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Review

Biochar-Based Adsorbents for Pesticides, Drugs, Phosphorus, and Heavy Metal Removal from Polluted Water

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Abstract: Water contamination is a ubiquitous issue for all countries and territories worldwide. Among others, pesticides, drugs, heavy metals, and phosphates play a special role in terms of pollutants due to their toxicity and large-scale applications in industrial and agricultural activities. In order to provide cleaner freshwater for the world's population, two types of actions are required: preventing/limiting the pollution that might occur during our daily activities and decontaminating the already exposed/contaminated water sources. One of the key points in the decontamination process is to create as few as possible side effects with the solutions applied. For this reason, in the case of the mentioned types of pollutants but not limited only to them, the use of environmentally friendly materials is more than welcome. Biochar qualifies as one of these materials, and its field of applications expands to larger scientific and industrial areas every day. Moreover, it can be functionalized in order to improve its properties in terms of pollutant removal efficiency. This paper summarizes the most recent developments in the field of water decontamination using biochar or biochar-based materials in order to remove pesticides, drugs, heavy metals, and phosphates from contaminated aqueous environments. Also, the removal of phosphorus from wastewater using biochar is considered. This removal can be a key controlling factor for the wastewater, which is obtained as a residual of agricultural activities. Indeed, due to the excessive use of chemical fertilizers, eutrophication in such kinds of wastewater can be a serious challenge.

Keywords: biochar-based adsorbents; water decontamination; pesticides; drugs; heavy metals; phosphorus

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1. Introduction

Biochar is a carbon-rich product resulting from the thermochemical conversion of carbonaceous materials in an oxygen-deficient environment at temperatures above 250 °C. Biochar has gained significant attention as one of a handful of greenhouse gas removal technologies with a critical role to play in achieving a net zero emission economy, and it is recognized by the Intergovernmental Panel on Climate Change as a carbon-negative technology. However, biochar's multi-functional nature enables additional application scenarios beyond its conventional use as a carbon sink in soil, ranging from water filtration and sensing application to its use as a building material, while largely retaining most of its carbon sequestration potential.

Biochar properties such as surface area, pore size distribution, structure, and electrical conductivity can be tailored to suit end application by changing process conditions such

as pyrolysis temperature, residence time, and career gas flow rates and by also including pre- and post-treatment steps such as doping, adding metal/metal oxide precursors, and activation to produce functionalized biochar.

Pine needle-derived biochar was demonstrated to sorb naphthalene, nitrobenzene, and m-dinitrobenzene effectively and can be used as an environmentally engineered sorbent for the removal of organic pollutants from aqueous contaminants, while straw-based biochar was used as a cheaper and more sustainable substitute for activated carbon, with high adsorption efficiencies for reactive brilliant blue and rhodamine B [1].

The market for bio-filters with good depollution results is constantly growing, and the authors started to investigate the potential of biochar as a filter medium for onsite wastewater treatment. Perez-Mercado et al., in 2018, investigated five sub-studies in this potential of biochar [2]. They compared pollutant removal from wastewater using pine–spruce biochar, willow biochar, and activated biochar filters. They concluded that willow and pine–spruce biochar could be considered suitable materials to replace or complete sand filters in onsite wastewater treatment systems, as they can efficiently remove organic matter and ammonium from wastewater, but further investigation will be necessary to establish the long-term performance of these materials.

Kaetzl et al., in 2020, completed this area with a similar study [3]. They compared Miscanthus biochar, used as filtration media, with sand as a common reference material. Biochar filters were efficient in the removal process of *E. coli*, which increased over experimental time ($R = 0.81$, $p < 0.01$), followed by a decrease in the normalized concentration of *E. coli*. By contrast, the sand filter removal efficiency decreased over experimental time, followed by an increase in normalized *E. coli* concentration.

The previous biochar reviews discussed biochar structure, biochar modification, the potential drawbacks, and the emerging applications for water pollution, such as metal sorption and catalytic degradation.

In the present work, the methods for biochar preparation and its applications as an adsorbent material for the removal of pesticides, drugs, and heavy metals from polluted water are presented (Figure 1).

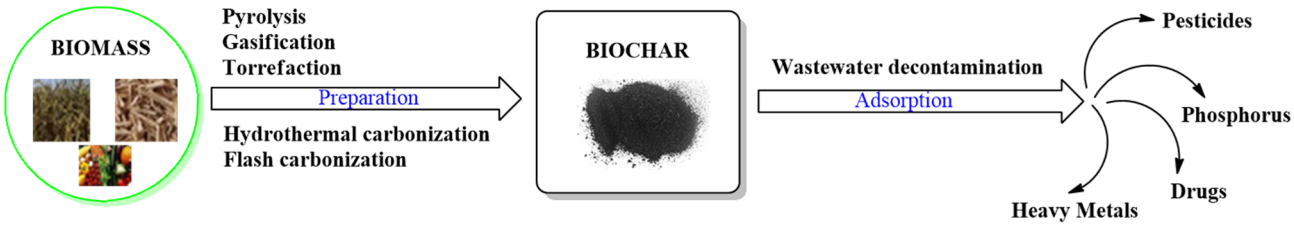

Figure 1. Biochar preparation and applications.

2. Preparation of Biochar

Unlike the relatively recently discovered carbon-based materials, biochar was used as a soil amendment for centuries. On the other hand, its application as an adsorbent material for targeted pollutants gained momentum in recent decades when the costs for most of the raw materials used on a large scale increased due to their high demand and limited availability. In this context, the relatively low production costs and the broadly available waste materials to be used as feedstock turned scientists' attention toward the use of biochar, either in their raw or in the functionalized/modified version, as possible solutions for the increasing pollution of freshwater sources.

2.1. Preparation and Characterization of Biochar-Based Materials

In order to obtain biochar-based materials, in most cases the biochar itself is produced followed by additional processes that reshape its physicochemical characteristics in order to improve its surface properties for the desired applications.

Several methods to turn the large variety of biomaterial available and usable as feedstock can be distinguished, pyrolysis being by far the most applied one. Other methods worth mentioning are gasification, hydrothermal carbonization, torrefaction, and flash carbonization.

2.1.1. Pyrolysis and Torrefaction

The pyrolysis process performed under an inert atmosphere at temperature ranges of 250 to 900 °C is used to recycle the waste biomass. The main factor controlling the efficiency of the pyrolysis process is the temperature [4]. In general, biochar production decreases with the increase in the reactor temperature, which leads to an increase in syngas production. Based on temperature, heating rate, residence time, and pressure, fast and slow pyrolysis processes are evidenced. In the case of fast pyrolysis, the feedstock is added to the reactor after raising its temperature to the desired value, implying a residence time for the reaction in the order of several seconds only. For a slow pyrolysis, the feedstock is added to the reactor at the beginning of the process, and it is characterized by residence time that ranges from half an hour to several hours [5]. The heating method adopted during the pyrolysis process can also differentiate between several types of processes, burning fuel, electrical heating, or microwaves [6]. Compared to other carbon-based materials (carbon nanotubes for example) preparation methods and pyrolysis as a biochar production technique is low-cost, easily applicable, and, in general, more sustainable from an environmental protection point of view.

Torrefaction is a mild pyrolysis process that uses a low heating rate (ranges from 200 to 300 °C) for feedstock conversion in biochar products. This process will be carried out in an inert atmosphere and under atmospheric pressure conditions [7]. Involving a relatively low heating rate below 50 °C/min, torrefaction comes with relatively large residence times of up to 1 h. The process leads to the partial decomposition of the biomass into condensing and noncondensing gases, the final product consisting of biochar and biocarbon, but the obtained biochar has a low adsorption capacity [8].

2.1.2. Gasification

The gasification process partially oxidizes the feedstock, occurring at high temperatures (>700 °C) in the presence of gasification agents (air, oxygen, steam, etc.). The gasification process produces gaseous products (e.g., CO, CO_2, CH_4, H_2) and solid and liquid products. It leads to low biochar yields because, in this process, the gaseous products are targeted. The production of hydrogen and carbon monoxide increases with temperature, while the carbon dioxide, methane, and hydrocarbon outcomes decrease. Before the main process, a drying process is usually needed [8].

2.1.3. Hydrothermal Carbonization

For the hydrothermal carbonization process, a mixture of feedstock and water will be slowly heated inside the reactor at a slow increase in temperature and pressure [8]. The temperature of the reactor is the most important parameter that influences the reaction products. It was observed that at temperatures lower than 250 °C (hydrothermal carbonization), biochar is produced, in the 250–400 °C temperature range, (hydrothermal liquefaction) bio-oil is produced, while for temperatures higher than 400 °C (hydrothermal gasification), different gaseous products are produced (e.g., CO, CO_2, H_2, CH_4) [4,9]. We can conclude that the hydrothermal carbonization process provides biochar with higher carbon content than in the case of the pyrolysis or gasification processes.

