

## Potential role of biochar in water treatment

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### ABSTRACT

Since the past decades, the water dearth has turned attention of researchers towards its restoration along with the remediation of contaminated water in lieu of rejuvenating valuable resources. Through the treatment of wastewater, it is possible to decrease the exploitation of natural water resources as well as alleviating the problem of water shortage. As a circular or closed loop economy solution, the organic waste such as biomass can be renewed in biochar, a carbon rich product by means of thermochemical conversion methods. Biochar demonstrates an incredible potential in water treatment for removing different pollutants considering low-cost, widely accessible feedstock, and easy surface modifications for enhancing contamination remediating properties as well. Hence, this manuscript focuses on an overview of remediating toxic pollutants employing biochar. The biochar production methods and different feedstocks have been discussed. Process parameters like selection of biomass as a raw material, pyrolyzing temperature, residence time, pre-treatment of biomass, and post treatment methods, etc. are the determining factors of carbonaceous biochar yields in a thermochemical conversion method. The key mechanisms like pore-filling, precipitation, complexation, ion-exchange, diffusion, partitioning,  $\pi$ - $\pi$  electron-donor-acceptor interactions, H-bonding, and electrostatic attraction, etc. drive the specific type of contaminant to be phased out from polluted environments whether organic/inorganic in nature. Activation/modification (physical/chemical) of biochar is another aspect for its rising utilization in the field of expelling specific contaminations. The application of biochar in water treatment has many limitations. In order to meet the challenges, biochar-based materials may be developed with improved physicochemical properties and efficiency of biochar, along with combined advantages of biochar and other materials. This manuscript covers different perspectives of biochar viz. biochar and production techniques, mechanisms involved in removal of toxic contaminants from aqueous medium using biochar, modification/activation methods used to improve the characteristics of biochar, biochars and different biochar-based materials for remediating aqueous environments, associated challenges and future directions. This compilation of evidences focused on biochar technology in water treatment will assist new researchers in their studies through developing a thorough understanding of the research and development of eco-friendly biochar-based environmental remediation.

**Keywords:** Biomass; Thermochemical conversion; Biochar; Pollution; Pollutants; Adsorption; Adsorbent; Water/wastewater treatment; Biochar-based materials

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## 1. Introduction

The majority of pollutants in aqueous solutions are caused by chemical pollution, which includes heavy metals, metalloids, and organic pollutants [1,2]. Heavy metals are not biodegradable and accumulate in living creatures through different trophic levels of food chains and result in biomagnification. Organic pollutants pose serious risks to human health due to their high persistence, difficult removal, ease of transmission, and high toxicity [3,4]. Faced with severe water contamination, it is critical to develop cost-effective methods based on low-cost materials. Adsorption is a widely-accepted and adopted method for adsorbing pollutants in wastewater treatment due to its comparatively high efficiency, less cost, eco-friendliness, and ease of operation [5]. The manufacturing of high-value products such as biochar, fuels, and building materials from waste matter is on high note for maintaining environmental harmony in this era. Out of these interesting approaches, biochar production is a key target under circular economy principles. The properties of biochar are somewhat similar to activated carbon so, reliable in removal of recalcitrant compounds and other impurities. Scientific communities are focusing on improvements in biochar yield and quality. The selection of appropriate feedstock and thermochemical conversion route is a deciding factor for feasible performance of biochar as an adsorbent [6,7]. Biochar is well-considered as effective, environmentally friendly, and economical material for adsorption of typical pollutants from aqueous medium, as well as microbial pollutants, heavy metal cations, inorganic contaminants, volatile organic compounds, personal care products, pharmaceuticals, and endocrine disrupting chemicals [8]. The adsorption of contaminants from adsorbates may occur through a number of mechanisms like pore-filling, complexation, precipitation, ion-exchange, H-bonding,  $\pi$ - $\pi$  electron-donor-acceptor interactions, and electrostatic attraction, etc. The removal capacities of biochar can be enhanced by employing either activation/modification processes, or impregnation of biochar with other materials, or new combined treatment strategies for effective pollution abatement [9,10].

