Advancements in the application of modified biochar for the removal of heavy metals and organic pollutants: short review

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Abstract

Water pollution, primarily caused by heavy metals and organic pollutants, poses a significant threat to environmental and public health. Traditional water treatment technologies, while effective, often face limitations such as high costs and secondary pollution. This review explores the advancements in the application of modified biochar for the removal of heavy metals and organic pollutants from contaminated water. We begin by discussing the various preparation methods of biochar, emphasizing the modifications that enhance its adsorption capabilities. The use of biochar in adsorptive removal of heavy metals is examined, highlighting the mechanisms and efficiencies involved. Additionally, the role of biochar-based adsorbents in the removal of organic pollutants is analyzed, focusing on adsorption processes and the incorporation of photocatalytic properties. The review also delves into biochar-based catalysts in sulfate radical-based advanced oxidation processes (AOPs), showcasing their potential in degrading complex organic pollutants. Furthermore, the application of biochar-based adsorbents in binary pollutant systems is reviewed, providing insights into their multifunctional capabilities. The paper concludes with future perspectives, suggesting pathways for further research and development to enhance the effectiveness and applicability of biochar in water treatment technologies. The findings underscore the promise of modified biochar as a versatile and sustainable solution for mitigating water pollution.

Keywords: biochar, heavy metals, adsorption, organic pollutants, AOPs

1.Introduction

Due to the rapid pace of global change, numerous advanced technologies and interventions have been developed to improve living standards and foster economic growth. However, this progress has come at a cost to the environment, with a multitude of disruptions occurring. Despite this, water, which covers two thirds of the planet, remains a fundamental need for all human beings. The widespread use of heavy metal compounds in the electroplating, textile, tanning, mining, wood production, pesticide, fertilizer and battery industries is responsible for their presence in industrial effluent, which causes soil contamination and water pollution if discharged untreated [1]. Heavy metal contamination of water bodies is a serious environmental issue, especially in developing countries [2]. Serious threats to human health and the environment have been caused by the excessive accumulation of heavy metals owing to their mobility and non-biodegradability [3]. Constant exposure to Cd may result in detrimental and irreversible damage to human body including metabolic disorders, neurological damage, renal failure, osteoporosis, and cancer [4]. Copper ions are also toxic for living organisms when intake intensive concentrations which resulted in dangerous impacts on kidney, liver functions and on nervous system [5]. Heavy metals can also disrupt on the food chain and food web owing to plants can accumulate it. For the above reasons, it is important to act in the treatment of heavy metals from polluted water and conventional methods need to be searched.

The visible water pollution emanating from the industries, responsible for producing a myriad of human-use clothes, and from printing and dyeing, pharmaceutical and food, and many other, organic dyes, poses a significant environmental challenge [6]. The wastewater discharged from this industry finds its way into rivers and lakes, leading to eutrophication. Algal blooms, a consequence of this pollution, not only degrade water sources but also infiltrate the food chain and web through aquatic organisms, thereby impacting human health.

Chemical precipitation, electrochemical, filtration, photocatalysis, advance oxidation process, membrane, bioremediation, ion exchange and adsorption methods, are most widely used methods to remove heavy metals and organic pollutants from water. Among them, the adsorption method is the top choice for the removal of heavy metals in recent years and the advance oxidation process is the best fit for the removal of organic pollutants. It is recognized as a promising technology owing to its high efficiency, ease of use, economic feasibility and environmental safety aspects [7]. Biochar, a sustainable and environment-friendly black carbon [8], has been employed to remove various pollutants from the aqueous medium owing to its strong adsorption abilities [9].

Biochar is a valuable byproduct of biomass pyrolysis; its use as an adsorbent for removing contaminants from wastewater has piqued the interest of researchers and industry alike [10]. Biochar, a type of charcoal produced through pyrolysis of organic materials, has gained significant attention in recent years due to its numerous environmental benefits. One of the most significant features of biochar is that it can be made from a variety of waste materials, such as food residue, agricultural residue (including rice husk, peanut shell, coconut shell, zea may husk, sugarcane bagasse), and various tree bark and leaves [11]. This is particularly important in today's world, where the concept of a circular economy is becoming increasingly popular. The circular economy is an economic system that aims to minimize waste and maximize resource utilization, and the use of waste materials for biochar production is a prime example of this approach [12]. By turning waste into a valuable resource, biochar production not only reduces waste disposal problems but also provides a sustainable source of soil amendment and carbon sequestration. Thus, the utilization of waste as a resource through biochar production has the potential to promote sustainable development and contribute to the transition toward a more circular economy. Furthermore, modifying biochar with activating agents such as salt, acid or alkali may improve its textural properties, morphological structure, and surface functional groups, as well as its contaminant removal capacity [13]. In this study, the removal of copper and cadmium by using various biochar will be discussed the removal efficiency. Overall, this study will provide valuable insights into the use of biochar materials for the removal of heavy metals and micropollutants from contaminated water and will provide important information on the optimal conditions for the efficient removal of heavy metals and micropollutants.