2.1.4. Flash Carbonization

In flash carbonization, the feedstock is converted into solid and gas products at a temperature of 300–600 °C under a pressure of 1–2 MPa, and the residence time is around 30 min [8]. Hydrophobic solid is obtained from biomass by baking it under inert conditions,

removing its water and oxygen [10]. The process occurred under high pressure and a flash fire [11].

2.1.5. Functionalization of Biochar-Based Materials

It was found that biochar composites incorporated with nanoparticles, nanometal oxides, or bimetallic parts are often used in the degradation of organic pollutants due to their electron carrier or morphological properties, and it could be concluded that these biochar composites are equally rich in physical–chemical properties compared to native biochar with good adsorptive removal ability of targeted pollutants from the environment. Unmodified biochar has a lower removal capacity than modified ones, especially in wastewater [12]. Tan et al. and Goswami et al. show the relation between the surface area and functionality of biochar with the sorption capacity [13,14].

Biochar metal oxide preparation aims to satisfy the homogeneous distribution of metals on biochar surfaces and despite the competitiveness and low price of pristine biochar, the biochar powder is difficult to separate from water. For this reason, researchers are trying to introduce a magnetic component (e.g., Fe_3O_4), obtaining a composite material that combines the advantages of biochar and iron oxides [15], allowing the magnetic separation of pollutants from aqueous solutions [16]. In addition, this combination increases the affinity for different compounds like phosphates, selenium, or organic pollutants [17,18]. The final cost of the sorbent should increase by introducing a magnetic part due to both the cost of the added component and extra synthesis steps [19,20].

The incorporation of iron particles within the biochar reduces adsorption capacity more than chemically activated biochar in the case of zero-valent iron particles supported on biochar produced from *Nephelium lappaceum* peel waste [21].

Combining biochar and metal oxides is a new route approached by researchers in the last few years. Due to the advantages of biochar and the physicochemical properties of nanometal oxides (e.g., MgO, ZnO, Fe_2O_3, binary oxides, such as $MnFe_2O_4$ and $MnAl_2O_4$, or ternary oxides, such as $CuZnFe_2O_4$) novel composites that are more dispersible and have a smaller crystallite size and a higher electron transfer can be obtained [22–25]. Nanometal oxide biochar, in addition to the ability to remove pollutants, is also interesting due to its low production costs and recyclability. In the future, it is important to develop large-scale, cost-effective, environmentally friendly methods of preparing these materials for the removal of emerging pollutants and eliminate the associated hazards and risks to organisms.

Khalil and co-authors, in 2021, after a literature search, presented a graph of the growing interest of the scientific community in the use of biochar: 2 papers in 2001, 221 in 2011, 1408 in 2016, 4225 in 2020, and 1289 in 2021 (until April 2021) [26]. They also presented the results of a bimetallic biochar, a CuNi-decorated biochar, which was prepared in the one pot method (olive pit powder particles were impregnated with copper and nickel nitrates and pyrolyzed together at 400 °C) that presented soft ferromagnetic hysteresis loops with zero remanence and zero coercivity and small sizes (up to 10 nm). CuNi-decorated biochar was found to be an efficient catalyst for the reduction in methyl orange dye. Their results open new horizons for the emerging topic of biochar-supported nanocatalysts [26].

The utilization of biochar for the control of environmental pollution is sustainable, eco-friendly, and cost-effective in terms of recycling waste materials into new resources. The use of them as catalysts, catalyst supports, and adsorbents for environmental remediation increased in the last year is due to the easy modification ability of biochar for a specific purpose, depending on the preparation methods and starting materials. Recently, metal-impregnated biochar and biochar-supported ZVI (zero-valent iron (Fe^0)) combination systems have been reported for environmental contaminant removal due to the anti-aggregation properties of the material [27].

The synthesis and consequent application of these nanocomposites can offer a variety of benefits including sustainability, low cost, and the achievement of the circular economy [28].

3. Application of Biochar-Based Adsorbents for Water Purification

3.1. Pesticides Adsorption on Biochar-Based Materials

The utilization of pesticides is beneficial to agricultural production and the economy, but excessive use of pesticides causes toxicity on non-target organisms and destruction of the ecological balance and human health. In the era of intensive agriculture, the introduction of pesticides and the reliance on the usage of pesticides have increased considerably in order to ensure constant annual yields, with minimal fluctuations in terms of quantities. Pesticide is considered any substance or mixture of substances used for preventing, destroying, repelling, or mitigating any pest that can deteriorate the crops and impact the whole harvest [29,30]. Biochar is applied with success as a distinctive remediation method in pesticide contamination treatment. Zhang et al., in 2018, produced maize straw biochar at 300, 500, and 700 °C to study thiacloprid sorption [31]. They found that sorption occurred probably via pore filling, hydrophobic interaction, and π–π interaction. The corn straw biochar prepared at 300, 500, and 700 °C and the other three adsorbents of acid, alkali, and iron magnetization-modified biochar prepared at 700 °C were studied for the adsorption of carbendazim from water [32]. The results revealed that the adsorption capacity of the adsorbents used for carbendazim removal decreased in the order iron magnetization, acid, alkali-modified biochar, followed by the biochar prepared at 700, 500, and 300 °C. Shi et al., in 2022, prepared biochar by pyrolysis of *Tenebrio molitor* frass and activated with KOH at 650, 750, and 850 °C and applied it for the removal of thiacloprid, nitenpyram, and dinotefuran. They found that the adsorption process might be mainly controlled by π–π electron donor–acceptor interactions and functional group interactions [33].

Biochar produced from sugarcane filter cake, after pyrolysis treatment at 380 °C, was used in the adsorption process of thiamethoxam in wastewater. The results indicated that the rate of thiamethoxam removal by biochar was approximately 70% over a period of 60 min [34]. The sugarcane bagasse-derived biochar encapsulated in alginate was used for the removal of chlorpyrifos from aqueous systems. The effect of contact time, initial pH, initial concentration of adsorbate, sorbent dosage, and temperature on the chlorpyrifos removal by biochar alginate beads was studied, and it was found that the adsorption capacity was 6.25 mg g^{-1} [35]. Also, for the removal of chlorpyrifos from polluted water, the performance of rice husk-based biochar as an adsorbent was evaluated. Percentage removal was 94.5 ± 5.23 for optimal conditions (2.8 mg L^{-1} initial concentration; 0.8 g of adsorbent dosage; pH of 5; and contact time of 30 min) [36]. The biochar obtained by pyrolysis of swine manure at 600 °C was used for imidacloprid sorption [37]. The results showed that pore filling is likely one of the dominant sorption mechanisms for this kind of polar chemical. Zheng et al., in 2010, investigated the sorption of two triazine pesticides, atrazine and simazine, on biochar. Based on different sorption conditions, the sorption ability of atrazine was 451–1158 mg g^{-1} and 243–1066 mg g^{-1} for simazine. When the two sorbates existed synchronously, there was competitive sorption on biochar. The sorption capacity of atrazine was 435–286 mg g^{-1} and 514–212 mg g^{-1} for simazine. The study also reported that the sorption process of both single and multiple triazine pesticides on biochar could be well-explained by the surface sorption mechanism [38]. Uchimiya et al., in 2010, produced broiler litter biochar by pyrolysis at 350 and 700 °C to remove deisopropylatrazine, a stable metabolite of atrazine, from water. They found that the biochar prepared at 700 °C had a higher surface area, was more microporous in a non-carbonized fraction, and had greater aromaticity. Thus, the target contaminant can be effectively removed, while the removal efficiency of biochar prepared below 500 °C was relatively low [39].

Srikhaow et al., in 2022, reported the application of biochar derived from eucalyptus wood chips for the removal of imidacloprid, acetamiprid, and methomyl from water. The maximum adsorption capacities for the investigated pesticides were 32.42 mg g^{-1} for methomyl, 14.75 mg g^{-1} for imidacloprid, and 4.87 mg g^{-1} for acetamiprid [40]. The efficacy of biochar prepared from the *Azardirachta Indica* waste biomass by pyrolysis process under limited oxygen conditions for the removal of bentazone was assessed

by Ponnam et al. [41]. They concluded that the bentazone adsorption capacity by biochar from aqueous solutions in optimal conditions was 79.40 mg g^{-1}. The ability of a wood-based biochar produced by slow pyrolysis from a mixture of about 80% hardwood and 20% softwood to adsorb bentazone, chlorpyrifos, diuron, glyphosate, and (4-chloro-2-methylphenoxy) acetic acid were studied by Cederlund et al. Their adsorption of the pesticides on the biochar was tested before and after it was subjected to treatments with heat and/or iron. It was found that biochar activation with heat (t = 450 °C) increased the specific surface area and the wettability of the biochar and increased the adsorption of bentazone and (4-chloro-2-methylphenoxy) acetic acid. Treatment with iron salts decreased the specific surface area of the biochar but increased the adsorption of glyphosate [42].