In context of the expanding demands of industrial wastewater treatment, cost-effective composite materials (chitosan-modified kiwi branch biochar; CHKB) were produced for the removal of cadmium ions from wastewater. Batch adsorption and characterization investigations revealed that adding chitosan to kiwi biochar (KB) significantly increased its adsorption ability. The primary processes in the sorption of cadmium ions on CHKB were cation exchange, surface complexation, electrostatic interaction, and precipitation. Adsorption isotherms and kinetics fitted well with Langmuir model and pseudo-second-order model indicating that it was a chemisorption-controlled monolayer process [11]. The innovative biochar composites (SFeS@biochar) were effectively generated by coupling peanut shell biochar with nanoscale ferrous sulphide and starch under nitrogen environment. SEM, BET, EDS, FT-IR, XRD, and XPS methods confirmed whether nanoscale ferrous sulphide particles and starch were effectively loaded on the surface of the biochar. Electrostatic attraction, precipitation, surface complexation, and

reductive reaction were postulated as reaction mechanisms for U(VI) adsorption by SFeS@biochar [12]. The feasibility of chitosan-modified magnetic biochar for heavy metal removal from aqueous solutions was assessed and optimized. Surface structure, specific surface area, pore characteristics, surface functional groups, and electromagnetism of the modified-biochar composite were analyzed and discussed. Furthermore, the operational parameters affecting adsorption process, such as solution pH, temperature, initial metal concentration, contact time, adsorbent dose, and the influence of interfering ions were also investigated. Authors studied the regeneration rates after cycles of heavy metal removal process and stability of modified-biochar as well [13]. In recent years, much interest has been shown towards the beneficial usage of sewage sludge in order to lessen the dangers connected with sludge disposal. In this study, researchers described recent advances in the use of sludge-based biochar for adsorption of pharmaceutical compounds from aqueous medium. The strategies for producing biochar from sewage sludge and their influence on the physicochemical properties of the resulting biochar along with reusability potential were discussed. The key challenges and concerns associated with the synthesis of sludge-based biochar and its uses were also explored, with emphasis on adsorption of pharmaceuticals from the aqueous phase [14]. Xiang et al. [15] critically reviewed and outlined the promising prospects of biochar technology in the treatment of a range of wastewaters, including municipal wastewater, agricultural wastewater, industrial wastewater (dye, battery manufacturing, and dairy wastewater), and stormwater [15]. Though BC-based composite materials have demonstrated great efficacy in the removal of inorganic or organic contaminants in comparison to pristine biochar, stability and biological toxicity of these composite materials still needs to be considered for a large-scale application in the water treatment sector to avoid secondary contamination in aquatic environments.

Thus, this article presents an overview on the different aspects of biochar production, biochar mechanisms involved in pollution mitigation, biochar modifications to enhance its characteristics and develop new biochar-based materials for effective removal of recalcitrant pollutants, its application in water treatment particularly to attain a clean technology for fixing the water pollution challenge, and associated challenges with the biochar technology usage along with future directions for more researches to be applied the same on a commercial/field levels.

## 2. Biochar and production techniques

Due to renewable properties, wide-availability, organic nature, and low cost, lignocellulosic biomass materials from agro-sources and forests are gaining more momentum. Lignocellulosic biomass encompasses three major components, that is, lignin, cellulose, and hemicellulose. Biochar is rich in carbon content which depends on lignocellulosic material, temperature, heating rate, thermochemical decomposition process, residence time, etc. Biochar can be prepared by combusting biomass in controlled oxygen environments. Since it is a carbonaceous organic substance so mostly used for improving the quality of soil, air, and

water. Biochar possesses a number of characteristics similar to charcoal and activated carbon but physically distinct [16–19]. Generally, two types of feedstocks, that is, nutrient rich feedstocks and lignin rich plant biomass feedstocks are used in preparation of biochar. The major techniques but not limited involved in producing biochar are pyrolysis (slow/conventional, flash/ultra-fast, and fast), gasification, hydrothermal carbonization as shown in Fig. 1 [20].

The two types of reactors, that is, horizontal and vertical reactors are generally used in pyrolysis as shown in Fig. 2 [21]. The reactor design plays a crucial role in operation and loading of feedstock.

