70% of their total use worldwide [8], and is the most alarming form of antibiotic use. Because antibiotics are given to livestock at low or sublethal concentrations, they allow bacteria to develop antibiotic resistance (antimicrobial resistance; AMR) through genetic modification [9], a similar consequence to the misuse of antibiotics by humans. AMR is alarming, as declared by the World Health Organization (WHO), because by 2050 as many as 10 million people are expected to lose their lives each year because of AMR [10]. Already it has been estimated that 1.27 million people lost their lives because of AMR in 2019 [10]. These values may be only the tip of the iceberg. Modern medicine may become obsolete in the near future because medical operations cannot be performed if all bacteria become resistant to antibiotics [11]. Other adverse but less-known effects of antibiotic consumption include the reduction in human immunity and the interference with human hormone secretion [12].

Historically, the USA was the most important producer and consumer of antibiotics, but today China and India have surpassed them in the production and consumption of

antibiotics [8]. Reports have indicated that global antibiotic consumption increased by 65% between 2000 and 2015 [13] and by 46% between 2000 and 2018 [14]. The global consumption of antibiotics was estimated to be between 100,000 and 200,000 tons 21 years ago [3,8,15,16]. Today, this figure is possibly much higher. It is also likely that, during the COVID-19 pandemic, therapeutic consumption of antibiotics was higher than in previous years [17]. It is expected that by 2030 total antibiotic consumption will increase by 67% for animal use [18] and by up to 200% for total consumption [8].

In recent years, the development of new antibiotics has not kept up with the occurrence rate of antibiotic-resistant bacteria [11]. New antibiotics have mainly been isolated and developed from soil microorganisms, particularly from bacteria of the actinomycete group [19], but this process seems to have faced a hiatus after the years between 1940 and 1960, known as the golden age of antibiotics discovery [19]. Because the discovery rate of new antibiotics has declined, known compounds have started to be rediscovered [5,19]. New methods of antibiotic development are currently under research, including genome mining and editing of different bacteria [19], as well as the application of artificial intelligence to model antibiotic activity and screen potentially new antibiotics from structurally different molecules [20].

At the same time, measures have been taken worldwide to restrict antibiotic use, particularly in livestock production. However, it is unclear whether they will effectively reduce the concentration of antibiotics in the environment in the short or medium term, particularly in the low- and middle-income countries (LMICs) [21]. Because the world's population has risen exponentially in the last 100 years, global food consumption will likely increase in the foreseeable future, leading to increased use of antibiotics in livestock production if strict measures are not put into effect. The therapeutic use of antibiotics in both human and animal medicine is also a source of concern, because only 10–70% of the administered antibiotics are used by the body, with the rest being excreted and ending up in aquatic environments [8,22,23]. Data on the production volume of antibiotics are scarce. However, it has been reported that China alone produces more than 150,000 tons of antibiotics each year [24,25]. Therefore, it is estimated that huge amounts of antibiotics are released to the environment each year, particularly into the water bodies. Another difficulty in estimating the total quantity of antibiotics in the environment arises due to their highly variable metabolism, stability, and solubility [26].

Antibiotics are classified as emerging pollutants in aquatic ecosystems, owing to their continuous input and persistence at low concentrations [3]. The traditional method of removing antibiotics from waters is sewage treatment by screening and sedimentation, followed by secondary biological treatment. A number of novel methods, such as advanced oxidation processes (AOPs) (including photocatalysis, Fenton, ozonation, and UV irradiation AOPs), application of nanofiltration and reverse osmosis membrane filtration, and membrane bioreactors, as well as chlorination [3,23,27–30], have been shown to be effective in removing antibiotics from wastewater at a small scale, but they have high capital and operation costs [31] or slow kinetics [32] and, therefore, their applicability in large-scale sewage treatment plants is unclear.

Conventional sewage treatment in wastewater treatment plants (WWTPs) is the most important process in removing antibiotics from wastewater. The WWTPs are the principal sources of the antibiotics that are released into the environment [31]. Conventional sewage treatment plants cannot effectively remove antibiotics from wastewater [33] because they include a large number of chemicals with different physicochemical properties that result in highly variable (17–90%) removal percentages; for instance, the removal percentage of tetracyclines may be as high as 90%, while it can be as low as 17% for  $\beta$ -lactams [34–36]. Certain antibiotics can be considered to be non-biodegradable or poorly biodegradable and present at ng/L or  $\mu$ g/L concentrations [37]. The low concentrations usually range from nanograms to micrograms per liter, and the half-lives are highly variable in wastewaters [4,22,38].

Adsorption is an economical and effective method of removing a number of pollutants from water, such as heavy metals, organic pollutants, and dyes, because adsorbents

are usually widely available, require little or no processing, and have good adsorption properties [39,40]. Different materials are currently being used as adsorbents, and their adsorption properties may be tuned by applying a thermal or chemical process. The activated carbons are possibly the most promising materials for the removal of organic pollutants from water, but they are costly. Alternative low-cost adsorbents such as microalgae [31] and carbon-based materials such as graphene-based nanomaterials, carbon nanotubes, hydrochars, and biochars [4,22,41] are currently being investigated for antibiotic removal. Biochars are promising adsorbents because they can be produced by using waste products as feedstocks, ranging from agricultural and forest residues to sewage sludges and manures. Their adsorption properties can be customized by changing the biomass feedstock and pyrolysis conditions to obtain distinct surface physicochemical properties for the adsorption of specific contaminants, such as antibiotics [42].

The objective of this review is to critically analyze the previous antibiotic adsorption studies, with particular attention to biochar sorbents and their properties (e.g., specific surface areas, pore structures, and surface functional groups), modification, and interactions with the different antibiotic classes to provide a state-of-the-art reference to screen biochars for different antibiotic adsorption processes, as well as to optimize their performance.

## 2. Biochars and Adsorption: A Bibliometric Survey

Biochars are carbon-based materials that are produced by pyrolysis processes of organic biomass (wood, leaves, manure, etc.) and used for non-fuel purposes such as adsorption [8,43], soil amendment [44,45], and as catalysts for chemical reactions [46]. The production of biochar is a carbon-negative process that contributes to mitigating the greenhouse effect [47,48]. Biochars typically have larger specific surface areas than raw biomass (generally  $<1 \text{ m}^2 \text{ g}^{-1}$  for lignocellulosic biomass), but their specific surface areas are generally much smaller than those of activated carbons ( $500\text{--}3000 \text{ m}^2 \text{ g}^{-1}$ ). The range of surface area and pore structure of different biochars is not well known. Biochars usually contain surface chemical groups, while in activated carbons these groups are modified or lost during the thermal or chemical activation processes.

Biochars have a significant cost advantage over activated carbons. The production of biochars costs between 0.35 USD/kg and 1.2 USD/kg [8], which is about one-sixth the cost of activated carbons [49]. Another interesting property of biochars is their high affinity for adsorbing organic pollutants [50]. This set of properties of biochars suggests their use for the removal of antibiotics from wastewater.

The favorable cost of biochars, along with their promising adsorption properties, has led to an increased usage of biochars for the removal of antibiotics [12]. Biochars show selectivity in the adsorption of antibiotics; for instance, they showed higher sulfamethoxazole removal capacities than multiwalled carbon nanotubes, graphite, and clay minerals [4]. The adsorption properties were compared based on adsorption coefficient values, which showed partitioning of antibiotics between the adsorbent and water [4]. This result is interesting because biochars adsorbed higher amounts of sulfamethoxazole antibiotics than carbonaceous adsorbents with low specific surface areas such as graphite ( $1\text{--}10 \text{ m}^2/\text{g}$ ) and multiwalled carbon nanotubes ( $100\text{--}1000 \text{ m}^2/\text{g}$ ). Tetracycline antibiotics showed stronger adsorption to graphite than to activated carbon and multiwalled carbon nanotubes, in spite of the latter's higher specific surface areas [4]. Therefore, specific surface area is not the only determining factor in the adsorption of antibiotics onto biochars.