Mandal and Singh, in 2017, used untreated and phosphoric acid-treated rice straw biochar in order to evaluate the atrazine and imidacloprid adsorption. The study suggested that rice biochar had a significantly higher potential to adsorb both pesticides [43]. In another study, Mandal et al. modeled the adsorption of atrazine, imidacloprid, and azoxystrobin in single-, bi-, and ternary-solutes systems on phosphoric acid-treated rice straw biochar. The simulations predicted that the phosphate ester group in the modified biochar increased the adsorption efficiency of the biochar surface in an aqueous medium, and non-bonding interactions between aromatic groups and electrostatic interactions with this phosphate ester group played an important role [44]. Another group studied the adsorption of a mixture of 15 different pesticides on untreated and treated (phosphoric acid) rice straw biochar and corn stover biochar from water. To compare the pesticide adsorption abilities of the tested adsorbents, they take into account the solid–water distribution coefficients [45].

The prepared P-dopant biochar from corn straw, cob, and starch using the phosphoric acid activation method has good results in the mechanistic removal of triazine from wastewater with an adsorption capacity of 79.6 mg g^{-1} [46]. Comparing the bare biochar and P-doped biochar for the adsorption of 2,4-dichlorophenoxyacetic acid, it was found that P-doped biochar can adsorb the pesticide more effectively [47]. Also, Fe_3O_4/Biochar nanocomposites were prepared from black wattle and tannin from tree bark. The results showed that magnetic biochar possesses a maximum removal capacity of 0.73 mg g^{-1} in the case of thiacloprid and 0.40 mg g^{-1} in the case of thiamethoxam, but attempts to desorb the pesticides adsorbed on the biochar resulted in low desorption that may be due to the existence of strong interactions, and further studies are needed [46,48,49]. CuO/biochar is a new material prepared and tested for the degradation of imidacloprid in water with the highest degradation efficiency at pH values over 11.0. The final results indicated that biochar support did not increase the activation efficiency of CuO particularly [50].

We can conclude that there is increasing evidence for the use of biochar as an attractive adsorbent material for the removal of several chemical and biological contaminants arising from its large surface area, recalcitrance, porosity, and presence of various surface functionalities, making it an efficient and cost-effective sorbent rooted in waste valorization and sustainability [51–53]. Also, biochar is largely used in soil remediation and amendment and can be designed to work as a slow-release fertilizer to improve soil quality and productivity with environmental and economic benefits [54–57].

3.2. Drug Adsorption on Biochar-Based Materials

Bacterial infections are a major cause of chronic illness and mortality. Antibiotics were, and still are, the preferred method of treatment for bacterial infections because of their cost effectiveness and good results. However, several studies have provided direct evidence that the widespread overuse of antibiotics has led to the emergence of drug-resistant bacterial strains. But the mechanisms of antibiotic resistance are irrelevant to nanoparticles (NPs) because the mode of action of NPs is direct contact with the bacterial cell wall, without the need to enter the cell. This raises the hope that NPs would be less likely to promote bacterial resistance than antibiotics. Therefore, the focus has been on new and interesting NP-based materials with antibacterial activity [58]. Contamination of aqueous environments with antibiotics by aquaculture effluents can be a major future

problem due to a very likely increase in bacterial resistance. The efficient treatment of those effluents before their release into the environment, in order to remove/reduce their antibiotic content, will be crucial [59–62]. Several studies report that nanoparticles could remove these compounds, even at low concentrations and under varying pH conditions [63]. For that reason, scientists are taking into consideration biochar as being a solution for the removal of several persistent contaminants, including pharmaceuticals. At the same time, antibiotics cannot be completely eliminated by conventional methods used for wastewater treatment [64]. Various types of antibiotics are usually detected in real livestock wastewater, including sulfonamides, tetracyclines, chloramphenicol, macrolides, or β-lactams. Zhao et al., in 2023, obtained and characterized alkaline-modified biochar with a larger surface area (130.520 m^2 g^{-1}), and by corroboration between experimental data and computational analysis based on the density functional theory, they concluded that the biochar surface –OH groups could serve as the dominant active sites for antibiotic adsorption due to the strong adsorption energies between them [65].

The removal of tetracyclines by a $ZnCl_2$/$FeCl_3$ solution-doped sawdust biochar was studied by Zhao et al., who obtained a removal rate of over 89% after three cycles [66]. Another study demonstrated that the maximum capacities of the humic acid-coated magnetic biochar prepared from potato stems and leaves for absorbing enrofloxacin, norfloxacin, and ciprofloxacin were 8.4 mg g^{-1}, 10.0 mg g^{-1}, and 11.5 mg g^{-1} [67]. Biochar based on rice straw pyrolysis at different temperatures had a 56.9% removal rate of tetracycline from wastewater [68]. In the last years, norfloxacin, a third-generation quinolone antibiotic, has been widely used due to its broad-spectrum antibacterial properties and its low toxicity to the human body and good oral absorption. Liang et al., in 2022, developed a new system of magnetic biochar obtained from the co-pyrolysis of poplar wood chips and $FeCl_3$/$CaCl_2$-mixed molten salt with promising results for removing antibiotics from water [69]. Also, Pang et al., in 2023, developed a new magnetic graphoxide/biochar composite derived from tea for the degradation and removal of sulfonamides and quinolones antibiotics. This degradation was based on synergistic adsorption and persulfate degradation [70]. H_3PO_4-activated sunflower seed husk biochar can effectively adsorb antibiotics via several different mechanisms (chemisorption, external diffusion, and intraparticle diffusion) and can be a promising material for the removal of antibiotics (in particular norfloxacin) from aquatic environments [71,72].

The biochar anaerobic membrane was demonstrated to be a promising solution for the removal of sulfonamide AB from swine wastewater [73]. The removal of sulfonamides and tetracyclines from aquatic environments, using biochar, was studied, and it was observed that the conditions of biochar pyrolysis influence the efficiency of decontamination [74]. Zeng et al., in 2018, observed that biochar produced at a high temperature (e.g., 700 °C) has a bigger adsorption capacity for doxycycline and ciprofloxacin than that produced at a low temperature (e.g., 300–500 °C). The antibiotic removal efficiency was higher than 80%, and it was in the following order: DOX > CIP [75]. Qalyoubi et al., in 2023, obtained textile-based biochar from cotton textiles and studied the abilities of this for the removal of ciprofloxacin antibiotics from synthetic water solutions. The results were very impressive, with the successful removal of ciprofloxacin (97.61%) after 4 h of contact time at pH 9. These results demonstrate the efficiency of using the low-cost, sustainable, and environmently friendly biochar adsorbent from textile waste. Future studies will be directed toward the investigation of the co-adsorption of other contaminants and applications on real wastewater [76].

Sun et al., in 2021, studied a new type of sludge-derived biochar material (Fe_3O_4-biochar) with high removal efficiency of tetracycline. They followed the adsorption effects and adsorption mechanism of three different materials for tetracycline removal: biochar (from waste sludge), Fe_3O_4, and Fe_3O_4-biochar. The adsorption effects decreased as follows: Fe_3O_4 (94.3%) > Fe_3O_4-biochar (88.3%) > biochar (65.7%). All characterization methods indicated that the removal of tetracycline by three adsorbent materials was based on pore filling, electrostatic effect, hydrogen bonding effect, or cation–π effect. The Fe_3O_4-biochar

can be recycled several times and can be an ideal channel for resource reduction in sludge waste. Due to different sources of sludge material used for biochar production, significant differences in the physicochemical properties of biochar are observed, causing differences in the adsorption efficacy of sludge-based biochar for tetracycline. For this reason, the possibility of removing other antibiotics or contaminants simultaneously and efficiently remains to be verified [77].

Huang et al., in 2017, used bamboo sawdust-like biomass to prepare a novel graphene oxide-coated biochar nanocomposite for the removal of sulfamethazine and concluded that about 30% of this was adsorbed by the chemisorption process due to the increasing surface functional groups of the new nanocomposites [78]. Later, in 2019, Liu et al. modified the surface of the biochar with chitosan and FeS_x for tetracycline removal, and the results showed a maximum removal capacity of the biochar and modified biochar of 51.78 and 193.01 mg g^{-1}, respectively. When chelation and silicate bonding increased on the modified biochar, silicate bonding was one of the main removal mechanisms in the case of tetracycline [79]. Silva et al., in 2021, presented a waste-based magnetic biochar/TiO_2 that can be used for the photodegradation of two antibiotics widely used in aquaculture: sulfadiazine and oxolinic acid [28].