2. Biochar

2.1. Preparation of Biochar

Biochar can be obtained by the carbonization of the biomass and byproduct. The carbonization process allows the valorization of diverse biomass sources like lignocellulosic residues from agro-industrial and forestry activities, animal manure, dewatered sludges, even micro algae, marine and aquatic species [14],15 .The term carbonization includes the technologies of pyrolysis, hydrothermal carbonization, flash carbonization, gasification and torrefaction. (1) pyrolysis is the most effective and efficient way to covert the biomass to get the biochar or charcoal. Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. It is the fundamental chemical reaction that is the precursor of both the combustion and gasification processes and occurs naturally in the first two seconds. The products of biomass pyrolysis include biochar, bio-oil and gases including methane, hydrogen, carbon monoxide, and carbon dioxide [16]. Depending on the thermal environment and the final temperature, pyrolysis will yield mainly biochar at low temperatures, less than 4500 °C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 8000 °C, with rapid heating rates [17]. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil. Pyrolysis can be performed at relatively small scale and at remote locations which enhance energy density of the biomass resource and reduce transport and

handling costs. Heat transfer is a critical area in pyrolysis as the pyrolysis process is endothermic and sufficient heat transfer surface must be provided to meet process heat needs [18]. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported biochar, which is the recent trending of research hotspot and, liquid, which can be successfully used to produce heat, power and chemicals A wide range of biomass feedstocks can be used in pyrolysis processes. The pyrolysis process is very dependent on the moisture content of the feedstock, which should be around 10%. At higher moisture contents, high levels of water are produced and at lower levels there is a risk that the process only produces dust [19]. High-moisture waste streams, such as sludge and meat processing wastes, require drying before subjecting to pyrolysis. The efficiency and nature of the pyrolysis process is dependent on the particle size of feedstocks. Most of the pyrolysis technologies can only process small particles to a maximum of 2 mm keeping in view the need for rapid heat transfer through the particle [20]. The demand for small particle size means that the feedstock has to be size reduced before being used for pyrolysis. (2) Biochar can also be produced by gasification, a process that differs from pyrolysis in that some oxygen is present and much higher temperatures are used [21]. Gasification has been used since the 1800s in energy generation from coal and biomass. Gasification is used to convert carbon-based materials into carbon monoxide, hydrogen, and carbon dioxide (syngas or producer gas) [22]. The gas mixture can then be combusted to generate power. While gasification technologies were designed for power, rather than biochar production, biochar can be produced with this approach. The main parameters of the gasification process are temperature, pressure, gasifier and the ratio of gasifier and biomass [23]. A drawback of this technology group is that the conversion efficiency of biomass to biochar appears to be limited to relatively low levels, though conversion efficiency depends on the specific technology used. (3) Hydrothermal carbonization is a promising technique among all conversion technologies, also known as wet pyrolysis. It is a thermochemical process for the pretreatment of high moisture content biomass under hot compressed water, making it applicable for various purposes. This process is performed in a closed reactor at a temperature range of 180–280°C under pressure (0.2–0.6 MPa) for 5 to 240 minutes [24]. The primary product of hydrothermal carbonization is a coal-like substance called hydro-char. It also produces aqueous phases (rich in nutrients) and gas phases (mainly CO_2) as byproducts. The water content in the wet biomass acts as an excellent solvent and reaction medium [25]. Water can function as both a base and an acid at temperatures between 200°C and 280°C because its ionic product is maximized. Furthermore, at these temperatures, the dielectric constant of water is reduced, so it behaves more like a nonpolar solvent. Key parameters such as residence time, process temperature, pressure, and water-biomass ratio are crucial in determining the properties of hydrocar [26]. The hydrothermal carbonization process is spontaneous and exothermic, resulting in various carbon compounds from the initial products being present in the final product. Compared to direct pyrolysis, which requires a high amount of energy for combustion and is endothermic, as well as releases SO_2 and NO_2 gases, hydrothermal carbonization is more environmentally friendly [27].

Researchers choose the appropriate methods according to their needs in the experimental preparation process. Among many methods in preparation of biochar-based composite, wet impregnation and co precipitation method are widely used.

2.2. Modification of biochar

Pristine biochar is also used in the removal of environmental contaminants by various methods. However, in recent years, modifications to biochar have been made to enhance its removal efficiency. There are many modification methods, but three prominent ones stand out [28]. Firstly, acid treatment introduces oxygen-containing functional groups (e.g., carboxyl, hydroxyl) on the biochar surface, enhancing its catalytic properties. Sulfuric acid (H_2SO_4) [29], nitric acid (HNO_3) [30], and phosphoric acid (H_3PO_4) [31] are frequently used for acid modification. Secondly, base treatment can increase the surface area and porosity of biochar, as well as introduce basic functional groups. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are typically used for this modification [32], [33]. Thirdly, biochar is modified with transition metals and used in advanced oxidation processes, significantly boosting its ability to generate reactive oxygen species and degrade organic pollutants. These modifications have been proven to greatly improve the efficiency and effectiveness of biochar in environmental remediation applications [34].