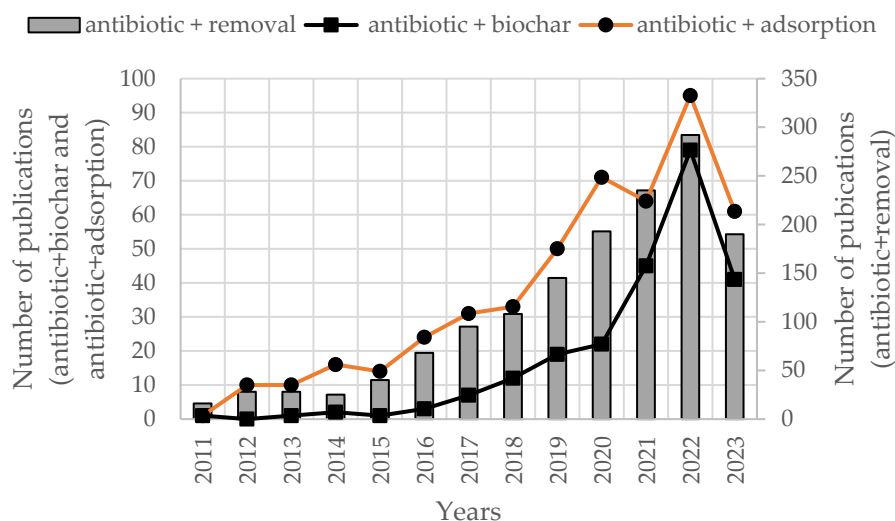
The pore structure and surface chemical groups of the carbonaceous materials also play an important role in the adsorption of antibiotics [41]. The pore structure is particularly important in the adsorption of bulky antibiotics such as tetracycline, where high-surface-area-bearing microporous activated carbons and carbon nanotubes demonstrated low affinity due to size exclusion and slow adsorption kinetics [51]. The size exclusion effect, on the other hand, may be beneficial in biochars containing macro- and mesopores [51], similar to reverse osmosis or nanofiltration membranes [27,52]. Surface chemical groups

such as hydroxyl, carbonyl, carboxyl, and amine groups also contribute to the adsorption through intermolecular interactions and covalent bonding.

Metal components of the inorganic biomass fraction also contribute to adsorption through surface complexation mechanisms [53]. The effect of the inorganic composition of the biochar is often ignored in adsorption studies.

The adsorption capacity of biochars may be further increased by physical or chemical treatments, as well as by metal oxide or heteroatom doping. Physical treatments are principally used to increase the surface area, while chemical treatments are applied to modify the surface chemistry and pore structure of biochars [8]. Metal oxides and hydroxides are frequently used to prepare biochar–metal composites. This application is essentially applied to convert the negative surface charge of biochars to positive [8], to produce magnetic biochars by using  $\text{Fe}_3\text{O}_4$  [54], and to increase the porosity [8].

The adsorption of antibiotics with biochars is a major issue, especially in the last decade, considering the efficiency and cost advantage of biochars. The number of adsorption studies with the keywords “biochar” and “antibiotics” on the Web of Science has increased in the last eleven years, particularly after 2021, indicating the importance of the topic (Figure 1).



**Figure 1.** Number of publications with the keywords “antibiotic + biochar”, “antibiotic + removal”, and “antibiotic + adsorption” on the Web of Science (WOS).

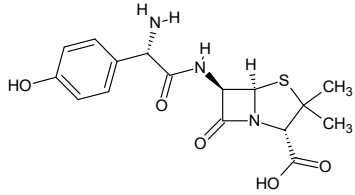
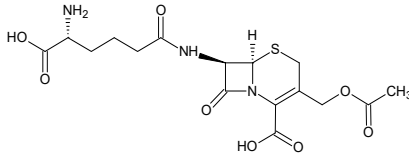
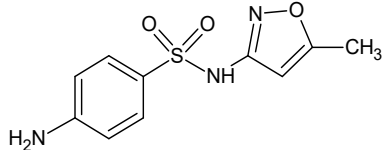
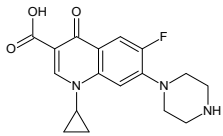
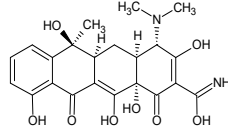
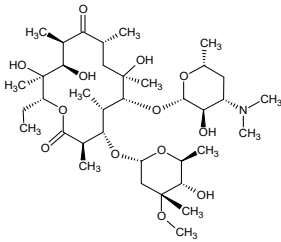
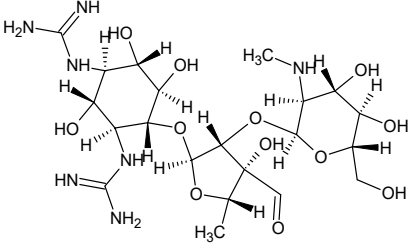
The specific search keywords “biochar” and “antibiotic” resulted in a total of 233 documents, where 94% were research articles and 4% were review articles. Environmental sciences (56%), environmental engineering (27%), and chemical engineering (17%) were the main contributors to these studies. China-based researchers dominated the studies, performing 78.5% of them, followed by researchers from the USA (12.5%) and South Korea (6.9%). The UN Sustainable Development Goal “clean water and sanitation” was the principal aim, making up 42.9% of the biochar and antibiotic studies.

The broader search keywords “antibiotic” and “adsorption” yielded a total of 527 documents, where 93% were research articles and 3% were review articles. The scientific areas mentioned above were also dominant in these studies. China-based researchers were also the principal contributors to the antibiotic and adsorption studies, with a 51.0% share, but the studies were distributed more evenly among a large number of countries, where Iran (7.4%), India (6.0%), and the USA (5.7%) were important.

The most relevant research topics in biochar and adsorption studies can be visualized by using a co-occurrence network map [55] (Figure 2). In this figure, it can be seen that tetracycline, quinolone, and sulfonamide antibiotics were frequently studied for adsorption. Antibiotic resistance genes, removal of antibiotics by magnetic biochar and activated



**Table 1.** Important properties of antibiotics (mechanism, spectrum, target bacteria, chemical structure, chemical formula, functional groups). Chemical structures are taken from <http://www.chemspider.com>, (accessed on 1 June 2023).