Another class of broadly used drugs that are considered environmental pollutants is anti-inflammatory (AI) drugs. For the removal of ibuprofen and diclofenac from water, partially graphitic biochar was also synthesized using peanut shell biomass and potassium ferrate [80]. Anfar et al. demonstrated that Fe_2O_3/biochar could potentially be applied as an effective adsorbent for ketoprofen and naproxen removal from aqueous solutions [81]. Pine wood biochar was found to have a good ability for salicylic acid and ibuprofen removal from aqueous solution ($\geq$40% removal rate) [82].

H_3PO_4-activated sunflower seed husk biochar has very good adsorption properties for the removal of ibuprofen and sulfamethoxazole from wastewater [71,72].

The incorporation of biochar into a matrix membrane represents a new good strategy leading to an increase in the adsorption capacity, reducing costs, and exceeding the limitation of these materials [83].

These results are very important because the antibiotics and anti-inflammatory drugs are not easily biodegradable, and the residual antibiotics can increase the resistance of water microorganisms with serious impacts on the ecological environment through bioaccumulation and demonstrate a high potential for application in the photocatalytic removal of antibiotics from aquaculture effluents; oxolinic acid displayed a much faster photodegradation than sulfadiazine. Moreover, the synthesis and consequent application of these nanocomposite materials can offer a variety of benefits including sustainability, low cost, and the achievement of the circular economy [28,84].

3.3. Phosphorus Removal from Wastewater Using Biochar

Phosphorus removal from wastewater using biochar is an effective and environmentally friendly method. When biochar is added to wastewater treatment systems, it can adsorb phosphorus, helping to reduce its levels in the effluent. Several recent reviews of the studies that have investigated the potential and challenges of using biochar for wastewater treatment are available in the scientific literature [15,84–87].

Here is how the process generally works: biochar is added to the wastewater treatment system, typically within a treatment unit like a settling tank or a filter. When wastewater comes into contact with biochar, phosphorus ions in the water are attracted to and adsorbed onto the surface of the biochar. The porous structure of biochar provides ample surface area for phosphorus to be trapped effectively. After adsorption has occurred, the treated wastewater undergoes further treatment processes, such as filtration or sedimentation, to separate the biochar carrying the adsorbed phosphorus from the cleaned water.

Interestingly enough, the biochar laden with phosphorus can be potentially reused as a soil amendment in agriculture, as it also has beneficial effects on soil fertility [85–91].

Alternatively, it can be disposed of safely, and the treated wastewater can be released into the environment or reused for non-potable purposes.

Advantages of using biochar for phosphorus removal from wastewater include low cost, as biochar production can be relatively inexpensive, especially if it is made from agricultural or waste residues; sustainability, since biochar is a sustainable material made from renewable resources, and it helps recycle organic waste; adsorption capacity, based on the biochar's high surface area and excellent adsorption capacity, which make it very effective in removing phosphorus and other contaminants from wastewater; and a reduction in the environmental impact of agriculture and other human activities implying a large use of phosphorous given that by removing phosphorus from wastewater before discharge, the risk of eutrophication in water bodies, which can lead to harmful algal blooms and oxygen depletion, can be drastically reduced.

However, there are some considerations to keep in mind when using biochar for phosphorus removal. First of all, it may be interesting to keep an eye on phosphorus recovery rather than its disposal. In fact, while biochar adsorbs phosphorus effectively, it may be desirable to recover the phosphorus for beneficial reuse rather than disposing of it. Another important issue is that of maintenance. i.e., the biochar media may require regular maintenance or replacement to ensure continued effectiveness. Last, but not least, there are site-specific considerations, which are necessary to take into account in implementing a biochar-based solution for phosphorus removal from wastewater, as the success of the biochar-based system may vary depending on the specific wastewater characteristics and the treatment process's design.

Overall, using biochar for phosphorus removal is a promising approach to address nutrient pollution in wastewater and contributes to sustainable water management. As with any wastewater treatment method, proper design, monitoring, and maintenance are essential to ensure optimal performance.

Recently, Strawn et al. studied the effects of iron modification on phosphorous sorption behavior and molecular characterization using biochar modified with 2% iron by mass [92]. This increased the biochar sorption capacities. Phosphorous K-edge X-ray absorption near-edge structure (XANES) spectroscopy then provided data on the sorbed phosphorous availability for subsequent release, i.e., important information for the future recycling as a slow-release soil fertilizer, of biochar used in wastewater treatment processes. The mechanisms for phosphate removal by means of iron-modified biochar and the regeneration of wastewater were also studied in the publication of Qin et al. where, in addition to the assessment of the adsorption capacity, care was paid also to study kinetics and isotherm models for the phosphate adsorption process [93].

In a comprehensive review of the adsorption capacity of both unmodified and modified (by various ions) biochar toward phosphate, though not including the most recent results in this rapidly growing field of investigation, it was pointed out that proper comparison between the different kinds of biochar and their composites in terms of adsorption capacity toward phosphate is complicated due to the diversity of experimental conditions [94]. This review also correctly points out several gaps that still need to be filled by further investigation in this area. Among them, we find that the major ones are twofold, i.e., that the research carried out so far at the laboratory level needs to be scaled up to a much higher level of technological maturity, and that there is a lack of study about the effect of coexisting ions on phosphate removal. Similar conclusions are drawn from the analysis carried out by Nobaharan et al. [86].

3.4. Heavy Metal Adsorption on Biochar-Based Materials

Heavy metals are among the most popular pollutants when considering water contamination by human intervention in the natural environments. A vast majority of human activities are releasing heavy metals in aqueous sources and environments, accidentally or by limited possibilities of preventing their spread/release. Most of the studies focus on limited elements when investigating both the effects of these elements on the living cells

and the methods for removing these pollutants which, consequently, limit their poisonous actions. Adsorption is one of the most used methods for heavy metal pollutant removal from aqueous environments. Among pollutant heavy metals well-studied are cadmium, copper, lead, zinc, chromium, arsenic, etc. In terms of the type of biochar-based adsorbents used, they might be both pristine and modified.

A good example where pristine biochar was successfully used was published by Komkiene and Baltrenaite in 2016 [95]. They used locally available Scot pine (*Pinus Sylvestris*) and silver birch (*Betula Pendula*) as biomasses for biochar production. After the drying and crushing steps, each wood type was subject to both slow and fast pyrolysis in order to produce the biochar samples ground at room temperature into pieces of 1–10 mm in size. The physical and chemical characterization of these samples showed less sensitivity for the Scots pine samples toward different production temperatures, with their specific surface area, porosity, and bulk density varying less with the treatment temperature than in the case of the silver birch. The initial heavy metal concentration in the aqueous solution for the investigated elements (Cd(II), Pb(II), Cu(II), Zn(II)) started from 0.04 mg L^{-1} and went up to 2.5 mg L^{-1}, and was related to the maximum contaminant level defined by the Water Framework Directive 2000/60/EC. In terms of cation exchange capacity (CEC), it turned out that the silver birch one is much higher than the Scots pine one (almost double), and it increases in the case of fast pyrolysis (performed at 700 °C) with respect to the value obtained using slow pyrolysis (performed at 450 °C) in the case of silver birch, while Scots pine decreases. Samples of both wood types and both pyrolysis types showed similar total carbon content. Also relevant in this study is the decrease in the adsorption efficiency by increasing the initial pollutant concentration in the aqueous solution. On the other hand, increasing the adsorbent dosage leads to an increase in the adsorption efficiency for both Scots pine and silver birch and all four metallic pollutants investigated.

In 2020, Zhang et al. published the results of an investigation where the removal from aqueous solutions of the same four metallic pollutants as in the previous study was analyzed, this time starting from invasive water hyacinth as the biomass source for biochar that was loaded with different amounts of manganese oxide nanoparticles [96]. For the surface modification/loading, a redox precipitation method was used. The manganese oxide weight percentages in the adsorbent samples investigated were 0.6% in the case of the pristine biochar sample and 12.3%, 18.4%, 26.6%, and 30.2% for the surface-modified biochar samples. While for the first two treated samples, the specific surface area increased to 135.9 m^2 g^{-1} and 181.9 m^2 g^{-1}, respectively, from 3.5 m^2 g^{-1} in the case of pristine biochar, the drop of this parameter to 120.2 m^2 g^{-1} and 12.5 m^2 g^{-1}, respectively, was reported for the samples with the highest manganese oxide nanoparticle content. A similar evolution was observed for the total pore volume and the pore diameter, proving that a pore-blocking mechanism was generated by the manganese oxide nanoparticles at higher concentrations. A strong increase in the adsorption for all four contaminants tested was observed when the pH values of the aqueous solution increased, an effect explained by balancing the competition between the heavy metal ions and the hydrogen ions. At the same time, the zeta potential dependence on the pH of the solution showed a lowering of the isoelectric point value in the case of manganese oxide-loaded biochar with respect to the pristine biochar from pH 6.3 to pH 2.8, which explains the abrupt increase in metal adsorption for pH values reported above. Another observation of this study is related to the selectivity of the adsorbents in complex multicomponent cations containing solutions given the fact that other ions like K(I), Na(I), Ca(II), or Mg(II) are common in most aqueous environments, like wastewater or natural water resources. In this sense, the adsorption capacity for the targeted Cd, Cu, Zn, and Pb decreased with the increase in the concentration of coexisting cations, proving the existence of the competition between different cations for the negatively charged surface adsorption sites. The X-ray photoelectron spectroscopy results suggested surface complexation as the dominant mechanism for heavy metal immobilization onto the manganese oxide nanoparticle-modified biochar. Although pristine biochar exhibits limited cation adsorption capacity due to its low cost and abundant surface functional

groups, it could be considered a reasonable option for hosting metal oxides in order to broaden its applicability in adsorption or catalysis experiments.