Lately, modification of biochar by single and bimetal have been widely used for the adsorption of heavy metals and organic pollutants. The most widely used production and modification of biochar was illustrated in Figure (1).
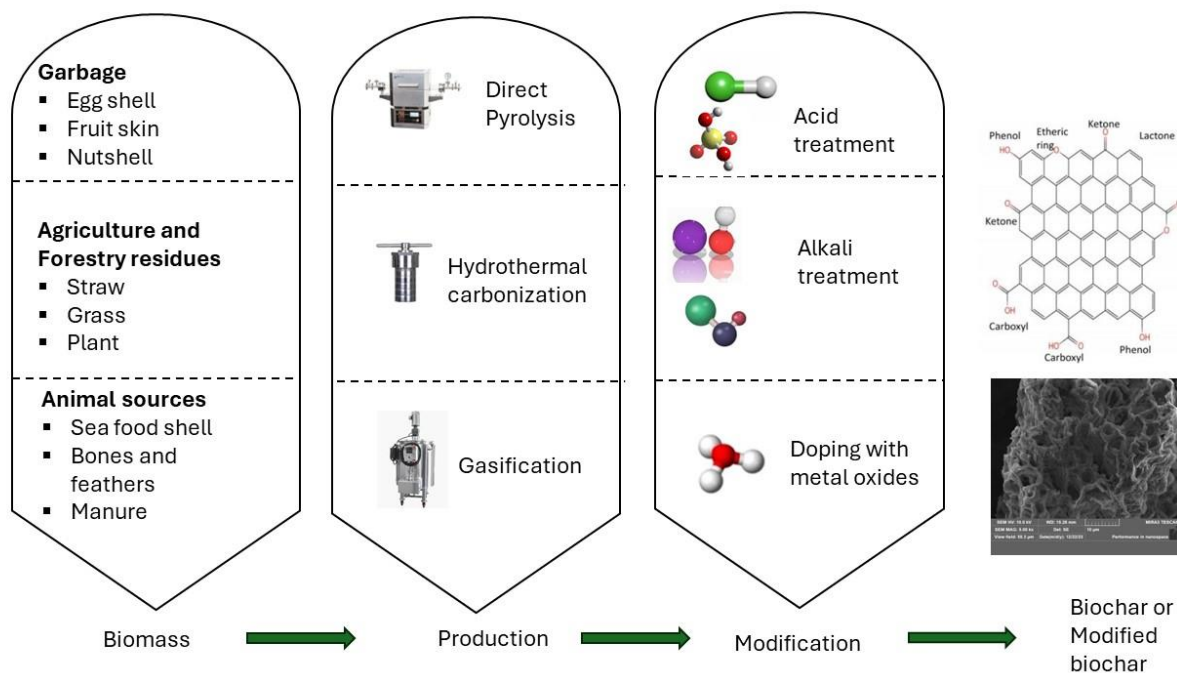
Figure 1. Illustration of production of biochar from biomass

3. Removal of heavy metals and organic pollutants

3.1 Removal of heavy metals

The public is increasingly concerned about the potential dangers posed by heavy metals and various anions in drinking water. These ions are sourced from chemical plants and landfills where metals can leach from solid waste. Many of these ions are highly toxic and carcinogenic, resulting in permanent damage to human health. The consumption of metal ions and anions can lead to chronic health problems rather than immediate effects, making it possible for individuals to suffer from long-term exposure to these contaminants without being aware of them. Recently, the removal of Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cr^{6+} from aqueous solutions is given more attention than the other ions, due to the economic values in the recovery of these ions, and the high level of hazards of these ions once released to the environment [35].

An African research team conducted an experiment in which they utilized eucalyptus tree bark to generate biochar. They subjected the biochar to pyrolysis at a temperature of 500 degrees Celsius and subsequently modified it using $ZnCl_2$ to create an adsorbent for extracting Cr(VI) from an aqueous solution [36]. They found that the application of activated eucalyptus tree shed bark biochar as an adsorbent was found to have a high affinity for Cr(VI) removal from aqueous solution and to be capable of adsorbing 94.82% of the adsorbate at an AEBB dosage of 0.3 g/L, a contact time of 140 minutes, and a pH of 6.0. Furthermore, they conducted research on the safe disposal of used biochar by calcining it at higher temperatures, and they discovered that this process completely eliminated Cr(VI).

Another study reveals for the removal of cadmium and zinc in a single or binary metal system using Hematite-KMnO4 modified biochar (MnFeB) [37]. They used MnFeB that displays a rugged surface structure, a significant specific surface area, a greater total pore volume, a profusion of functional groups, and a substantial amount of iron oxide, all of which contribute to an increased adsorption capacity for Cd^{2+} and Zn^{2+}. In the case of single metal systems, the maximum adsorption capacities of MnFeB for Cd^{2+} and

Zn^{2+} were 1.88 and 1.79 times higher, respectively, than those of unmodified biochar (CSB). In the binary metal system, the maximum adsorption capacities of MnFeB for Cd^{2+} and Zn^{2+} were 2.73 and 2.65 times higher, respectively, than CSB. And also, they sum up their conclusion for future suggestions like in a way like that MnFeB had a high adsorption capacity for Cd^{2+} and Zn^{2+}, exceeding that of CSB in both single and binary metal systems. The adsorption capacity for Cd^{2+} was particularly noteworthy. The key mechanisms behind Cd^{2+} and Zn^{2+} adsorption by MnFeB included electrostatic interaction, co-precipitation, π-π interaction, complexation, and ion exchange. Future research should explore the comparative adsorption capacities of MnFeB with other materials and its efficiency in removing various organic and inorganic pollutants.