In the traditional method of producing charcoal, slow pyrolysis is used [22]. It comprises the heating of feedstock material without oxygen at a slow heating rate, that is, 10°C/min and long residence time (5–30 min) between 400°C–500°C [23]. Slow pyrolysis’s key products are bio-oil (liquid tar), biochar (solid char), and gases (syngas). The residence time, heating rate, heating temp., and size of biomass particles affect the quality and yield of biochar [24]. Fast pyrolysis involves the disintegration of complex feedstock molecules into small molecules in lack of oxygen under intense heating conditions at a high rate of heating, that is, 100°C/s and less contact time (0.5–2 s) between 400°C–700°C. The major products of fast pyrolysis are bio-oil (thinner), biochar (solid char), and gases. Flash pyrolysis is done for dissociation of feedstocks in absence of oxygen at a high rate of heating, that is, >500°C/s and less residence time (<0.5 s) between 700°C–1,000°C. The major key products of fast pyrolysis are bio-oil and gases [25–30].

Gasification temperatures are higher in comparison to pyrolysis. Gasification converts carbon-rich products into gaseous fuel, that is, mixture of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and air nitrogen at a high temperature in presence of a moderating agent (steam) and gasifying agent (oxygen, air, oxygen-enriched air, etc.). The hydrogen yields from pyrolysis and steam gasification increase on rise in temperature. The hydrogen yields are higher in gasification as compared

to pyrolysis. The yield from steam gasification increases with an increase in water to sample ratio. In steam gasification, the steam combines with carbonaceous biomass followed by drying, pyrolysis, reduction, and combustion to produce syngas. Hydrothermal gasification converts wet biomass into synthesis gas by consuming water within biomass. Hydrothermal gasification uses hot and compressed water for feedstock gasification. The supercritical state water or sub-critical liquid water generally gasifies wet biomass type of feedstock. Since the main aim is to convert feedstock into syngas thus, the process is optimized and maximized for producing gas. The biochar yields are very low from the gasification process but high in calorific value that is the most suitable foundation for activated carbon manufacture [31–37].

Carbonization manifests pyrolysis methods closely related to conventional charcoal manufacturing. It generates biochar containing a very high carbon content. Charcoal has been used as a substitute for fossil-derived coke in some projects of Brazil under the clean development mechanism. HTC (hydrothermal carbonization) is generally considered as an induced coalification method in which the raw biomass material is converted into a coal-like product, that is, hydrochar rich in carbon content and having high calorific value. It is also said to be wet pyrolysis or wet torrefaction which can be employed for wet agricultural residues, municipal solid waste comprising organic matter, algae and aquaculture residues, and sewage sludge. Unlike conventional dry pyrolysis, HTC paves a way for treating substrates having high moisture content (75%–90%) in high-pressure compartments (10–50 bar) at temperature between 180°C–250°C for 0.5–8 h in absence of air without undergoing the drying process. Biomass is dehydrated, decarboxylated, and decarbonylated for converting it into a carbon-densified product, namely, hydrochar, which can be utilized for a range of applications [38]. As a final comment, pyrolysis is the optimal technique for increasing biochar yields since solid char obtained by gasification does not meet

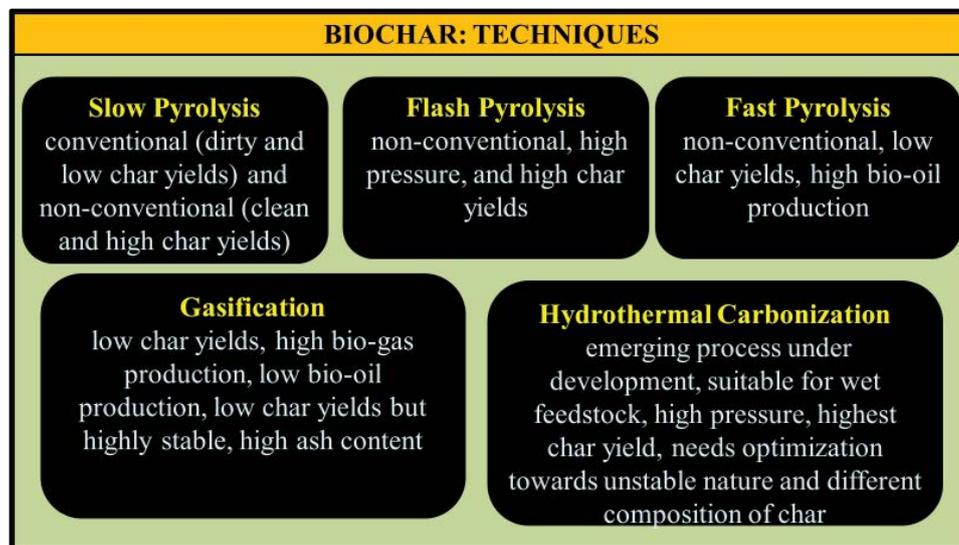


Fig. 1. Techniques used for biochar preparation [10].