From the myriad of other studies that are focusing on cadmium pollutants and their removal from aqueous solutions using biochar-based adsorbents produced from different biomass sources, we will mention only a few and try to bring attention to relevant and recent investigations [97–106].

In their recent study, Qu et al. used ball milling as a new method to modify the surface of biochar obtained from cotton straw, corn straw, and rice husk [102]. By adding (Fe/Mn) oxides, they obtained binary metal-oxide ball-milled biochar samples. The functionalization leads to increased specific surface area (with a factor of 100), more oxygen-containing surface functional groups, and a rougher surface. Cd^{2+} adsorption showed a rapid first phase of about 20 min for both pristine and functionalized biochar samples, gradually slowing down after the mentioned time and depicting a saturation of the adsorption sites after 4 h for pristine and 3 h for functionalized biochar. The adsorption capacity, on the other hand, was much larger for the modified biochar, an increase that was ascribed to the increase in the specific surface area and the number of surface functional groups. As the isoelectric point as a function of the solution pH for the surface-modified samples varies for the four different samples from pH 1.78 to pH 3.06, the strong increase in the adsorption efficiency for solution pH values above 3 is not surprising. The Cd^{2+} adsorption in the presence of different cations in the solution was also investigated as a function of coexisting cations valence, leading to the conclusion that trivalent ions exert a stronger adsorption-inhibiting effect than divalent ions and monovalent ions. The inhibiting strength was as follows: $Al^{3+} > Ca^{2+} > Na^{+}$.

In a publication from 2018, Akgül et al. started from industrial tea waste in order to obtain biochar samples that were later modified by impregnation using Mg, Fe, Mn, and Al salts to improve their adsorption properties [103]. They tested their composites for cadmium and phosphate adsorption from aqueous solutions. Of the four modified biochar samples, the one containing Mg was the most efficient for the removal of both pollutants, the anionic $(PO_4)^{3-}$ and cationic Cd^{2+}. Another conclusion of their study is that functionality (more surface functional groups) plays a stronger role than porosity in the efficiency of the removal of both pollutants.

Changing the pollutant, we would like to address the publication by Liu et al., where the targeted contaminant was chromium and the biomass used to produce biochar was apple wood [107]. Their X-ray photoelectron spectroscopy results and X-ray absorption near-edge structure (XANES) showed that the majority of the chromium on biochar was reduced Cr(III), suggesting electrostatic attraction, Cr(VI) reduction, Cr(III) complexation, and ion exchange were main processes to remove Cr(VI) from aqueous solutions using pristine biochar.

In a 2021 publication by Zhou et al., the Cr(VI) removal from aqueous solutions using magnetic biochar was investigated [108]. The addition of iron oxide nanoparticles increased the specific surface area of the biochar. The biochar was produced using wet and dry electromagnetic induction pyrolysis out of cellulose from a local chemical supplier. The samples prepared by wet electromagnetic induction showed a higher Cr(VI) removal capacity, a higher specific surface area, and surface functional groups.

Over time, due to its improved surface and magnetic properties, many of the studies involving biochar-based adsorbents for water purification purposes migrated toward magnetic biochar, a modification of the biochar surface mainly obtained by impregnation of the pristine biochar with magnetic nanoparticles (iron oxide for example) [109–111].

Beyond the vast and interesting research articles available in the literature concerned with (toxic) heavy metal removal from various aqueous solutions, there are also good review papers, some of them covering other closely related scientific fields of interest, and we strongly recommend them to our readers [112–117].

As shown in Table 1, a large variety of biomass materials is used as feedstock, and different temperatures are applied in order to produce biochar for the adsorption of different classes of pollutants.

Table 1. List of selected references proving the broad feedstock bio-sources and scattered preparation conditions used for pristine or modified biochar preparation applied for the removal of very different types of pollutants.

Reference Publication	Adsorbent Feedstock Material/Functionalization	Preparation Method/Temperature (°C)	Contaminants Addressed
Zhang et al. [31]	Maize straw and pig manure-based biochar	Pyrolysis 300 °C, 500 °C, 700 °C	Thiaclopirid insecticide
Wang et al. [32]	Corn straw (functionalized with HCl, NaOH, and $FeCl_3$)	Pyrolysis 300 °C, 500 °C, 700 °C	Carbendazim (methyl-2-benzimidazolecarbamate)
Fernandes et al. [34]	Sugarcane filter cake	Pyrolysis, 380 °C	Thiamethoxam
Jacob et al. [35]	Sugarcane bagasse	Pyrolysis, 450 °C	Chlorpyrifos pesticide
Okoya et al. [36]	Rice husk	Pyrolysis, 700 °C	Chlorpyrifos
Jin et al. [37]	Rice straw, wheat straw, swine manure	Pyrolysis 300 °C, 450 °C, 600 °C	Imidacloprid, isoproturon, atrazine
Zeng et al. [76]	Rice straw	Pyrolysis 300 °C, 500 °C, 700 °C	Doxycycline, ciprofloxacin
Qalyoubi et al. [77]	Textile waste (cotton straps)	Pyrolysis 900 °C	Ciprofloxacin
Sun et al. [78]	Sludge from municipal sewage-based biochar functionalized with Fe_3O_4	Pyrolysis 500 °C	Tetracycline
Essandoh et al. [83]	Pine wood	Pyrolysis 425 °C	Salicylic acid, ibuprofen
Strawn et al. [94]	Lodgepole pine, dairy manure-based biochar (Fe-modified)	Pyrolysis 550 °C, 650 °C, 750 °C	Phosphorous
Qin et al. [95]	Iron-modified lychee twig-based biochar	Pyrolysis 600 °C	Phosphate
Komkiene et al. [97]	Scots pine, silver birch-based biochar	Slow and fast pyrolysis 450 °C, 700 °C	Cd, Pb, Cu, Zn
Zhang et al. [98]	Water hyacinth-based biochar (functionalized with MnO_2 nanoparticles)	Pyrolysis 700 °C	Cd, Cu, Zn, Pb
Akgül et al. [104]	Industrial tea waste biochar (modified with Mg, Fe, Mn, and Al salts)	Pyrolysis 500 °C	$(PO_4)^{3-}$, Cd^{2+}
Hasan et al. [108]	Pinewood-based biochar (functionalized with nanoscale zerovalent iron)	Pyrolysis 600 °C	Cu^{2+}, Cd^{2+}, Zn^{2+}
Son et al. [111]	Kelp and hijikia-based biochar (functionalized with iron oxide particles)	Pyrolysis 500 °C	Cd^{2+}, Cu^{2+}, Zn^{2+}

4. Adsorption Mechanisms in Biochar-Based Water Decontamination

Adsorption mechanisms in biochar-based water decontamination are complex processes involving interactions between the biochar surface and pollutants in the water. Biochar, a carbon-rich material formed by the pyrolysis of biomass, has unique physicochemical features that make it an efficient adsorbent for a variety of contaminants. Understanding the adsorption mechanisms is critical for improving the efficacy of biochar in water purification [118,119]. The primary adsorption mechanisms of biochar-based water decontamination are based on physical adsorption, chemical adsorption, ion exchange process, and π–π stacking interactions (Figure 2), as described below.

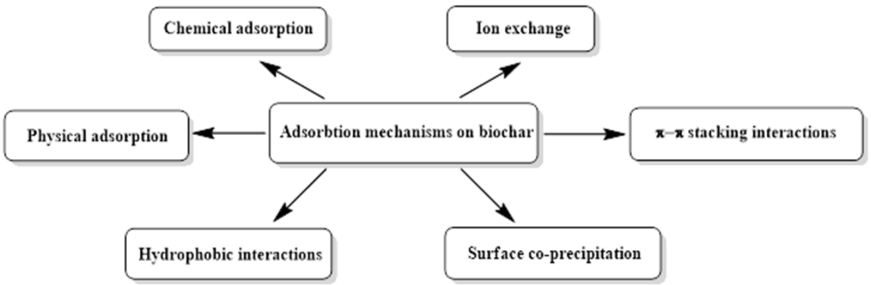

Figure 2. Adsorption mechanisms involved in water decontamination with biochar.