A study in India uses $FeSO_4$ to modify *zea may* husk in the sequestration of Ni(II) and Cu(II) [38]. They study the impact of different variables, such as pH levels (ranging from 2 to 12), adsorbate concentration (ranging from 10 to 100 mg/L), contact time (ranging from 5 to 240 minutes), and temperature (ranging from 288 to 308 K), on the adsorption process was investigated in batch mode. The optimal conditions for the process were found to be pH 6, an initial concentration of 50 ppm, and equilibrium times of 120 minutes and 90 minutes for the removal of 98.00% of copper and 97.44% of nickel, respectively. They concluded that Ferrous Sulphate modified magnetic *Zea mays* biochar is an appropriate adsorbent for wastewater treatment for the removal of Cu^{2+} and Ni^{2+}.

Another study prepares an adsorbent with discarded mollusk shells in combination with PVA (polyvinyl alcohol) by means of a solution casting method [39]. Initially, the researchers prepared oyster shell particles for the unmodified sample to enable a comparison with the modified composite. Subsequently, they created a PVA/OSP composite. According to the Langmuir model's fitting of thermodynamic data, it was found that the adsorption capacities of Cu^{2+} and Cd^{2+} onto the PVA-OSP composite were approximately 6.64 and 7.83 times higher, respectively, compared to the OSP's average adsorption capacity. This indicates that the PVA-OSP composite is highly effective at removing these heavy metal ions from water.

A study provided information about the use of biochar and fertilizer together. They created a fertilizer called biochar-based infiltration urea fertilizer (BIUF) using infiltration technology to use the biochar in the removal of cadmium and to study in the release of fertilizer [40]. The researchers investigated the urea slow-release performance and Cd (II) adsorption ability of BIUF. They compared the slow-release rate of BIUF with that of urea and found that the slow-release rate of BIUF decreased significantly during the urea release process. Furthermore, they tested the equilibrium adsorption capacity of BIUF and discovered that it was 1.73 times that of biochar, reaching a value of 14.24 mg/g. Additionally, the researchers studied the Cd (II) adsorption of BIUF and found that it fit the pseudo-second order model better. This suggests that chemical adsorption was the dominant mechanism at play. These findings provide important insights into the potential use of BIUF as a slow-release fertilizer and as an effective adsorbent for Cd (II) in contaminated soil.

The use of biochar made from agricultural waste has become increasingly popular as an affordable solution for treating water contaminated with metals. A recent study examined the effectiveness of non-activated biochar made from corn cob and sugarcane bagasse for removing metals such as Pb, Ni, and Cu from water [41]. The researchers conducted a thorough analysis of the physical, chemical, and structural properties of the biochar to better understand its performance. The study aimed to investigate the efficacy of biochar derived from corn cob and sugarcane bagasse for removing metals such as Pb, Ni, and Cu from an aqueous medium. The researchers conducted various physical, chemical, and structural characterizations of the biochar before conducting batch sorption experiments using the Langmuir and Freundlich equations. The results showed that the separation factor (RL) values were between 0 and 1, indicating productive adsorption. The optimal dosage for metal adsorption was found to be 30 g/L. The researchers also identified the ideal conditions for adsorption to occur, which included a pH of 6.5 and 5.5, an adsorbent dose of 1.5 g, and an equilibrium time of 180 minutes for both types of biochar. The study found that at a pH of 6.5, the

maximum adsorption capacities of Pb, Ni, and Cu were achieved, with values of 11.34, 15.71, and 11.96 mg/kg for corn cob biochar and 8.96, 15.46, and 12 mg/kg for sugarcane bagasse biochar, respectively. These findings demonstrate the potential of corn cob and sugarcane bagasse-derived biochar as an effective and affordable method for removing heavy metals from contaminated water.

As mentioned earlier, the combination of PVA and oyster shell powder has shown promising results in the removal of heavy metals. However, in addition to this method, researchers are exploring the possibility of using plastics to produce biochar as an alternative approach. The idea behind this is to reduce the amount of plastic waste and promote the use of biochar. Experiments are being conducted to determine the effectiveness of this approach in removing heavy metals from contaminated water. If successful, this method could provide a solution to two problems at once - the reduction of plastic waste and the remediation of contaminated water. This research is particularly important as plastic waste has become a major environmental concern, with large amounts of plastic waste polluting oceans and harming marine life. Finding ways to repurpose plastic waste could help to reduce its impact on the environment. Additionally, the use of biochar has been shown to have numerous benefits, including soil improvement and carbon sequestration, making it a valuable resource in sustainable agriculture and environmental management.