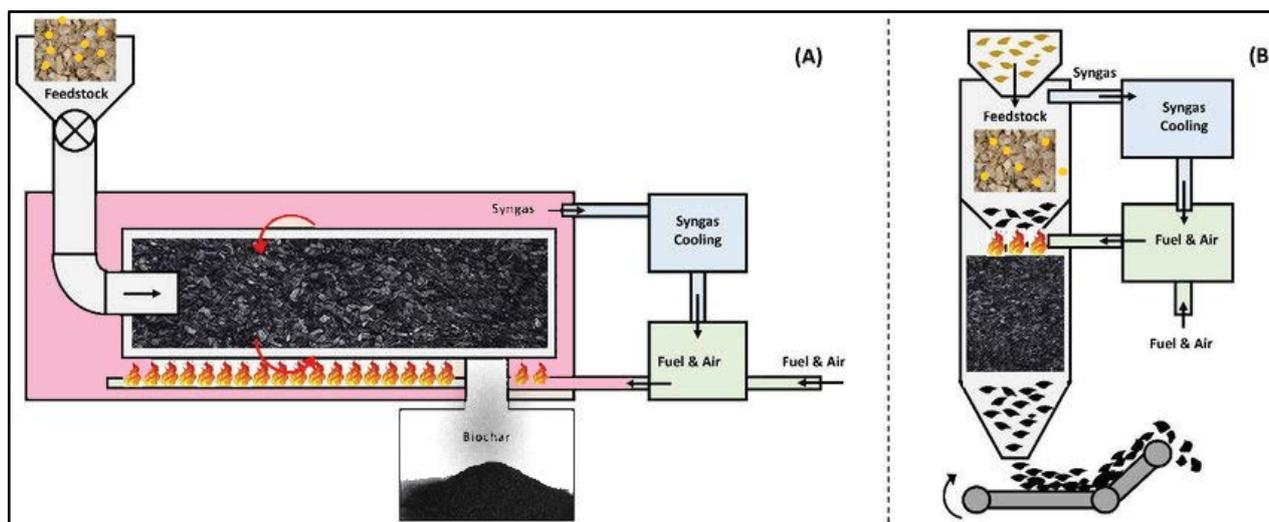


Fig. 2. Pyrolysis reactor (A) horizontal and (B) vertical [11].

the requirements for being classified as biochar. A range of feedstocks and thermochemical conversion methods used in biochar production are tabulated in Table 1.

A summary comprising pyrolysis methods, feedstocks used, typical products, applications and uses of these products is given in Fig. 3 [94].

The chemical and physical characteristics of biochar mainly depends upon selection of feedstock such as energy crops, crop residues, wood chips, manure, municipal waste, etc., and experimental conditions, that is, temp. and residence time. According to Kuwagaki (1990) as cited in Sohi et al. [94], the measurement of seven characteristics viz., volatile compound content, pH, ash content, bulk density, surface area, end functional groups, porosity, pore volume, acid-base behaviour, and water holding capacity is necessary for quality assessment of biochar. These characteristics have a dominant effect on biochar performance in environmental applications and decide its fate as a feasible option. The elemental composition of pyrolytic products may be significantly affected by processing temperature and residence time for a particular feedstock. pH of biochar also observed alteration in its value from 7.6 at 310°C to 9.7 at 850°C. As per study conducted by Day et al. (2005) cited in Sohi et al. [94], an increase was observed in surface area from 120 to 460 m<sup>2</sup> g<sup>-1</sup> upon raising temperature from 400°C to 900°C. It connotes that the biochar prepared at higher temperatures are analogous to activated carbon while biochar prepared at lower temperatures may be found suitable for controlling the release of fertilizer nutrients. However, the lower temperature biochar's surface is hydrophobic and thus, may limit the capacity to store water in soil [94]. The factors governing preparation of biochar with biochar characteristics are illustrated in Table 2 [94].

### 3. Mechanisms involved in adsorption of contaminants using biochar

In recent years, researchers have explored that biochar has the ability to adsorb pollutants and remove them from

soil and aquatic environments. Several pathways of sorption are employed during remediation of different types of contaminants in accordance with the properties of the pollutants as well as biochar. Fig. 4 demonstrates major processes involved in remediation of the heavy metal cations and organic pollutants [95].