Antibiotics	Mechanism	Spectrum	Target Bacteria	Chemical Structure	Chemical Formula Functional Groups
Penicillins	Inhibition of cell wall synthesis	Broad-spectrum, last resort, narrow-spectrum	Gram-positive bacteria (first-generation) Gram-positive and Gram-negative bacteria (second-, third-, and fourth-generation)		$C_{16}H_{19}N_3O_5S$ (L-amoxicillin) $\beta$ -lactam ring COOH NH NH <sub>2</sub> OH CH <sub>3</sub>
Cephalosporins	Cell wall disruption	Broad-spectrum, last-resort	Gram-positive bacteria (first- and second-generation) Gram-positive and Gram-negative bacteria (third- and fourth-generation)		$C_{16}H_{21}N_3O_8S$ (+)-cephalosporin C) $\beta$ -lactam ring COOH NH NH <sub>2</sub> CH <sub>3</sub>
Sulfonamides	Inhibition of folic acid metabolism	Broad-spectrum	Gram-positive and Gram-negative bacteria		$C_{10}H_{11}N_3O_3S$ (sulfamethoxazole) SO <sub>2</sub> NH NH <sub>2</sub> CH <sub>3</sub>
Fluoroquinolones	Inhibition of DNA replication	Broad-spectrum	Gram-positive and Gram-negative bacteria		$C_{17}H_{18}FN_3O_3$ (ciprofloxacin) COOH C=O
Tetracyclines	Inhibition of protein synthesis (30 s ribosome)	Broad-spectrum	Gram-positive and Gram-negative bacteria		$C_{22}H_{24}N_2O_8$ (tetracycline) C=O OH R <sub>3</sub> N C=N
Macrolides	Inhibition of protein synthesis (50 s ribosome)	Broad-spectrum	Gram-positive and Gram-negative bacteria		(-)-Erythromycin  $(C_{37}H_{67}NO_{13})$ C=O OH CH <sub>3</sub>
Aminoglycosides	Inhibition of protein synthesis (30 s ribosome)	Broad-spectrum	Mostly Gram-negative bacteria and certain Gram-positive bacteria		Streptomycin  $(C_{21}H_{39}N_7O_{12})$ NH NH <sub>2</sub> C=N OH

The cellular structure and organization of the bacteria are helpful in understanding bacterial diseases and in the development of antibiotics. Therefore, bacterial cytology is briefly analyzed below.

#### *Characteristics of Bacterial Cytology*

Bacterial cytology is the study of bacterial cellular structure and organization. It is a useful tool to identify pathogenic bacteria, understand the disease mechanisms, and target antibiotics [57]. The identification of bacteria is the first step in bacterial cytology. Bacterial cells can be visualized by light, electron, or fluorescence microscopy. Usually, light microscopy observations are performed. Before the light microscopy observations, bacterial cells are stained with crystal violet ( $C_{25}H_{30}ClN_3$ ). The Gram-positive bacteria retain the stain and exhibit a purple color when observed under the microscope, while the Gram-negative bacteria do not retain the stain and appear pink. After the staining, the bacterial cell morphology is determined. Spherical bacteria are cocci, rod-shaped bacteria are bacilli, and spiral-shaped bacteria are spirochetes. This information, together with staining, is helpful in the determination of bacterial genus and species. However, Gram staining cannot be applied to all bacteria, because not all bacteria contain peptidoglycan cell wall layers that retain the stain, such as mycoplasma. Mycobacteria contain a complex cell wall with high contents of mycolic acids and are thus identified by acid-fast staining. Certain morphological properties of bacteria give clues to their pathogenicity. These properties include the presence of capsules (helping bacteria to evade the immune system), pili and flagella (helping with adhesion to hosts), endospores, intracellular inclusions, etc. [58].

Protein synthesis and DNA replication are the fundamental processes in all living organisms. Thus, bacteria synthesize proteins and replicate DNA. The protein synthesis of bacteria is similar to human and animal protein synthesis, but bacterial ribosomes (70 s ribosome), composed of 50 s and 30 s subunits, are smaller than eukaryotic ribosomes (80 s ribosome). Certain antibiotics, such as streptomycin, erythromycin, and tetracycline, inhibit protein synthesis by selectively binding bacterial ribosome subunits. Fluoroquinolones such as ciprofloxacin inhibit DNA replication directly by binding topoisomerase IV and DNA gyrase enzymes. Another way to inhibit DNA replication is to inhibit folate synthesis by binding the dihydropteroate synthase (DHPS) enzyme, which is necessary for DNA replication. Sulfonamide antibiotics inhibit DNA replication by blocking folate synthesis. The most commonly used antibiotics,  $\beta$ -lactams such as penicillin, target peptidoglycan synthesis by inhibiting the transpeptidase enzyme, which is used for crosslinking reactions of the peptidoglycan layers [59]. Thus, it is not surprising that  $\beta$ -lactams are highly successful against Gram-positive bacteria.

This mode of action of antibiotics provides insights into the engineering of adsorbents. Successful adsorbents can be produced by generating pore structures in biochar that allow for the diffusion of antibiotics and create similar surface functional groups to those contained by antibiotic-binding enzymes. The modification of the biochars for the removal of antibiotics is reviewed in the next section.

#### **4. A Critical Review of Biochar-Based Adsorption Processes**

Currently, four different processes are applied to remove antibiotics from water sources, including the conventional process (i.e., filtration and sedimentation, followed by biological processing), oxidation (advanced oxidation), disinfection (chlorination), and adsorption, as well as combined processes [12]. The conventional wastewater treatment process consists of primary mechanical (filtration and sedimentation) and secondary biological (activated sludge) processes. Antibiotics are partially removed through these processes. The activated sludge process is the main process for the removal of organics in WWTPs. Alternative biological processes, such as fixed-bed bioreactors, moving-bed biofilm reactors, and membrane bioreactors, are less common compared to the activated sludge process [60]. Some wastewater treatment plants also apply a final disinfection with UV irradiation, or by using chlorine in the final step of the water treatment. These latter processes have been

shown to be effective in the removal of antibiotics. Advanced oxidation processes based on the generation of reactive radicals such as hydroxyl or sulfate radicals [61] are highly effective against organic pollutants such as antibiotics. Biochars can be integrated into the AOPs as activators for the generation of radicals [61,62]. This latter approach seems to be particularly promising for the simultaneous removal of heavy metals and antibiotics [63,64].

Adsorption has certain advantages over conventional and oxidation processes, such as high efficiency at low concentrations, being easy to scale up, low cost, and the possibility of utilizing a wide range of waste materials, including plastics [12,65,66].

Adsorption also has disadvantages, such as the production of concentrated waste and the generation of secondary pollution when the adsorbent is modified to enhance the adsorption, as in the case of doping the biochars with metals [42]. Yet another disadvantage of the adsorption is the time-consuming separation of the adsorbent from water [67].

It is possible to apply a wide range of adsorbents for the removal of antibiotics from water resources, including clay and minerals, metal oxides, polymeric resins, polymers, chitosans, gels, carbon-based materials, and metal–organic framework (MOF) materials [65].

Carbon-based materials (mainly in the form of activated carbons, carbon nanotubes, graphene, and biochars) are commonly used for the adsorption of antibiotics [12,53] because of their four characteristics that contribute to adsorption:

1. Specific surface area;
2. Micro- and mesopore structures;
3. Surface functional groups;
4. Mineral content and composition.

These characteristics are determining factors in the adsorption of antibiotics, along with the antibiotic properties and the adsorption conditions [12]. Therefore, they are evaluated below for biochar adsorbents.

#### 4.1. Biochar Properties

The most relevant properties of biochars in relation to their adsorption ability are the specific surface area (i), the pore size distribution (ii), and surface functional groups (iii) such as hydroxyl, carboxyl, carbonyl, etc. [68]. The mineral content and composition (iv) of biochars are also important in the adsorption of bulky antibiotics such as tetracyclines through surface complexation [53,69].

The biochar's properties contribute to the available active sites for adsorption, improving the adsorption capacity [70]. The pore structure is formed due to the release of volatile compounds and water loss in the dehydration process during pyrolysis. Thus, the feedstock and the pyrolysis conditions, especially the temperature, significantly affect the biochar's pore structure and, consequently, the adsorption capacity of the biochar [49,71,72].