In a recent study, biochar was produced using three different types of biomass materials: bamboo, sugarcane, and neem and additionally, plastic char was produced using PET, PE, and PVC plastics [42]. The objective of this study was to investigate the process of pyrolysis of waste biomass and plastics and evaluate the effectiveness of the produced biochar in removing heavy metals from aqueous solutions. Batch experiments were conducted using Fe, Ni, Cu, Cr, Cd, and Pb with both biochars and plastic chars to determine the impact of various parameters such as feedstock, contact time, adsorbent dose, pH, and pyrolysis temperature on the removal of heavy metals. The results of the study revealed that the sorption capacities of biochars were higher compared to those of plastic char, as demonstrated by the isothermal sorption models. The maximum removal efficiency observed for both biochars and plastic chars was 99.86% and 99.93%, respectively, at a pH of 4. This research is significant as it highlights the potential of using waste biomass and plastics to produce biochar for the removal of heavy metals from aqueous solutions. The findings suggest that this approach could be a cost-effective and environmentally friendly method for addressing the issue of heavy metal contamination in water. The adsorption of heavy metals was described in table (1)

Table (1) Removal of heavy metals by biochar

Types of biochar	pH	Target metals	Concentration range (mg/L)	Langmuir adsorption capacity (mg/g)	References
Pinewood char	5	Pb^{2+}	2-1036	4.13	[43]
Peanut straw char	4.5	Cu^{2+}	6-318	12.52	[44]
Soybean straw char	4.5	Cu^{2+}	158-954	33	[45]
Rice husks 5 24	5	Cu^{2+}	1-20	3.49	[46]
Pig manure biochar	5	Zn^{2+}	0.065-0.2	62.13	[47]
Dairy manure biochar	-	Cd^{2+}	0-6575	32.03	[48]
Oak Wood char	2	Cr^{6+}	1-100	3.03	[49]
Pine needle biochar	6	U^{6+}	5-30	2.12	[50]
Corn straw	5	Hg^{2+}	0-139	-	[51]
Pinewood biochar	2	F^-	1-100	7.66	[52]
Banana peels		Pb^{2+}	70-250	87.5	[53]
Corn straw	5	As^{3+}	0-7	-	[54]
Corn straw	5	Hg^{2+}	140	5.03	[55]
Sugar beet tailing biochar	2	Cr^{6+}	50-800	123	[56]

4. Removal of organic pollutant

4.1 Removal of organic pollutant by adsorption

Organic pollutants such as phenols, antibiotics, herbicides can be highly adsorbed onto biochar [57]. In livestock wastewater, similar organic contaminants and pollutants are always found; as a result, biochar has become a major focus in agricultural resources and the environment. Antibiotic substances such as a fluoroquinolone, sulfamethoxazole can be adsorbed by biochar in their aqueous phase mainly through hydrogen bonding, π–π electron transition and cationic interactions. For example, the fluoroquinolone adsorption ability of biochar was investigated by [58]. Their biochar was prepared using pyrolysis of sludge at 500 °C for 1 h, and the maximum adsorption capacity was 19.8 mg/L and Langmuir capacity is 0.4 mg/g. It was also found that the adsorption of fluoroquinolones was positively correlated with the amount of volatile matter contained in the raw sludge. Similar results were reported by [59] to produce biochar from Arundo donax using microwave-assisted pyrolysis to adsorb sulfamethoxazole. They observed that increasing the pyrolysis temperature decreased the adsorption capacity of biochar. It was reported that biochar has a significant impact on the adsorption of organic pollutants, such as phenols, compounds with high-chromatic content, herbicides [60]. The mechanism of adsorption can be either physical or chemical. It depends mainly on the aromatic and/or special functional groups and on the polarity of both the biochar and the organic pollutants. The nature of intermolecular gravitation and electrostatic force between the biochar and the pollutants is the determining factor for the physical adsorption, while the chemical adsorption mainly depends on the chemical interactions between the biochar and the organic pollutant, which can be π bonds, hydrogen bonds and coordination bonds [61]. They prepared biochar from different raw materials (Cole, peanut and rapeseed straw) after pyrolyzing at 350 °C. The methyl violet adsorption capacity of their biochar was in the range of 123.5–195.4 mg/g. Rapeseed straw gave the highest adsorption at room temperature. The presence of electrostatic attraction between methyl violet and biochar was confirmed by zeta potential and FTIR analysis. The results revealed that the methyl violet was mainly adsorbed on the hydrophilic and ─COO-sites. Mohan et al obtained methyl blue removal efficiency of 99.5, 99.3 and 86.1% using biochar prepared from anaerobic digestion residue, palm bark and tree, respectively [62]. The organic materials were pyrolyzed at 400 °C for 30 min, and the conditions during the treatment were pH 7, 40 °C and 4 mg/L of the dye. It was found that the pyrolysis temperature had a significant effect on the treatment of methyl violet. They also prepared biochar from peanut shells and wheat straw and obtained a maximum adsorption capacity of 58.82 and 20.61 mg/g, respectively. These organic materials were pyrolyzed at 400 and 600 °C, respectively. The adsorption capacity of biochar prepared from mixed wood wastes, pyrolyzed at 450 °C for 1 h, was investigated, and maximum adsorption capacities of 1066 and 1158 mg/g were obtained for two herbicides, namely simazine and atrazine, respectively [63]. The authors claimed that better adsorption performances were obtained in acidic conditions. The removal of organic pollutants by biochar adsorption was listed on table (2).