4.1. Physical Adsorption

Physical adsorption, also known as physisorption, occurs when nonpolar pollutants are drawn to the hydrophobic surfaces of biochar via weak van der Waals forces and London dispersion interactions. The enormous surface area and porous nature of biochar provide multiple sites for these interactions and mainly depend on the carbonization temperature. For instance, Liu et al. reported that biochar derived from pine (700 °C) and switchgrass (300 °C) could efficiently remove Cu and uranium through physical adsorption [120]. The efficient removal of uranium (VI) is a great challenge for nuclear wastewater treatment, and tremendous research is underway to solve this issue. Recently, Hu et al. investigated the adsorption of uranium (VI) on bamboo shoot shell biochar at 298 K, achieving an adsorption of 32.3 mg g^{-1} [121]. They demonstrated that solution pH, adsorbent dosage, contact time, and initial uranium content all have a significant impact on the adsorption capacity. Physical adsorption is often reversible and is controlled by parameters, such as biochar surface hydrophobicity and temperature [122]. The primary factors influencing the adsorption capacity of biochar include specific surface area, pore structure, and biomass pyrolysis at high temperatures, which leads to the development of biochar with a substantial surface area and cavities. This considerably enhances the contact area between biochar and contaminants, increasing the physical adsorption in aqueous media [123,124]. The physical adsorption method is particularly appealing due to a number of advantages, including simple operational conditions, no harmful byproducts, flexibility, low cost, and being capable of adsorbing various drugs on the biochar surface. It has been demonstrated that the nature of the feedstock and the pyrolysis conditions greatly affect the features of biochar, and the biochar's potential to remediate pesticides in the soil is determined by the soil and pesticide types, solution pH, biochar dose and application systems, and environmental factors. For instance, the optimal adsorption capacity of biochar for glyphosate was 82.0% at pH 4. However, the adsorption was decreased to 56.0% at pH 10. From Freundlich and Langmuir's isotherm models, it was confirmed that glyphosate adsorption was governed by the physisorption mechanism [125]. Soybean and corn straw biochar revealed exceptional adsorption and removal capacities for atrazine, which were attributed to the pH value and pore volume of the biochar [126].

4.2. Chemical Adsorption

Chemical adsorption, referred to as chemisorption, involves the interaction between polar contaminants and oxygen-containing functional groups, namely hydroxyl (-OH), carboxyl (-COOH) and phenolic (-Ph-OH), which are present on the surface of biochar. Hydrogen bonding and electrostatic interactions with polar molecules are made possible by these functional groups. The adsorption process is more powerful than physical adsorption and is influenced by factors such as pH, ionic strength, and the existence of competing ions. For instance, Wang et al. investigated the adsorption study of highly toxic metals on $KMnO_4$-treated hickory wood biochar obtained via pyrolysis at 600 °C [127]. Their findings revealed that the resultant biochar has an adsorption capacity of 153.1, 34.2, and 28.1 mg g^{-1} for Pb (II), Cu (II), and Cd (II), respectively. The observed variations in adsorption can be ascribed to the distinct affinities of the aforementioned metals that exhibit various valences with regard to the biochar. According to Kalderis et al., the KOH-oxidized pine tree biochar demonstrated outstanding adsorption capability toward U(VI) in aqueous media, with a maximum adsorption capacity of 800 mg g^{-1} [128]. They found that the surface interaction with the oxygen-containing groups in biochar was governed by physical interaction with the pore structure. In addition, acid-base modifications result in the formation of functional groups, such as C-OH and C-H, which have a notable impact on the chemical adsorption mechanism of biochar, altering its adsorption capacity [129]. For instance, Chu et al. demonstrated that the modification of biochar with phosphoric acid creates micropores in biochar, which are substantially larger due to the cross-linking and acid catalysis compared to the untreated biochar [130]. This significantly increases the specific surface area of the biochar. Wang et al. reported that the adsorption capa-

bility of biochar modified with acid and base for enrofloxacin was enhanced by 27.80% and 54.08%, respectively [131]. Likewise, bisphenol A, ciprofloxacin, and tetracycline contaminants were removed via the chemical adsorption mechanism using acid/base-modified biochar [132–134]. According to Chakhtouna et al., the removal efficiency of $CoFe_2O_4$-modified banana-pseudo-stem (Co-BP350) biochar for amoxicillin was 92% after five consecutive cycles [135]. Sayin et al. demonstrated that the newly fabricated H_3PO_4-modified waste-based biochar (MPCWSB500) derived from a sour cherry stalk revealed 100% adsorption capability for ciprofloxacin at optimal conditions (time = 40 min, pH = 6.3, biochar dose = 15 mg) [136]. Several researchers have used biochar and its modified forms for the removal of pesticides from agricultural wastewater. Among various pesticides, atrazine and pentachlorophenol are the most commonly used in agriculture, and their removal from agricultural wastewater is highly desired. For instance, Mandal et al. utilized bare rice straw and H_3PO_4-modified rice straw biochar in the adsorption of atrazine and imidacloprid pesticides from agriculture wastewater [43]. They observed that the adsorption capability of H_3PO_4-modified rice straw biochar for both of the pesticides was remarkably enhanced.

4.3. Ion Exchange

In the ion exchange mechanism, the liquid and solid phase ions undergo a reversible reaction. In order to maintain electrical neutrality in an aqueous solution, certain ions present in the liquid phase are absorbed by an ion exchange solid material. Subsequently, the solid material releases similar ions back into the solution [137]. Due to the presence of charged functional groups, biochar has a net surface charge. This electrical charge allows for ion exchange, in which ions in the water exchange positions with ions on the biochar surface. The cation exchange capacity of biochar is an estimation of how many cations it can contain and is especially significant for eliminating heavy metals and inorganic ions from water. The solution's ionic strength and the concentration of ions in the water both influence the ion exchange process. The fundamental principle of this mechanism involves the interaction of proton and ionized cation on the biochar's surface. The efficacy of biochar in removing contaminants is dependent on the size of the contaminants and the functional groups present on the surface of the biochar [138]. According to a previous report, the stronger the ion exchange ability of biochar, the higher will be the metal adsorption [139]. In contrast, when the pyrolysis temperature exceeds 350 °C, ion exchange capability decreases. For instance, El-Shafey explored the removal of Zn^{2+} and Hg^{2+} from wastewater via the biochar derived from rice husk at a pyrolysis temperature of 180 °C [140]. They demonstrated that Hg ions adsorbed substantially more over the surface of biochar than Zn^{2+} ions. Likewise, Trakal et al. explored the adsorption of Cd and Pb metals using biochar derived from various feedstocks, such as graph stalk, grape husk, wheat straw, nutshell, and plum stone [141]. They observed that iron oxide-containing feedstocks exhibit higher removal capacity for Pb and Cd, and the iron-containing biochar feedstock was found to remarkably improve the cation exchange capability of biochar. According to Tan et al., ion exchange strongly increased the Cd adsorption from 20 to 40 mg g^{-1} by exchanging Ca ions of municipal sludge-derived biochar with Cd [142]. Similarly, the ion exchange adsorption mechanism was dominant in the case of Cd^{2+} adsorption on the rice husk biochar [143].

4.4. π–π Stacking Interactions

Through π–π stacking interactions, biochar has the unique capacity to interact with aromatic contaminants. The process of electron transfer occurring between the electron donor and acceptor species is responsible for the binding of the adsorbent and adsorbate species [125]. π–π stacking is very useful for removing certain organic pollutants from water. This adsorption mechanism is crucial in the adsorption of contaminants over a variety of carbon-based compounds [144]. The π-aromatic biochar systems function as an electron acceptor at temperatures below 500 °C. However, at temperatures above 500 °C, biochar assumes the role of an electron donor by binding the withdrawing electron