A high pyrolysis temperature has been linked to a larger surface area, higher microporosity, and graphitic structures, due to the increase in volatilization at higher temperatures [73–77]. On the other hand, at low pyrolysis temperatures, the functional groups are retained and they contribute to adsorption [69,78]. Therefore, generally, moderate temperatures (400–700 °C) are more suitable for the development of favorable pore structures [74]. The aromatic carbon groups (C=C), carbonyl groups (C=O), and aliphatic groups (CH<sub>2</sub> + CH<sub>3</sub>) were determined for four biochars produced by carbonizing corn crop residue (*Zea mays* L.) and wood shavings of oak (*Quercus* spp.) at 350 °C and 600 °C using slow pyrolysis. The results showed that the aromatic carbon content increased with temperature for both biochars, while the carbonyl and aliphatic groups decreased [79,80], which is in agreement with the results of Fu et al. [81]. Thus, a high pyrolysis temperature is almost always advantageous for the adsorption process, although the biochar yield decreases with increasing pyrolysis temperature and the economic viability of the process is reduced.

Several pore measurements have been reported for biochars. The most common measure is the total pore volume, which includes all pores. According to the International Union of Pure and Applied Chemistry (IUPAC), pores can be divided into three main groups: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) [71].



However, some authors also use the term “nanopores” to indicate micropores, probably because they are in the nanometer range. The role of each type of pore in adsorption is different. Macropores are primarily linked to the diffusion of substances, mesopores serve as channels for mass transfer, and micropores provide space for trapping [71,82]. The high temperatures in pyrolysis have been stated to be responsible for the presence of pores with sizes around 1.2 and 1.0 nm—the so-called micropores—leading to an increased surface area [83]. Nevertheless, the surface area only increases with the pyrolysis temperature up to a maximum, after which the surface area decreases [68]. For instance, some authors state that there are two competing phenomena: the first increases the volatile release and, consequently, the surface area; and the other is thermal deactivation that leads to char melting, pore fusion, and structure ordering, which decrease the surface area and pore volume [84–86].

The heating rate is also important in the formation of the pore structure. For example, tests conducted at two different heating rates (10–30 °C/min and 50 °C/min) showed that at the lower heating rate the volatiles formed were released from the surface, leading to an open fiber structure with the formation of cavities and, therefore, increasing the surface area [87]. On the other hand, a higher heating rate led to a decrease in surface area and pore volume, which was believed to be due to some of the pore walls becoming too thin and breaking [87]. The same effect was also observed with pyrolysis residence time. Thus, the severity of the pyrolysis conditions (i.e., maximum pyrolysis temperature, heating rate, and solid residence time) increases the surface area to some extent, but it decreases after a certain limit (which is dependent on biomass, chemical and anatomical composition, and the heat and mass transfer rate). This phenomenon has two practical implications: (i) it is not always necessary to apply the most severe conditions, and (ii) energy savings can be achieved by applying the optimal pyrolysis conditions.

The determination of the surface area available for adsorption faces some problems. For instance, the prevailing method to determine the surface area, N<sub>2</sub> adsorption at 77 K, has a kinetic diffusion limitation for N<sub>2</sub> in small micropores [88]. The kinetic limitation arises from the inflexibility of the matrix, leading to an artificially lower surface area for some chars. This phenomenon has been reported by several authors, for instance for oak, pine, and grass chars, where the N<sub>2</sub> surface area was 225, 285, and 77 m<sup>2</sup>/g, respectively, while the CO<sub>2</sub> area for the same materials was 528, 843, and 427 m<sup>2</sup>/g, respectively [89]. Similar results were presented for sewage sludge and wood chip char [90]. The higher surface area estimation by CO<sub>2</sub> has been reported to be due to the higher kinetic energy associated with the smaller kinetic diameter of CO<sub>2</sub> (3.3 Å vs. 3.64 Å for CO<sub>2</sub> and N<sub>2</sub>, respectively), which allows CO<sub>2</sub> to diffuse more easily into the small pores [89,91,92].

Argon has also been used to measure char's surface area at 77 K and 87 K. The results showed that at 87 K the surface area was slightly greater than at 77 K, which was attributed to the increased mobility of Ar molecules at higher temperatures. On the other hand, the low values of surface area measured by Ar were believed to be due to the lower amount of mesopores [93].

The size of the pores also affects the sorption, because the filling of micropores involves a higher number of contact points than the filling of mesopores, and pore filling has been characterized as being influenced by size exclusion effects [88]. A comparison of the adsorption-relevant properties of different biochars is presented in Table 2.

The results of Table 2 show that biochar properties are highly variable between different precursors and applied pyrolysis temperatures. However, data analyses allow for certain conclusions:

1. The specific surface area of biochars is usually between 0 and 100 m<sup>2</sup>/g;
2. Wood biochars have the greatest specific surface area (up to 738 m<sup>2</sup>/g);
3. The pore volume of different biochars is between 0 and 0.2 cm<sup>3</sup>/g;
4. The ash content of biochars is highly variable; it is highest in sewage sludge, algae, and manure biochars, and lowest in wood biochars.

**Table 2.** Pyrolysis temperature, char yield, surface properties, and ash content of different biochars.

Feedstock	Pyrolysis Temperature (°C)	Char Yield (%)	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	Ash Content (%)	Reference
Sewage sludge	750	-	60.7		-	[94]
Sewage sludge	400	76.1	23.7		-	[95]
Sewage sludge	600	-	92.3		-	[96]
Sewage sludge	500	-	25.4	0.056	74.2	[97]
	900		67.6	0.099	88.1	
Sewage sludge	700	65	26.70	0.159	86.8	[98]
Palm oil mill sludge	400	54.2	47.7	0.007	44.8	[99]
	800	-	193.1	0.065	59.5	
Pine needles	400	30	112.4	0.044	2.3	[83]
	700	14	490.8	0.186	2.2	
Pine needles	700	25	390	0.12	18.7	[73]
Used tea leaves	350–550	-	8.1	0.012	-	[100]
<i>Ponderosa pine</i> wood	500	28.4	196		2.1	[101]
<i>Ponderosa pine</i> wood	700	22.0	347		1.7	
Tall fescue straw	700	28.8	139		19.3	
<i>Quercus lobata</i> wood			225 285 77		3.7	
<i>Pinus taeda</i> wood	650		(N <sub>2</sub> ) 528		1.1	[89]
<i>Tripsacum floridanum</i> grass			643 427		15.9	
			(CO <sub>2</sub> )			
Beech wood	800	12.5 ± 0.2	70.2	0.003		[86]
	1200	10.0 ± 0.7	110.2	0.047	-	
	1600	8.3 ± 0.4	48.7	0.040		
	2000	8.3 ± 0.5	22.2	0.032		
Poplar wood	600	-	411	0.182	4.7	[87]
Durian wood ( <i>Durio zibethinus</i> )	550	24.6	221	0.008	20.8	[102]
<i>Paulownia elongata</i> wood	-	-	310		4.1	[103]
<i>Pinewood sawdust</i> ( <i>Pinus radiata</i> )	800	11.6	738.0	0.244	1.9	[104]
Oak bark	450	22.8	1.9	1.060	11.3	[105]
Corn stover	450	15	12		58.0	[106]
Corn stover	500	17	3.1		32.4	[107]
Soybean stover	700	21.6	420.3	0.190	17.2	[108]
Cotton stalk	500		1.5	0.007	2.7	[81]
Duckweed	500	44	12	0.014	9.5	[109]
Rice husk	500	-	34.4	0.028	42.2	[110]
Rice husk	550	-	181		-	[111]
Rice straw	400	-	4.4	0.015	40.7	[112]
	700		161.2	0.086	52.5	

Table 2. Cont.