Table (2) Removal of organic pollutants by biochar adsorption

Type of biochar	pH	Target pollutant	Concentration range (mg/L)	Langmuir adsorption capacity (mg/g)	References
P-(acrylamide)-wood biochar	-	Phenol	5-50	23.14	[64]
Rice husk biochar	-	Phenol	100-15000	409.8	[65]
Hardwood (Laurel oak, Quercus)	-	Humic acid	0-13	13	[66]
Orange peel biochar	-	Naphthalene	18	-	[67]
Wood char	7	Pyrene	0.002-0.12	-	[68]
Pine needle biochar	-	m-dinitrobenzene	0.02-1.0		[69]

Peanut straw char	5-9	methyl violet	40–816	104.61	[70]
kenaf fibre char	8.5	methylene blue	50–200	18.18	[71]
Rice straw-derived char	5	Malachite green	25–300	128.14	[72]
Bamboo biochar	-	Acid black 172	50–500	358.14	[73]
Sewage sludge		2,4-Dichlorophenol	100		[74]
Corn straw	5	Bisphenol	91.05	-	[75]
Miscanthus-derived biochar	5	Naphthalene	3000		[76]
Bamboo hydrochar	-	Congo red	100	-	[77]
Sugarcane bagasse biochar	7	Malachite green	3000	-	[78]
Corn straw	5	Atrazine	70	-	[79]
Macadamia nutshell	7	Phenanthrene	60	-	[80]

4.2 Removal of organic pollutant by photocatalysis

Pure biochar can directly generate reactive oxygen species (ROS) without oxidants for organic pollutant degradation under UV light radiation. It was reported that 100%, 95% and 89% of 5.0 mg/L diethyl phthalate were degraded in pine needles, wheat and maize straw biochar (pyrolysis at 300 °C) suspensions in the presence of O_2, respectively, with the reaction time of 24 h [81]. In this process, Free radicals (FRs) in biochar transferred electrons to O_2 to produce the $O_2^{•-}$ and H_2O_2, which reacted further with FRs to produce $^{•}OH$. Biochar carbon matrix (BCM) and dissolved organic matters (DOM) can induce the generation of ROS under solar irradiation. Titanium dioxide, as the most commonly used photocatalyst, provides a set of beneficial redox properties. However, the photocatalytic activity is hampered by limited light absorption and the high recombination of charge carriers [82]. To mitigate this limit, different approaches have been explored for the material's assembly, such as nanocrystals' shape and facet engineering, heterojunction construction, and metal co-catalyst deposition [83]. Previous research had indicated that biochar can serve as a support for TiO_2 to remedy the above shortcomings. The TiO_2/ biochar composite exhibited a higher decolorization efficiency of 96.88% than that of single TiO_2 for methyl orange [84]. Other photocatalysts were also used to couple with biochars. Liu prepared Ag/Ag_3PO_4 support amino-modified biochar composite, which exhibited greatly enhanced photocatalytic performance, and almost 80% amoxicillin was decomposed in 120 min, whereas only 65% with pure Ag_3PO_4 [85]. The CdS load activated biomass carbon composite displayed excellent photocatalytic ability toward methyl orange and methylene blue degradation with the efficiency of 97.8% at 60 min and 96.3% at 150 min, respectively [86]. Additionally, biochar based photocatalysis were stated in table (3).

Table (3) biochar based photocatalysis degradation

Type of nano particles catalysis	Targeted species	Concentration range (ml-mg/L)	References
Starbon-TiO 2	Phenol	150–50	[87]
Softwood pellets-TiO$_2$	Phenol	150–50	[88]
Pinewood- TiO$_2$	Bisphenol	50–20	[89]
Waste plum stones-N- TiO$_2$	Methylene blue	125–25	[90]
Bamboo- TiO$_2$	Methylene blue	200–30	[91]
Chestnut leaf-g-C3N4	Methylene blue	20–4.8	[92]
Sludge/wheat	Reactive Blue	100–20	[93]

husks- TiO$_2$			
Reed straw- TiO$_2$	Sulfamethoxazole	160–10	[94]
Corncob- TiO$_2$	Sulfamethoxazole	100–10	[95]