molecules [145–147]. According to Yu et al., N-doped biochar fabricated via the direct annealing of crop straws revealed exceptional adsorption capacity for Cu^{2+} and Cd^{2+} metals [148]. The adsorption mechanism between the N-doped biochar and the heavy metals followed a strong π–π stacking interaction. Tetracyclines are an important class of antibiotics used in agriculture and medicine, but their efficacy is at risk due to rising resistance. They are among the most prescribed antibiotics and were ranked third in clinical drugs in the USA in 2010 [149]. Thus, tetracyclines pose a significant concealed risk to human health. Zhou et al. used an alkali-acid-binding approach to modify municipal sludge biochar from solid waste, utilizing it in tetracycline removal from wastewater [150]. The modified biochar effectively removed tetracycline from an aqueous solution (200 mg L^{-1}), with an adsorption removal performance of 86%. On the other hand, carbamazepine is an anti-epileptic drug that can influence the developing embryos and larvae of fishes in aquatic environments [151]. Shan et al. fabricated an ultrafine magnetic biochar/Fe_3O_4 composite that was modified with coconut, pine nut, and walnut shells [152]. The biochar-based hybrid exhibited an exceptional carbamazepine removal rate. Further addition of quartz sand to the biochar/Fe_3O_4 hybrid significantly improved the mechanochemically removal of carbamazepine, with a removal percentage of 98.4% at a dosage of 0.3 g quartz sand g^{-1} adsorbent. Recently, Min investigated the adsorption capability of NaOH-activated and hematite-modified biochar for sulfamethazine, ionizable tetracycline, erythromycin, norfloxacin, and chloramphenicol antibiotics in a single and competitive sorption dynamic system [153]. The sorption of antibiotics on NaOH-activated biochar was shown to be substantially greater compared to hematite-modified biochar. The affinity coefficients of the NaOH-activated biochar for tetracycline, erythromycin, and norfloxacin were found to be 100 times greater than those predicted for hematite-modified biochar. The rate of absorption of the target antibiotics was shown to be higher in single-solute systems compared to the ternary-solute systems. The sorption capability of all antibiotics adsorbed over the NaOH-activated or hematite-modified biochar was remarkably inhibited in the competitive system. The π–π stacking (EDA) interactions regulated the antibiotic sorption by the biochar. According to the previous literature, biochar containing oxygen functional groups provides abundant active sites for the adsorption and removal of various drugs [145,154,155]. A π–π interaction exists between the drugs and biochar due to these functional groups. Additionally, a π–π interaction also exists between the agriculture pesticides and biochar via the oxygen-containing functional groups in the biochar. For example, Liang et al. utilized unmodified and Fe/Mn-modified biochar in the adsorption and removal of atrazine [156]. The Fe/Mn-modified biochar revealed remarkably high adsorption and removal capacity for atrazine, and it was confirmed that the adsorption mechanism of atrazine on the modified biochar is governed by a π–π interaction. Likewise, the adsorption mechanism of Tenebrio molitor frass biochar and neonicotinoid pesticide also followed a π–π electron donor–acceptor interaction [33].

4.5. Hydrophobic Interactions

Hydrophobic interactions are a type of noncovalent force that occur in aqueous solutions, wherein nonpolar species have a tendency to aggregate, reducing the overall interfacial area across hydrophobic species and molecules of water. These interactions are thermodynamically favorable and are associated with a corresponding change in the entropy of the entire system. The water molecules exhibit a state of arrangement, which is evident by the decreased entropy of the system in its equilibrium state. Nevertheless, the introduction of nonpolar species into the system imposes a constraint on the water molecules, restricting their ability to freely orient themselves. Consequently, the resolution of this undesirable interaction occurs through the reduction in water molecule interaction with the nonpolar interface. This, in turn, facilitates the clustering of nonpolar chemicals and hydrophobic biochar inside an aqueous solution [157,158]. Choi and his co-worker conducted an investigation into the adsorption mechanism of bisphenol A and sulfamethoxazole onto biochar produced from alfalfa. The primary adsorption processes were considered by the

authors to be hydrophobic and π–π interactions. The hydrophobic nature of the biochar, characterized by low O/C and H/C ratios, was identified as the contributing factor. Furthermore, the neutral states of these organic compounds at a pH range of 3 to 5 were indicative of non-electrostatic interactions [159]. The study conducted by Chen et al. focused on evaluating the sorption of perfluoro octane sulfonate on biochar derived from maize straw. The elimination occurred through hydrophobic contact, which was facilitated by the organic pollutant's high hydrophobicity. The adsorption of perfluoro octane sulfonate molecules exhibited a positive correlation with the rise in pyrolytic temperature. The observed phenomenon can be ascribed to the reduction in the quantity of polar functional groups present on the surface of the biochar, which can be linked to the temperature at which the pyrolysis process was conducted [16]. The study conducted by Zhou et al. aimed to examine the adsorption mechanism of sparfloxacin and ciprofloxacin onto Fe_3O_4/graphene-coupled biochar. The authors concluded that the adsorption of sparfloxacin and ciprofloxacin was significantly influenced by hydrophobicity since more hydrophobicity led to a stronger positive association between the adsorbent and adsorbate [160]. The study conducted by Li et al. explored the predominant mechanism underlying the adsorption of ionizable organic contaminants, including benzoic acid, p-chlorobenzene acid, and o-chlorobenzene acid, which was determined to be the hydrophobic interaction [161].

4.6. Surface Co-Precipitation

Precipitation occurs when insoluble materials are formed either by co-precipitation with a macro-component or when a chemical approaches its solubility threshold. The occurrence of this mechanism is typically attributed to fluctuations in the solution pH or the existence of substances on the surface of the biochar, including minerals, enzymes, and polymers, which have the potential to induce precipitation on the biochar surface or within the solution. Nevertheless, it is important to note that while precipitation does aid in the elimination of specific adsorbates, it is crucial to avoid the solubility threshold in adsorption tests. This is because exceeding the solubility limit would render the adsorbate unable to be eliminated through adsorption. Therefore, the adsorption process is solely influenced by precipitation occurring on the biochar surface or through co-precipitation [162]. The mechanism for the adsorption of Pb^{2+} ions onto biochar derived from anaerobic waste was studied by Ho et al. The authors proposed that the presence of a significant amount of phosphorus on the surface of biochar leads to surface co-precipitation. This process involves the interaction between the phosphorus and Pb^{2+} ions, resulting in the formation of a precipitate known as Pb phosphate. The validity of these findings was confirmed by the utilization of X-ray elemental dot mapping and X-ray diffraction (XRD) analysis [163]. Cao et al. investigated lead (Pb) precipitation over the surface of biochar rich in phosphates, which were produced from manures. The addition of biochar to a solution has the potential to increase its pH, dependent upon the initial pH of the solution. This increase in pH may result in the formation of metal hydroxides, which typically exhibit low solubility [164]. The study conducted by Deng et al. focused on investigating the adsorption behavior of Pb^{2+}, Cd^{2+}, and Cu^{2+} ions onto biochar derived from wood waste. The researchers identified biochar modification by introducing chlorine and phosphorus, leading to an increased development of precipitates on the surface of the biochar [165]. The study conducted by Wu et al. evaluated the mechanism for the adsorption of Cd(II) on biochar produced from lignin, which was confirmed by following the co-precipitation mechanism [166]. In their study, Cui et al. explored the mechanisms involved in the adsorption of Cd^{2+} ions onto biochar obtained from Canna indica. Following the adsorption process, the researchers observed the presence of white granular crystals on the surface of the biochar. Through the utilization of electron microscopy and X-ray analysis, these crystals were recognized as $CdCO_3$. Furthermore, researchers observed that the release of $(CO_3)^{2-}$ from the biochar exhibited a notable decrease as the initial amount of Cd^{2+} ions was enhanced. This finding implies a potential correlation between the amount of Cd^{2+} ions and the development of co-precipitate on the surface of the biochar [167].

Overall, the biochar's efficiency as an adsorbent for water decontamination is determined by a mixture of these adsorption mechanisms, which are affected by factors such as biochar features, feedstock type, pyrolysis environments, pH, temperature, and the types of pollutants in the water. Optimizing these interactions and developing customized biochar-based adsorbents can result in more efficient and long-lasting water decontamination processes. It is important to highlight that the use of biochar for wastewater treatment requires careful consideration of particular contaminants and site-specific conditions in order to achieve successful and accurate results.

5. Limitations and Risks Associated with the Use of Biochar as Adsorbent

Considering its enormous surface area and porous texture, biochar received tremendous attention as a potential adsorbent that is capable of adsorbing numerous pollutants and toxins from soil, water, and air. However, like any other method, using biochar as an adsorbent has limitations and hazards, as briefly described below [113,168–171].