Feedstock	Pyrolysis Temperature (°C)	Char Yield (%)	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	Ash Content (%)	Reference		
Rice straw	700	-	20.6	0.019	-	[113]		
Rapeseed	550	-	25.4 (BET) 18.3 (Micro) 7.1 (Meso)	0.0480	24.9	[114]		
Rapeseed	700	29.6	19.3	1.254	14.4	[115]		
Maize	600	29.54	70	0.06	27.2	[116]		
Sugarcane bagasse (SGB)	300	-	224.1		4.2	[117]		
	400		361.8		4.2			
	500		291.4		4.1			
Giant <i>Miscanthus</i>	500	27.2	181		-	[118]		
	700	25.1	369					
Peanut shell	700	21.9	448.2	0.200	8.9	[108]		
Palm kernel shell	400	46.7	4.5	0.011	8.1	[77]		
	500	37.5	12	0.086	5.2			
	600	35.4	260	0.17	8.9			
	700	32.8	370	0.19	8.4			
Olive stones	400	-	476.3		36.2	[119]		
	600		173.3		41.2			
Alfalfa ( <i>Medicago sativa</i> )	500	-	31.1		31.3	[120]		
Orange peel	700	22.2	201.0	0.035	2.8	[121]		
Tire rubber	400	59.3	24.2	0.080	15.4	[122]		
	600	54.5	51.5	0.120	15.6			
	800	43.0	50.0	0.110	10.5			
Grape seeds	700	28	124 (N <sub>2</sub> ) 454 (CO <sub>2</sub> ) 66 (Ar77)		-	[93]		
	600	31	110 (N <sub>2</sub> ) 424 (CO <sub>2</sub> ) 57 (Ar77)					
Wood Straw Green waste Dry algae	600	23.3	127		1.3	[123]		
		25.2	22		24.5			
		24.4	46		13.4			
		22.9	19		73.0			
Cow manure	500	57.2	21.9	0.028	67.5	[124]		
Pig manure		38.5	47.4	0.075	48.4			
Shrimp hull		33.4	13.3	0.039	53.8			
Bone dregs		48.7	113	0.278	77.6			
Wastewater sludge		45.9	71.6	0.060	61.9			
Waste paper		36.6	133	0.084	53.5			
Sawdust		28.3	203	0.125	9.9			
Grass		27.8	3.33	0.010	20.8			
Wheat straw		29.8	33.2	0.051	18.0			
Peanut shell		32.0	43.5	0.040	10.6			
<i>Chlorella</i>		40.2	2.78	0.010	52.6			
Waterweeds		58.4	3.78	0.009	63.5			
Spruce wood		525	-	40.4			4.7	[125]
Poplar wood				55.7			6.8	
Wheat straw	14.2			12.7				

Table 2. Cont.

Feedstock	Pyrolysis Temperature (°C)	Char Yield (%)	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	Ash Content (%)	Reference
Pine sawdust (air lim.)	300		12.1		6.7	
Maize straw (air lim.)	300		7.8		15.4	
SCB (air lim.)	300		25.3		11.8	
Pine sawdust N <sub>2</sub>	300	-	8.2		4.6	[126]
Maize straw N <sub>2</sub>	300		2.6		11.3	
SCB N <sub>2</sub>	300		12.2		8.9	
Pine sawdust N <sub>2</sub>	500		68.4		6.9	
Maize straw N <sub>2</sub>	500		33.2		17.6	
SCB N <sub>2</sub>	500		97.8		12.3	
Wheat straw		24.6	177	0.110	12.0	
Corn straw	600	26.7	7	0.012	18.0	[127]
Peanut-shell		28.5	185	0.110	11.0	
Broiler litter	350	-	60.0	0.000	-	[128]
	700		94	0.018		
Poultry litter	600	46	5.79		60.8	[129]
Feedlot manure	700	32.2	145.2		92.0	[76]
Goat-manure	600	37.9	13.9	0.008	-	[130]
	800	33.8	93.5	0.049		
Yak manure	700	-	82.9	0.074	-	[131]
<i>S. dimorphus</i>	500	-	123		43.3	[132]
Microalgae	600		89		44.2	
<i>Laminaria japonica</i> microalgae	600	38.0	79.9	0.044	55.1	[133]
Waste marine Macroalgae	400	67.7	70.3	0.112	41.9	
( <i>Undaria pinnatifida</i> roots)	600	47.8	61.8	0.078	48.7	[134]
	800	39.3	44.5	0.057	50.4	
<i>Saccharina japonica</i> macroalgae	600	-	266 (unwashed) 543 (washed)	0.132	-	[135]
				0.266		
			277.3			
			266.7			
			228.6			
			382.8			
Bamboo	550		143.4	0.173		
	650		(S <sub>BET</sub> )	0.162		
Industrial waste	750	-		0.144	-	[136]
	850		221.6	0.254		
	950		228.7	0.142		
			200.8			
			320.7			
			99.7			
			(S <sub>mic</sub> )			
Rice straw	700	30.7	32.9	0.049	-	[137]
Pig manure		38	20.5	0.045		
Douglas fir wood		16.0	500	0.2		
Hybrid poplar wood	600	20.4	416	0.17	-	[138]
Douglas fir bark		29.6	423	0.17		

Table 2. Cont.

Feedstock	Pyrolysis Temperature (°C)	Char Yield (%)	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	Ash Content (%)	Reference
Sewage sludge			165	0.047		
			87	0.027		
Sludge and food waste	-	-	683 (CO <sub>2</sub> )	0.186		
			97	0.153	-	[90]
Wood chips			84	0.133		
			261 (N <sub>2</sub> )	0.160		

#### 4.2. Modification of Biochars

A number of methods have been developed to tailor and maximize the adsorption capacity of biochars used in water treatment and soil remediation, as well as in energy storage [139]. The modified or engineered biochar is the derivative of pristine biochar that has undergone physical, chemical, or biological treatments to improve its properties, such as its specific surface area, porosity, cation-exchange capacity, surface functional groups, pH, etc. [140–142]. The engineered biochars contain a large number of carbons, including activated carbons. Interestingly, most biochar engineering methods are less expensive and easier processes than the typical carbon activation processes [68].

Currently, different physical or chemical modifications (Table 3) are applied to biochars to improve their adsorption capacity [12]. These modifications are discussed below.

**Table 3.** Critical comparison of the advantages and disadvantages of the main biochar modification methods.

Treatment No.	Treatment	Advantages	Disadvantages
1	Acid treatment	Removal of metals; increased surface area	Lower biochar yield due to acid hydrolysis; inefficient removal of silica; high cost
2	Alkali treatment	Removal of silica; increased surface area	Lower biochar yield due to alkaline hydrolysis; inefficient removal of metals; high cost
3	Deminceralization with hot water	Efficient removal of metals and silica	Energy- and time-consuming; additional drying step required
4	Ball milling	Increased surface area	High cost; less effective than chemical methods
5	Steam activation	Increased surface area	Reduced biochar yield
6	Doping with organic compounds	Addition of surface functional groups	High cost
7	Surfactant modification	Addition of acidic or basic surface functional groups	Leaching of surfactant; high cost
8	Mineral impregnation	Addition of metal oxides on the biochar surface	Secondary contamination by leaching of mineral
9	Mineral impregnation: iron	Addition of iron atoms on the biochar surface; easy removal of magnetic particles from water	Secondary contamination by leaching of iron
10	Composite-forming clays	Enhanced ion-exchange mechanism	Environmental impact of clay processing
11	Composite-forming by carbon	Addition of adsorption sites	High cost
12	Composite-forming by heteroatom doping	Addition of surface functional groups	High cost; heteroatom leaching; specialized process
13	Molecular imprinting	Production of a specialized type of biochar selective to target (imprint) molecules; reusable	High cost; specialized process

Acid or alkali activation is the most widely used and effective way to enhance biochars' surface area and porosity. Both acid and alkali treatments increase the porosity of biochars by altering the biochar's structure and surface functional groups via depolymerization, dehydration, and dehydrogenation reactions (i), creating micro- and mesopores inside the biochar's structure (ii), and removing the inorganic compounds (iii) [49,143–145].