4.3 Removal of organic pollutant by Sr-AOPs

Lately, Nowadays, the Advanced Oxidation Process (AOPs) method has become more sophisticated, enabling more effective activations. The radicals generated by activating peroxymonosulfate (PMS) or peoxydisulfate (PDS), such as $SO_4^{\bullet-}$, $^{\bullet}OH$, ($^1O_2$) singlet oxygen, and ($O_2^{\bullet-}$) superoxide radicals, possess longer radical half-lives (30–40 μs), a more potent oxidation potential (2.5–3.1 V), and greater stability compared to the traditional hydroxy radical-based AOP [96]. In sulfate radical-based AOP, PMS can be activated using methods like heat, ultrasound, transition metals, and heterogenous catalysts to efficiently degrade pollutants. In PMS activation, heterogenous catalysts involving transition metals such as (Fe, Mn, Zn, Cu, Co, Ni, etc.) oxides and their composite are often employed due to their lower production cost, modest energy requirement, and minimal release of metal ions [97]. Concerning the synergistic properties of BC as the support materials for enhancing pollutant removal, a recent research study confirms the effectiveness of nZVI/BC composite for methyl orange dye removal as compared with nZVI alone or BC alone [98]. The superior removal by nZVI/BC composite was attributed to the uniform dispersion of nZVI into BC matrix which enhances its reactivity as compared with less reactive aggregated nZVI. Moreover, the porous structure of BC acts as a protective layer to avoid the rapid oxidation of iron nanoparticles which lead to the passivation of nZVI or decrease in the reducing ability of iron nanoparticles. Simultaneous occurrence of both reduction and adsorption of methyl orange by BC-based nZVI was considered the main factor for decolorization progress. A study from Chen et al confirmed the significance of the introduction of BC during Co$_3$O$_4$ fabrication. Extraordinary activation for PMS and ofloxacin degradation performance were noted by applying Co$_3$O$_4$ modified BC (BC-Co$_3$O$_4$) [99]. Park et al [100] applied Fe-impregnated sugarcane BC catalyst (FSB) for the degradation of azo dye orange G through Fenton-like reaction. Under optimum reaction conditions, maximum removal efficiency of 99.7% was obtained within 2 h. FSB exhibited good stability and reusability within consecutive 4 runs with orange G removal efficiency higher than 89.3%. Several other metal oxides are also used to incorporate with biochar in the advanced oxidation processes. Although, cobalt is the best activator to in the advanced oxidation process, due to its toxicity to environment and human, Iron is frequently use in the AOPs. The degradation of organic pollutants by biochar composite were listed in table (4).

4.4 Application of biochar in binary pollutants system

There are one or more pollutants in the natural wastewater system. So, scientists are also trying to track this problem by using biochar and its composite. The coexistence of heavy metals and antibiotics in the environment always results in greater toxicity compared to the individual precursors. Therefore, efficient and economic technology for the simultaneous removal of antibiotics and heavy metals is essential. A study revealed that the adsorption of heavy metals in binary and ternary system [101]. Surprisingly, it was found that the adsorption for only single metal system was 99.6% and when it combines in a binary system with Pb^{2+}, a complete removal efficiency occurred. When Hg^{2+}, Pb^{2+} and Cd^{2+} are put together for the adsorption, Hg^{2+} and Pb^{2+} can completely adsorb while the removal of Cd^{2+} reaches 99.05%. This shows the mixed pollutants system can enhance the adsorption ability of biochar. However, another study investigated the binary pollutant system had negative impact on the adsorption for the competitive of the species, the removal efficiency decreased than that of the single metals system [102]. Song et al synthesized an *Enteromorpha prolifera* -based biochar for the adsorption of dye and metal binary system. The adsorption ability for MO only reached 71.18 mg/g and for Cr^{6+} alone was 115.41 mg/g. For the binary pollution system, the adsorption capacity for MO decreased from 74.88 % to 47.65% and for Cr^{6+} dropped from 62.33% to 42.4%, respectively. Competition between MO and Cr (VI) in the dual system can be attributed to the presence of amino and hydroxyl groups. The MO–Cr complex, which was more compact in structure than a single contaminant, was formed, allowing few reactive groups to be exposed to the surface [103].

Another study investigated the adsorption of cassava peel biochar on the methylene blue (MB), malachite green (MG), and rhodamine B (RhB) for single, binary and ternary system [104]. The maximum adsorption capacities for three dyes in single system are 286.41 mg/g for MB, 282.64 mg/g for MG, and 265.36 mg/g for RB; in binary dye system, the maximum adsorption capacities are 129.06 mg/g for MB(MB+MG), 51.07 mg/g for MB(MB+RB), 92.59 mg/g for MG(MG+MB), 111.67 mg/g for MG(MG+RB), 14.82 mg/g for RB(RB+MB), and 14.05 mg/g for RB(RB+MG). Besides, three kinetic models were used in single dye system including the pseudo-first-order model, the pseudo-second-order model, and the intraparticle model. The pseudo-second-order model was adequate to describe the adsorption kinetic. Finally, the thermodynamic study showed that the adsorption of the three dyes in single, binary, and ternary mixture was controlled by physisorption, spontaneous, and endothermic in nature. In the adsorption of binary pollutant systems using biochar-based adsorbents, several mechanisms often occur simultaneously or sequentially, contributing to the overall removal efficiency. The interactions between different pollutants can lead to synergistic effects, enhancing the overall adsorption efficiency. For example, the presence of one type of pollutant can alter the surface properties of biochar, making it more favorable for the adsorption of the second pollutant. The results are more controversial because some binary system support each other for the effective adsorption of organic pollutants but in some cases, the competition for the adsorption site is the inevitable process, causing the reduction in the removal efficiency and some may cause the inhibitory effect. Therefore, this complexion indicates the future research spots. Additionally, there are a few research available on the binary pollution system and invisible organic pollutants removal research are less compared to organic dyes binary system.