5.1. Variable Adsorption Capability

The biochar's adsorption capacity varies according to its source material, pyrolysis temperatures, and activation processes. Due to this disparity, predicting the efficacy of biochar as an adsorbent under various environmental conditions might be challenging [125]. For example, biochar samples (CCB350 and CCB650) were acquired through the pyrolysis process of corn stalk biochar (CB350 and CB650) at temperatures of 350 °C and 650 °C, respectively. These samples were then subjected to artificial oxidation using hydrogen peroxide (H_2O_2). The qualitative and quantitative analysis of the impact of Pb^{2+} and Cd^{2+} on newly produced and aged biochar was conducted by batch adsorption studies in conjunction with characterization techniques. The experimental findings from the adsorption isotherm analysis indicate that the adsorption capacity of Pb^{2+} and Cd^{2+} was reduced as a result of the aging treatment. Additionally, the aging treatment was found to hinder the competing adsorption behavior of heavy metals. In the context of a single metal system, the primary mechanisms of adsorption for CB350 and CB650 were identified as precipitation and cation exchange. The respective proportions of these mechanisms were found to range from 40.07 to 48.23% for precipitation and from 38.04 to 57.19% for cation exchange. The presence of both Pb^{2+} and Cd^{2+} ions led to an escalation in the relative significance of mineral precipitation, while concurrently diminishing the role of the cation exchange mechanism. The process of aging has been found to have a significant impact on the adsorption of Pb^{2+} and Cd^{2+} on biochar. Specifically, it has been observed that aging leads to an increased contribution of surface complexation to the adsorption process, particularly in biochar that has been subjected to low temperatures. Conversely, the role of mineral precipitation in the adsorption of these metals is diminished as a result of aging [172].

5.2. Selectivity and Specificity

It is possible that biochar may not be particularly selective toward specific contaminants. While it has the ability to adsorb a wide range of contaminants, it might not be able to properly target specific pollutants of interest, thus leading to partial removal [173].

5.3. Slow Kinetics

In comparison to other adsorbents, the adsorption process of biochar is typically slow. Slow kinetics may be impractical for large-scale or time-critical applications that demand faster remediation techniques [174]. For instance, Maghsoodi et al. conducted an investigation on the release kinetics of NH_4^+ from urea-impregnated biochar and other reference adsorbents. The release kinetics were studied by exposing the adsorbents to a 2 M KCl solution at various time intervals. Based on their findings, it was observed that a substantial amount of urea (i.e., 76.5%) was transformed into NH_4^+ over a period of 20 days. Furthermore, it was noted that the concentration of extractable NH_4^+ exhibited an

initial increase, followed by a subsequent decline after a period of 20 days. The findings of this study indicate that the biochar that was impregnated with urea exhibited a gradual release of the urea, possibly leading to a reduction in nitrogen loss [175].

5.4. Leaching of the Adsorbed Contaminants

In some cases, the toxins adsorbed onto biochar may escape over time, thereby re-entering the environment and giving rise to secondary contamination. This can occur under extremely high pH, temperature or extensive exposure to water [176]. For instance, Oleszczuk et al. conducted a study that indicated that biochar formed from Miscanthus exhibited a greater concentration of toxic metals compared to other types of biochar. Consequently, there is a potential risk of heavy metal leaching into the surrounding environment [177]. Von Gunten et al. conducted a study in which they observed that heavy metals, specifically zinc (Zn) and manganese (Mn), were predominantly present as monovalent and divalent cations in wood biochar produced from pine wood chips, bamboo, or oak. These heavy metals were shown to be present in significant quantities. Hence, it can be observed that the heavy metals exhibit a low degree of adsorption onto the biochar matrix and can be readily released, even when subjected to mild conditions [178].

5.5. Saturation and Regeneration

Biochar can undergo regeneration and be utilized in many adsorption cycles. However, the effectiveness of the adsorbent diminishes over time due to the gradual accumulation of contaminants and variations in the surface properties of the adsorbent, leading to its eventual depletion. Furthermore, the utilization of newly produced biochar may present a more cost-effective alternative compared to regenerative biochar, which is mostly attributed to the readily available and relatively low cost of feedstock materials. In this specific case, it is necessary to replace and appropriately dispose of the depleted biochar, thereby requiring a regular supply of biochar [179]. Regeneration techniques can be complicated and costly, and many cycles of adsorption–desorption may reduce biochar's overall efficacy as an adsorbent [180].

5.6. Harmful Compound Release

Relying on the feedstock and pyrolysis factors, biochar may contain hazardous substances, such as heavy metals or polycyclic aromatic hydrocarbons. These compounds can be discharged into the environment during the application of biochar if not precisely identified and managed [181]. Thus, the biochar might be at risk of the introduction of potentially hazardous elements originating from the source material. Furthermore, the process of biochar formation has the potential to produce other harmful substances, including dioxins, persistent free radicals, volatile organic compounds, and metal cyanide. The presence of such toxins has the capacity to entail hazards for both human health and surroundings, including but not limited to ecotoxicity, phytotoxicity, neurotoxicity, and cytotoxicity [182]. For example, the presence of biochar containing higher levels of polycyclic aromatic hydrocarbons and potentially toxic elements has been observed to enhance the generation of reactive oxygen species within the cellular structures of animals and plants. This phenomenon subsequently leads to increased levels of cytotoxicity and genotoxicity in human lung epithelial cells. Hence, it is imperative to conduct a comprehensive assessment of possible ecological risks associated with the utilization of biochar [183].

5.7. Inhibition of Bioavailability and Biodegradation

The existence of biochar in the soil could reduce the bioavailability of vital nutrients and organic molecules to plants, thereby inhibiting growth. It can also interfere with the biodegradation of some organic contaminants, deteriorating soil health and ecosystem dynamics [184]. Tian et al. conducted a study in which they examined the impact of biochar on the bioavailability of cadmium (Cd) and arsenic (As) in soils. Their findings revealed that the presence of biochar resulted in a considerable reduction in Cd bioavailability by

50.12%. Conversely, the bioavailability of As in soils was seen to have a slight rise of 2.39% when biochar was introduced. The findings indicate that the application of biochar has the potential to decrease the levels of As and Cd in plants by approximately 25.48% and 38.66%, respectively. The observed trends in the decreasing percentage of As and Cd across different tissues were as follows: root < stem < leaf < grain for As, and root < leaf < stem < grain for Cd. Based on the investigation of key variables, it was determined that the utilization of manure biochar, a pyrolysis temperature below 400 °C, an application rate below 2%, and a high soil organic carbon content exceeding 30 g kg^{-1} were found to be more favorable in reducing the simultaneous bioaccumulation of As and Cd in co-contaminated soils [185]. In their study, El-Naggar et al. observed the inability of woody plants to successfully establish and endure due to the substantial buildup of charcoal and the resulting micronutrient insufficiency, resulting from enhanced soil pH emerging from the application of soil biochar [186]. The rise in soil pH caused by biochar application may potentially enhance the hydrolysis of N-acyl-homoserine lactone (AHL), a signaling molecule employed by gram-negative bacteria to facilitate intercellular communication. Consequently, this process could lead to a reduction in the bioavailability of AHL [187].

5.8. Land and Resource Competition

The feedstock utilized in the synthesis of biochar encompasses a wide range of biomass sources, including crop and forestry residuals, specifically cultivated plants, animal waste, and wastewater sludge [188]. As demand for biochar grows, competition for land and biomass resources may arise, potentially leading to deforestation or the transition of cropping land from food production to biochar production [174,189].

5.9. Uncertainty about Long-Term Implications

The long-term environmental implications of the use of biochar still remain unclear. The extensive and long-term use of biochar as an adsorbent may have unforeseen implications on soil fertility, water quality, and ecological balance [171,190]. For example, the environmental reactions that biochar undergoes during its evolution might lead to detrimental impacts on the environment due to variations in its features. These changes not only impact the biochar itself but also influence the interface of the media. During the transport of biochar, it is possible that a cycle including soil, water, and gas may be induced. The potential transport mechanisms of biochar include migration and leaching, leading to its movement from soil to water; runoff, resulting in its transfer from water to soil; wind erosion and weathering, causing its movement from soil to the atmosphere; and free settling and precipitation, facilitating its deposition from the atmosphere to soil or water [173].

5.10. Inadequate Regulatory Standards

The lack of advanced testing techniques and standards of regulation for the use of biochar as an adsorbent may result in varied practices and a lack of confidence in its safe and effective use [191].

6. Conclusions

Biochar is an attractive material used more and more for water decontamination due to its unique characteristics such as high surface area, a wide range of pores, electrical conductivity, low price, and being environmentally friendly. It can be used as pristine or functionalized. Usually, functionalization is achieved with metal oxides aiming to obtain a magnetic material that is easy to separate from water and has a high surface or affinity for different pollutants.

One of the many advantages of this material is that it can be used with great efficiency for the removal of organic and inorganic pollutants, from various drugs to heavy metals. At the same time, the possibility to adsorb numerous contaminants can also be considered a limitation because specificity is necessary in some cases. Unfortunately, the final cost of

the sorbent could be increased by the functionalization procedure. However, changing the operating conditions like pH, temperature, and contact time can be achieved at a low cost, thus allowing for an improvement in the specificity of the method.

In summary, while biochar offers promise as an adsorbent for environmental remediation, its limitations and potential hazards must be considered. Addressing these challenges through proper studies, in-depth and breadth characterizations, and regulations will ensure that biochar is used responsibly and effectively as an adsorbent in a variety of environmental applications.

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