Acid–base combined treatments can be considered for low-porosity biochars bearing limited surface functional groups, such as municipal sewage sludge biochars [49,146,147]. These treatments seem to be superior to the single acid or alkali treatments [49]. However, the available data are still scarce. More experimental results with a broader range of biochars are required to better understand the effects of the combined acid–base treatments.

Physical treatment methods, such as coating with carbonaceous materials, ball milling, and template formation, can also result in surface enhancement. Ball milling seems to be a feasible method to produce biochar nanoparticles [148]. Future research should focus on developing technologies to simultaneously achieve enhanced functionality and porous structure of biochars.

Cationic or anionic surfactants such as cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) are used to alter the adsorbent's surface and, in particular, to change the surface charge [149]. Certain organic compounds, such as humic acid (HA) [150], methanol [151], and chitosan [152–154], have been used in the modification of biochars because they introduce supplementary functional groups (e.g., carbonyl (-C=O-), amino (-NH<sub>2</sub>) and hydroxyl (-OH)) to the surface of biochar [49]. However, organic compound modification has cost disadvantages, which limit its development [49]. Metal or metal oxide modification provides a higher number of adsorption sites and creates a larger surface area in biochars [49,146,155–157]. The metal modification is particularly effective in the recycling of biochars after adsorption. However, metal modifications generate contamination of water bodies through metal ion shedding [49].

Doping with carbonaceous materials is the introduction of carbonaceous materials (e.g., graphene and carbon nanotubes) into the surface structure of biochars to improve their adsorption efficiency [49,158]. The increased number of adsorption sites and the increased specific surface area of the biochar improve its adsorption capacity [49,159,160]. However, graphene, graphene oxide, and carbon nanotubes are highly expensive materials and cannot be considered practical for large-scale adsorption applications [49].

Non-metallic or heteroatom doping of biochars using nitrogen [161–163], oxygen [162], sulfur [163], or phosphorus [162] is an efficient modification method to offer increase the stability and adsorption efficiency of adsorbents [49]. The heteroatom doping of biochar provides additional surface functional groups and active sites for adsorption. However, the available research is currently scarce [49].

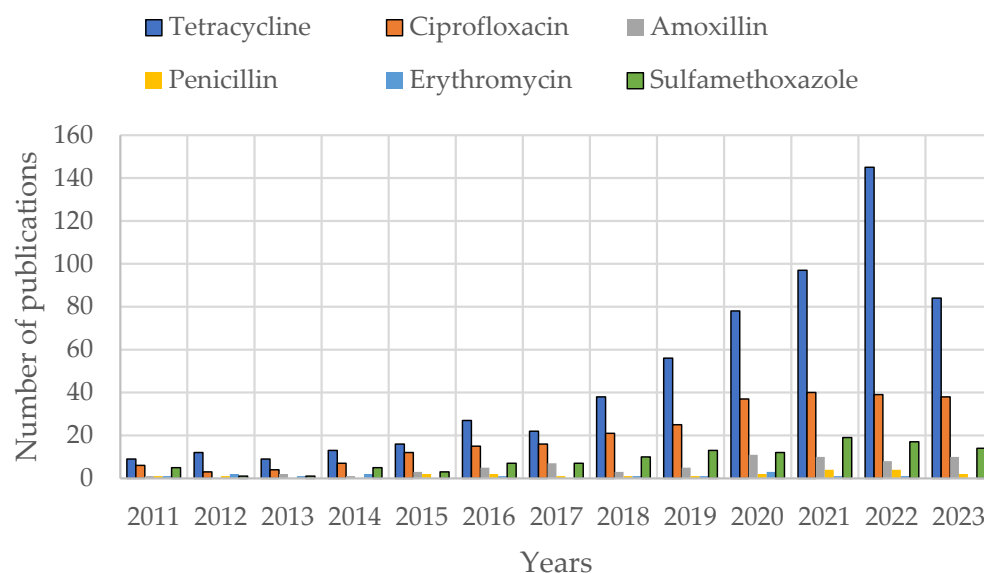
Other physical modifications, such as steam activation [164] and ball milling [158,165], generate a higher specific surface area, a higher number of functional groups, and pores in biochars. Physical modifications are environmentally friendly, as they do not use any chemicals during biochar modification [49]. However, they are comparatively less effective than chemical modifications [49].

Molecular imprinting improves the specific adsorption of biochars by creating selective active sites [49]. Molecularly imprinted biochars can be used to remove low-concentration and highly toxic pollutants [49,166]. Molecularly imprinted biochars have already been used to detect and quantify antibiotic residues at trace levels in food and environmental samples [49,167,168]. Molecularly imprinted biochars are reusable, which is their major advantage compared to other biochars [48]. Similar to other modified biochars, molecularly imprinted biochars usually exhibit better adsorption properties for antibiotics than pristine biochars [49].

#### 4.3. An Overview of Biochar-Based Adsorption Studies

In the bibliometric survey section, it was shown that antibiotic adsorption studies are increasing in number, while in the antibiotics and bacterial cytology section, antibiotics were

grouped into different classes based on their chemical structure. It is important to observe the adsorption studies of each major antibiotic group. Figure 3 provides an overview of adsorption studies with different antibiotics. Adsorption studies were predominantly performed on tetracycline, fluoroquinolone, and sulfonamide antibiotics. This is consistent with the co-occurrence map (Figure 2) and suggests that these antibiotics are selective to carbonaceous adsorbents.



**Figure 3.** Number of publications with “adsorption” and “different antibiotics” titles on the Web of Science (WOS).

Previous studies on biochar-based removal of antibiotics were mainly performed on modified biochars. The usage of pristine biochars for the removal of antibiotics is currently limited to biochars prepared by pyrolysis, which are termed pristine biochars (PBs) [68]. However, in order to modify the adsorption performance of biochars, the first step is to understand the adsorption performance of pristine biochars by studying the biochars’ properties and adsorption mechanisms.

The adsorption mechanisms of different carbonaceous materials are not identical, although certain mechanisms, such as  $\pi$ - $\pi$  electron donor–acceptor (EDA) interactions and hydrogen bonding, are considered both for high-surface-area carbon nanotubes and for biochars, indicating the role of intermolecular interactions in the adsorption [169]. According to Du et al. (2023), at least seven different mechanisms, including hydrogen bonding,  $\pi$ - $\pi$  interactions, surface complexation, electrostatic interactions, pore filling, ion exchange, and hydrophobic interactions, can contribute to the adsorption of antibiotics onto biochars [49]. This excellent review also showed that antibiotic adsorption studies with biochars were mostly performed with modified biochars (approximately 65% of the studies) [49].

Table 4 provides a comparison of proposed antibiotic adsorption mechanisms and maximum adsorption capacities for pristine biochars and modified biochars.

The results of Table 4 suggest that the modification of biochars significantly affects their antibiotic adsorption capacity. The antibiotic adsorption mechanisms were principally studied on modified biochars, and  $\pi$ - $\pi$  interactions were the most commonly proposed mechanisms for both types of biochars.