5. Future perspectives

Current development of BC-based heterogeneous Fenton and AOPs catalyst is reviewed in this study with specific focus on tailoring the BC properties before using it as supporting media for catalyst loading on its surface to obtain dual benefits of adsorption and degradation of pollutants simultaneously. BC is a kind of suitable supporting media due to its multiple advantages, such as low cost and adsorption affinity for organic pollutants due to available oxygen functional groups. These groups available on BC surfaces such as –COOH, C=O, and –OH groups can activate PS or PMS with production of $SO_4^{\bullet-}$ radicals [115]. Regarding the future application of BC for advanced oxidation processes, there are several perspectives should be considered. (1) Until now, most of the works are limited to the laboratory stage and theory based. Few reports can be found regarding large-scale applications of modified or engineered BC. From industrial perspective, large-scale production and application of BC for a specific purpose are still in its infancy or initial stage and require more studies to design and develop most efficient and simple routes for mass production of BC materials at low cost. (2) Biochar based mate techniques in dealing with the pollutants which are anionic properties and should consider more advanced modification techniques to mitigate this drawback. (3) develop strategies to mitigate the risk of secondary pollution from biochar-based adsorbents. Ensure the long-term sustainability and safety of using biochar in environmental remediation. (4) Boost collaboration between researchers from different fields (e.g., materials science, environmental engineering, chemistry). Encourage innovation and comprehensive approaches to solving complex environmental challenges.

Table (4) The degradation of organic by biochar based AOPs

Catalysts	Reaction condition	Rate constant	References
Fe^0/Fe_3O_4/biochar	[Methylene blue] =20 mg/L, [PMS] = 0.4 g/L, [Cat]= 0.3 g/L, [pH]= 7, [Time]= 60 min, T=25 ºC	0.1550 min^{-1}	[105]
MnO2@SBC	[Methylene blue] = 35 mg/L, [PMS] = 0.5 mmol/L, [Cat]= 0.3 g/L, [pH]= 7, [Time]= 180 min, T=25ºC	0.17796 min^{-1}	[106]
Cu-MBS	[Methylene blue] = 100 mg/L, [PM	0.17796 min^{-1}	[107]

	S] = 2.0 g/L, [Cat]= 0.5 g/L, [pH]= 6.5, [Time]= 40 min, T=25ºC		
0.50-CeO2/ZIF-9	[Methylene blue] = 20 mg/L, [PMS] = 150 mg/L, [Cat]= 50 mg/L, [pH]= 6.4, [Time]= 30 min, T=20ºC	0.195 min^{-1}	[108]
CuO/Fe3O4	[Methylene blue] = 20 mg/L, [PMS] = 1 mmol/L, [Cat]= 0.1 g/L, [pH]= 7.55, [Time]= 30 min, T=20ºC	0.1223 min^{-1}	[109]
CuCo@GCNS	[Tetracycline]= 20 mg/L, [PMS] = 0.5 mM, [Cat]= 0.1 g/L, [pH]= 5.47, [Time]= 30 min, T=25ºC	0.182 min^{-1}	[110]
Co-Cu@g-C$_3$N$_4$	[SMX]= 50mg/L, [PMS] = 0.5 mmol/L, [Cat]= 50 mg/L, [pH]= 7, [Time]= 20 min, T=25ºC	0.137 min^{-1}	[111]
RHB-CuCO$_2$O$_4$	[Acid orange] = 50 mg/L, [PMS] = 1 mM, [Cat]= 100 mg/L, [pH]= 7, [Time]= 30 min, T=25ºC	0.095 min^{-1}	[112]
Co-FE@PPBC	[Tetracycline]= 50 mg/L, [PMS] = 1 g/L, [Cat]= 0.1 g/L, [pH]= 7, [Time]= 60 min, T=25ºC	0.03295 min^{-1}	[113]
FeCu/OPB-1	[BPA]= 200 mg/L, [PMS] = 0.1 g/L, [Cat]= 0.3 g/L, [pH]= without adjustment, [Time]= 90 min, T=25ºC	0.025 min^{-1}	[114]

6. Conclusion

This review has primarily focused on the production of environmentally friendly biochar and its applications in the adsorption of heavy metals and organic pollutants. Additionally, the utilization of biochar and its composites in the oxidation reactions for degrading organic pollutants was thoroughly discussed. The findings indicate that biochar-based adsorbents exhibit significant potential for the removal of heavy metals due to their high surface area, porosity, and functional group-rich surfaces. However, the risk of secondary pollution remains a critical challenge that needs to be addressed through innovative material modifications and post-treatment strategies. Photocatalytic degradation utilizing biochar composites has shown promise for the effective breakdown of organic pollutants under light irradiation. Nonetheless, the high energy consumption associated with these processes underscores the need for research into more energy-efficient and sustainable photocatalytic systems, possibly harnessing solar energy. Advanced oxidation processes (AOPs) incorporating biochar have demonstrated effectiveness in degrading a wide range of organic contaminants. However, the degradation efficiency of anionic dyes by carbon-based materials remains an area for improvement. Future research should aim to enhance the performance of these materials to expand the applicability of AOPs.

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