#### 3.1. Inorganic contaminants

Metal ions in the aquatic systems are mostly accumulated from anthropogenic sources like casting, mining, effluents from the electronic manufacturing industry, etc. A biochar-based method to remove heavy metals from wastewater has been proposed by various researchers. Lu et al. [96,97] studied that sludge-derived biochar had the ability to bind lead. They found that a small quantity of Mg<sup>2+</sup> and Ca<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> had been liberated from biochar, which they believed was the consequence of metal exchanges with Pb<sup>2+</sup> in the biochar material. Zhang et al. [98] investigated the mechanisms of sorption of cadmium on the biochar surface. Nearly equal quantities of total sorbed Cd on biochar and discharged cations from the biochar (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) suggested that the cation-exchange mechanism was the most significant factor in cadmium sorption and removal [98]. It is widely proven that biochar may remove a variety of heavy metals and other inorganic ions [99–101], for example, anionic pollutants such as F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> [102,103], and arsenic [104,105]. Biochar's selectivity and molecular sieving capabilities are vital for heavy metal removal, and hence its pore shape, porosity, and cation exchange capacity are all important aspects to consider [106,107]. It is also important to consider the radius of hydrated ion of a metal ion in relation to the pore size [99], the species having smaller hydrated ionic radii will be preferentially adsorbed in comparison to those having larger ionic radii [108].

The selectivity of metal adsorption by sesame straw-derived biochar in a multi-component solution was observed as Pb<sup>2+</sup> > Zn<sup>2+</sup> > Cd<sup>2+</sup> in an experiment. Pb<sup>2+</sup> was the

Table 1  
Feedstocks and thermochemical processes involved in biochar production

S. No.	Feedstock	Method	Reference
1.	Soybean stover	Slow pyrolysis	[39]
	Peanut shell		
2.	Pinewood	Slow pyrolysis	[40,41]
	Wood bark		
3.	Paper mill sludge	Slow pyrolysis	[42]
4.	Herb residue	Slow pyrolysis	[43]
5.	Rice husk	Slow pyrolysis	[44]
6.	Dairy manure	Slow pyrolysis	[45]
7.	Rice straw	Slow pyrolysis	[46]
	Wheat straw		
8.	Pine wood	Fast pyrolysis	[47,48]
9.	Pine sawdust	Fast pyrolysis	[49]
10.	Sawdust	Fast pyrolysis	[50–52]
11.	Grass	Fast pyrolysis	[53–55]
12.	Rice husk	Fast pyrolysis	[56–59]
13.	Straw pellet	Microwave	[60]
	Willow chips		
14.	Corn stover	Microwave	[61]
	Pine wood		
15.	Switchgrass sludge	Microwave	[62]
16.	Peanut shell	Microwave	[63–67]
	Groundnut shell waste		
17.	Bamboo	Pyrolysis	[68,69]
18.	Castor plant	Pyrolysis	[70]
19.	Bagasse/sugarcane	Slow pyrolysis, vacuum pyrolysis, microwave-assisted carbonization	[71–74]
20.	Tomato plant residue	Pyrolysis	[75]
21.	Corn cob	Pyrolysis	[76,77]
22.	Wasted food	Pyrolysis/gasification	[78,79]
23.	Cow dung	Pyrolysis/fast pyrolysis	[80,81]
24.	Poultry manure	Slow/fast pyrolysis	[82,83]
25.	Sewage sludge	Slow pyrolysis, microwave pyrolysis	[84,85]
26.	Rice straw	Slow pyrolysis with carbonization at low temperature	[86,87]
	Cotton hay		
27.	Pine needle	Pyrolysis	[88]
28.	Shrimp hull	Pyrolysis	[89,90]
29.	Oak wood	Fast pyrolysis	[91,92]
	Oak bark		
30.	Orange peel	Pyrolysis	[93]

most selective metal adsorption on straw of sesame biochar followed by  $Zn^{2+}$  and  $Cd^{2+}$  in a multi-metal solution [109]. Biochar's mineral components are also important for the removal process, as they serve for additional sorption sites and contribute to heavy metal sorption by the process of precipitation by working as a catalyst for precipitation [110,111].