**Table 4.** Mechanisms of antibiotic adsorption onto biochars; modified from [12].

Biochar Biochar Precursor	Pyrolysis Temperature (°C)	Proposed Mechanism	Modification	Antibiotic Used	Maximum Adsorption Capacity ( $Q_m$ ) (mg/g)	Reference
Pristine biochars						
<i>Pinus radiata</i> wood sawdust	600–800	n.a	n.a	Tetracycline (TC)	163	[104]
Bamboo sawdust	500	n.a	n.a	Enrofloxacin (EF) Ofloxacin (OF)	45.9 (EF) 45.1 (OF)	[170]
Spent coffee grounds	200–700	$\pi$ - $\pi$ EDA	n.a	Sulfadiazine (SDZ), sulfamethoxazole (SMX)	0.12 (SDZ) 0.13 (SMX)	[171]
Modified biochars						
Sunflower seed husk	600	Multiple: chemisorption, external diffusion, intraparticle diffusion	H <sub>3</sub> PO <sub>4</sub>	Tetracycline (TC), ciprofloxacin (CIP), sulfamethoxazole (SMX)	429.3 (TC) 361.6 (CIP) 251.3 (SMX)	[172]
Bamboo	380	Hydrogen bonds, $\pi$ - $\pi$ EDA, Lewis acid–base	H <sub>3</sub> PO <sub>4</sub>	Sulfamethoxazole (SMX)	88.10	[173]
Poplar wood	500	Pore filling, $\pi$ - $\pi$ interactions, surface complexation, hydrogen bonding, and electrostatic interactions	KOH Fe <sub>3</sub> O <sub>4</sub>	Tetracyclines (TCs) Fluoroquinolones (FQs)	70.3–89.6 (TCs) 35.5–60.3 (FQs)	[174]
Palm fibers	500	Pore filling, surface electrostatic interactions, hydrogen bonding, complexation, and $\pi$ - $\pi$ EDA interactions	Fe–N co-doped	Sulfamethoxazole (SMX)	42.9	[175]

#### 4.4. Thermodynamic and Kinetic Considerations

Thermodynamic and kinetic (rate and mechanism) studies are the two essential tools in adsorption studies because they answer fundamental questions such as whether an adsorption process works, how it works, how to optimize it, and how to design better adsorbents.

Thermodynamics determines the feasibility of an adsorption process under various temperature and pressure conditions. The thermodynamic analysis of adsorption involves the calculation of thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy ( $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ , respectively), which can be used to assess the thermodynamic feasibility of the adsorption process. For instance,

- If  $\Delta G < 0$ , the process is thermodynamically favorable, and adsorption will occur spontaneously;
- If  $\Delta G > 0$ , the process is thermodynamically unfavorable, and adsorption will not occur spontaneously;
- If  $\Delta G = 0$ , the process is at thermodynamic equilibrium.

Enthalpy change ( $\Delta H$ ) is another thermodynamic parameter that is used to assess the feasibility of adsorption. If the adsorption is exothermic ( $\Delta H < 0$ ), it releases heat and is more favorable at lower temperatures. If the adsorption is endothermic ( $\Delta H > 0$ ), it absorbs heat and is more favorable at higher temperatures. Entropy change ( $\Delta S$ ) is the final factor to assess the feasibility of adsorption. An increase in entropy ( $\Delta S > 0$ ) favors the adsorption process.



These factors are related according to the following equation:

$$\Delta G = \Delta H - T\Delta S$$

In order for  $\Delta G$  to be negative, either the enthalpy change ( $\Delta H$ ) should be negative (exothermic process) and greater than the  $T\Delta S$  product (typically positive), or, in the case of endothermic reactions, the entropy change ( $\Delta S$ ) should be large enough to offset the positive enthalpy change ( $\Delta H$ ) and temperatures ( $T$ ) should be high.

Exothermic adsorption ( $\Delta H < 0$ ) involves relatively strong adsorbate–surface interactions, such as chemical sorption or strong van der Waals forces, while endothermic adsorption involves weak adsorbate–surface interactions such as physical sorption (weak intermolecular interactions). The entropy change ( $\Delta S$ ) may be positive or negative in chemical sorption, but it is usually negative in physical sorption.

Pressure can also affect the adsorption process, but its impact in liquid adsorption is less pronounced than temperature. High pressures increase the entropy and favor the adsorption process, but they may also lead to degradation of the adsorbent.

Thus, in order to optimize the adsorption of antibiotics onto biochars, it is necessary to calculate the thermodynamic properties. If the adsorption is exothermic, it should be performed at low temperatures, and if the adsorption is endothermic it should be performed at high temperatures. If the adsorption occurs due to surface chemical reactions, the adsorbent's surface should be modified with metal oxides or heteroatoms to increase the number of available complexation sites and drive the adsorption process in a thermodynamically favorable manner. If the adsorption occurs through physical sorption, oxygenated surface functional groups should be introduced to the biochars to increase the intermolecular interactions, such as hydrogen bonds. It should be noted that the adsorption of antibiotics is a complex reaction and involves both surface chemical reactions and physical sorption [172]. Therefore, different experimental conditions should be tested to optimize the adsorption process.

A particular case of thermodynamic studies is the study of adsorption isotherms that describe the equilibrium relationship between the concentration of adsorbate molecules and the amount of adsorbate adsorbed onto the surface of the adsorbent. Thus, they provide information about the adsorption capacity and the adsorbent–adsorbate surface interactions. The Langmuir isotherm and Freundlich isotherm are the most frequently used adsorption isotherms. According to the Langmuir isotherm, the adsorbent's surface is homogeneous, and adsorption occurs as a monolayer until all available sites are occupied by adsorbate molecules and there are no interactions among the adsorbed molecules. The Freundlich isotherm assumes a heterogeneous adsorbent surface, multilayer adsorption, and interactions among the adsorbed molecules.

Kinetic models of adsorption describe how adsorbate molecules are adsorbed onto the surface of an adsorbent material as a function of time. The kinetic models explain the reaction rate and the mechanisms, and they provide insights into the dynamic aspects of adsorption. The most frequently used kinetic models are the pseudo-first-order model, pseudo-second-order model, Elovich model, and intraparticle diffusion model. The pseudo-first-order and pseudo-second-order models consider the surface reaction as the rate-limiting step, while the intraparticle diffusion model considers the intraparticle diffusion as the rate limiting step. According to the pseudo-first-order kinetic model, the adsorption rate ( $dq/dt$ ) is proportional to the difference between the equilibrium concentration ( $q_e$ ) and the concentration at a given time ( $q$ ), while according to the pseudo-second-order kinetic model the adsorption rate is proportional to the square difference between the equilibrium concentration and the concentration at a given time. The Elovich model assumes that rate of the adsorption is not constant over time and that there are interactions between the adsorbate molecules. The intraparticle diffusion model describes the rate of intraparticle diffusion.

The adsorption of tetracycline antibiotics onto zinc chloride activated biochar was described by the pseudo-second-order kinetic model and the Langmuir isotherm, with a maximum (monolayer) adsorption capacity of 200 mg/g tetracycline. Hydrogen bonding

and electrostatic interactions were the main proposed mechanisms [176]. The adsorption of quinolone antibiotics onto magnetic biochar also resulted in a similar trend. The adsorption was described by the pseudo-second-order kinetic model and the Langmuir isotherm, with a maximum adsorption capacity of 68.9 mg/g [177]. Similarly, the adsorption of tetracycline, quinolone, and sulfonamide antibiotics onto H<sub>3</sub>PO<sub>4</sub> activated biochar was described well by the Elovich and pseudo-second-order kinetic models, as well as by the Langmuir isotherm [172]. Interestingly the results of this latter study indicated that the adsorption of antibiotics is an endothermic and spontaneous process with negative Gibbs free energy and a positive entropy change. Both chemical and physical adsorption occurred simultaneously [172]. The endothermic character of antibiotic adsorption on activated carbon was also reported for the adsorption of heavy metals [178]. On the other hand, the adsorption of sulfonamide antibiotics onto H<sub>3</sub>PO<sub>4</sub> activated biochar resulted in a spontaneous and exothermic process that was favorable at low temperatures [179]. The adsorption was described by the Langmuir isotherm and the pseudo-second-order kinetic model, similar to previous studies [179]. The study of Srivastava et al. (2002) also showed a similar trend. The adsorption of quinolone and tetracycline antibiotics onto modified biochar was exothermic and was described by the Langmuir isotherm and the pseudo-second-order kinetic model [180].

The above examples were the modified biochars, which are the biochars most frequently used as adsorbents. The kinetic models and isotherms for the adsorption of antibiotics onto pristine biochars seem to follow the same trend (i.e., Langmuir isotherm and pseudo-second-order kinetics). However, there are still few studies on pristine biochars providing insights into their adsorption mechanisms. For instance, the adsorption of tetracycline antibiotics onto wheat-stalk biochars was described well with the Langmuir isotherm as well as the pseudo-second-order and intraparticle diffusion kinetic models [148]. A similar kinetic model was reported for the adsorption of sulfonamide antibiotics onto a biochar based on spent coffee grounds. The adsorption kinetics of sulfadiazine (SDZ) and sulfamethoxazole (SMX), two common sulfonamide antibiotics, was better described by a pseudo-second-order model, implying that the adsorption of antibiotics onto biochars is controlled by the chemisorption mechanism [171].

The overall results indicate that the adsorption of antibiotics onto pristine or modified biochars predominantly occurs as a monolayer through surface reactions and intraparticle diffusion mechanisms. Thermodynamic studies of the adsorption of different antibiotics have shown that the adsorption of antibiotics on biochars can be exothermic or endothermic and should be determined for each adsorption case to improve the adsorption efficiency.

## 5. Knowledge Gaps, Critical Evaluation, and Future Directions

The application of biochars in the adsorption of emerging pollutants such as antibiotics is still in the development stage. The number of scientific studies on the adsorption of antibiotics is increasing, but only a few studies have used pristine biochars for adsorbents. On the other hand, biochar modification seems to be a promising approach to increase the adsorption capacity of biochars.

In order to maximize the potential of biochars in adsorption, the first step is to determine the knowledge gaps. This review allowed us to identify the following knowledge gaps:

1. Currently, there is deficient monitoring of specific antibiotic compounds in water sources.
2. Biochars' surface structure and chemical properties are highly variable among different biochars. Waste biomass materials are usually applied for biochar production, but they have limited potential compared to porous wood biochars.
3. The effect of ash contents on adsorption is usually ignored, although inorganics are involved in the surface complexation. More studies are required to screen biochars for ash composition.

4. Most antibiotic adsorption studies were performed at the batch scale, which is not representative of real water conditions. Also, studies on the simultaneous removal of antibiotics and other pollutants are still scarce.
5. Thermodynamic and kinetic studies on the adsorption of antibiotics on biochars are scarce. The adsorption mechanisms of different antibiotics on pristine chars are not well known.
6. Heteroatom doping and iron doping of biochars are promising approaches to increase the adsorption capacity of biochars, but they are costly.
7. Molecular imprinting of biochars is another possible way to improve the adsorption capacity of biochars, but this process is also costly.
8. The combination of biochars with other antibiotic removal methods, such as the activation of AOPs, seems to be a promising approach.

Previous studies have demonstrated that biochars are efficient adsorbents for the removal of antibiotics, while it is important to screen target antibiotics for adsorption. Among the different antibiotics,  $\beta$ -lactams are the most frequently used, but they are not stable in water because of the instability of the lactam ring; therefore, they are usually not detected or are detected at low concentrations in the wastewater [33]. The high-molecular-weight tetracyclines are the sorbents most readily adsorbed onto biochars [12], suggesting the size exclusion effect and the role of surface chemistry in adsorption. Another implication of this result is that biochars are low-cost alternatives to nanofiltration and reverse-osmosis membranes [27], as well as activated carbons [181], for tetracycline removal. Hydrothermally produced chars (hydrochars) may be preferentially used for the removal of tetracyclines because they usually retain surface chemical groups better than biochars.

The adsorption process can be integrated into the activated sludge process as a tertiary process where antibiotics that are not retained by the activated sludge can be targeted. For this aim, the octanol–water partition parameter criterion ( $\log K_{ow}$ ) can be applied. According to the classification of Rogers (1996) [182], the antibiotics can be grouped as low-sorption (i.e., tetracyclines, sulfonamides, aminoglycosides;  $\log K_{ow} < 2.5$ ), medium-sorption (i.e.,  $\beta$ -lactams, macrolides;  $2.5 < \log K_{ow} < 4.0$ ), and high-sorption (i.e., glycopeptides;  $\log K_{ow} > 4.0$ ) [60]. However, this result should be interpreted with caution, because environmental conditions such as the pH of the solution can affect the sorption of antibiotics [33].

However, in all cases, the principal adsorption targets of biochars should be low-sorption and medium-sorption antibiotics that cannot be removed by activated sludge.

As mentioned earlier, the adsorption of antibiotics using biochars leads to the production of secondary waste, either due to the concentration of antibiotics in the biochar or through metal-doping-related secondary pollution. It is highly unlikely to reuse the antibiotic-loaded biochars, except for molecularly imprinted biochars. Therefore, they should not be used for soil amendment, as antibiotics may leach from the biochars and reach surface waters. However, it should be noted that antibiotic leaching depends on the biochar type, biochar–antibiotic interaction, and environmental conditions. Therefore, high antibiotic retention may be observed in different biochars, as in the case of activated carbons [183].

In fact, this problem is not exclusive to biochars. All adsorbents, membranes, and activated sludge also confront this post-antibiotic-removal problem. The most frequently used adsorbent, activated sludge, is incinerated to avoid secondary pollution. In recent years, it has not been allowed for fertilizer use in some countries [60]. A thermochemical conversion strategy can be applied to antibiotic-loaded biochars by using high temperatures to produce activated carbons and to remove the antibiotics. The activated biochars can be used again for the adsorption of antibiotics. The activated carbons can be incinerated similarly to activated sludge once they have been used for antibiotic removal.

The main problems of biochars are their small particle size and low density, which make it very difficult to remove them from the water after the adsorption [184]. The small particle size and low density of biochars lead them to be suspended in water, preventing

solid–liquid separation or settling. Magnetic modification seems to be the unique solution to this problem.

## 6. Conclusions

Antibiotics are natural or synthetic pharmaceuticals that are used to combat bacterial infections. They are considered to be emerging pollutants, and their concentrations are continuously increasing in the environment, causing bioaccumulation in animals and the occurrence of antibiotic resistance, which is an alarming issue according to the World Health Organization.

It is not possible to completely avoid the use of antibiotics, but their accumulation may be reduced by using adsorption methods. Adsorption methods are selective for the removal of low-concentration pollutants. A number of adsorption methods and adsorbents are currently used for the removal of antibiotics from water sources. Biochars are low-cost adsorbents that show promising potential for antibiotic removal. The antibiotic adsorption properties of biochars are comparable to those of activated carbons. The adsorption capacities of biochars can be further improved by different modification methods. The adsorption of antibiotics onto biochars predominantly occurs as a monolayer and follows pseudo-second-order kinetics, and the adsorption may be exothermic or endothermic.

Tetracyclines, quinolones, and sulfonamide antibiotics are the most-tested antibiotics with biochars. The biochar surface properties, such as specific surface area and pore structure, as well as ash content and ash composition, are highly variable between different precursors. Wood biochars should be selected for the adsorption of non-bulky antibiotics, due to their high surface areas, while ash-rich non-wood biochars should be selected for the adsorption of bulky antibiotics, due to their surface chemical groups.

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