### 3.2. Organic contaminants

The potential of biochar in removal of organic pollutants has also been evaluated and the most significant

mechanisms of organic pollutants sorption using biochar included pore-filling, hydrophobic effect, electrostatic attraction, and hydrogen bonding, depending on the physical and chemical characteristics of the contaminants and biochar [112,113]. Chen et al. [114] found that the pyrolysis temperature of biochar has an impact on surface area of biochar, which affects the absorption rate of naphthalene (NAP) in solutions. At higher temperatures, organic constituents within biomass were carbonized to a greater extent, resulting in biochar with a greater carbonization degree, a bigger surface area, and more developed micropores, all of

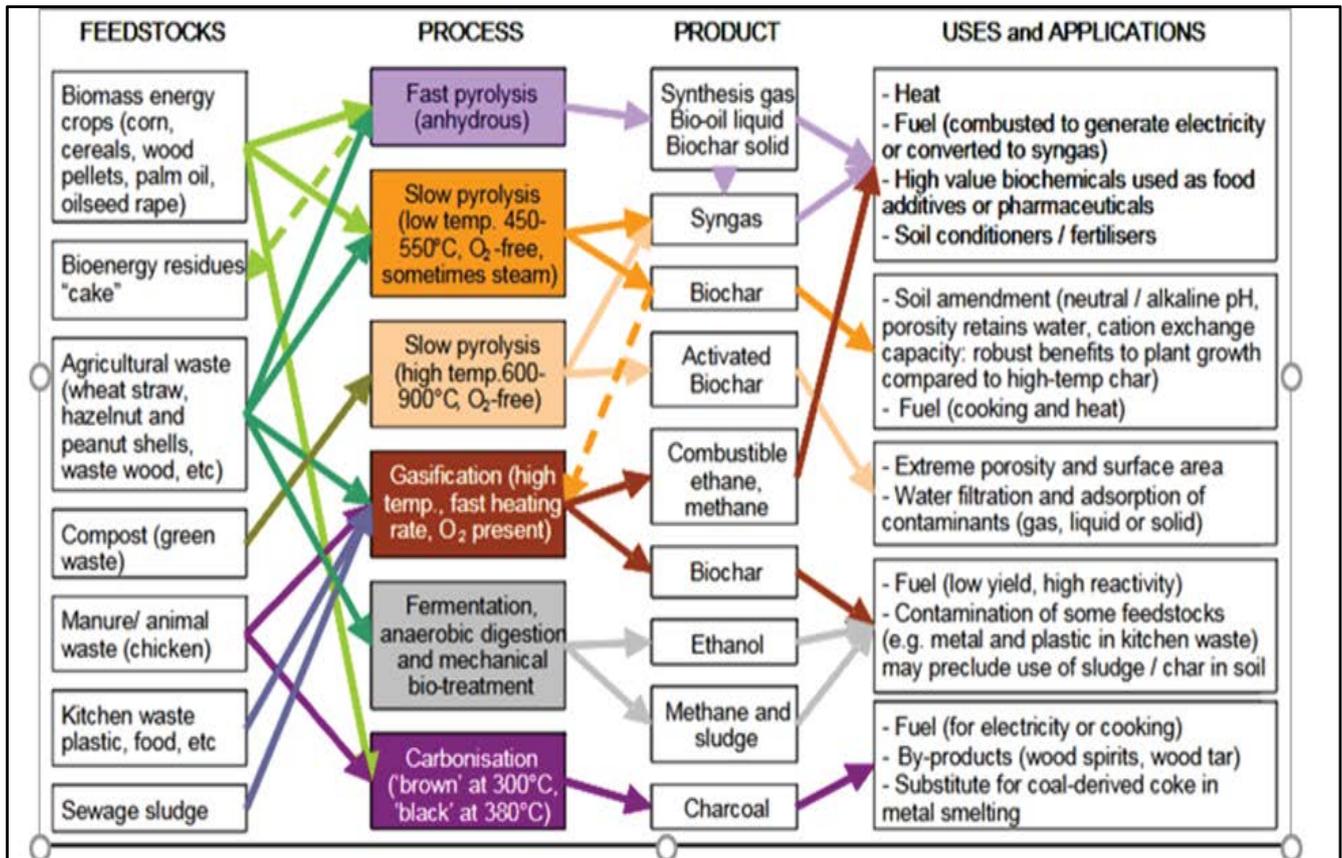


Fig. 3. Summary of pyrolysis methods, feedstocks used, typical products, applications and uses of these products [84].

which led to a higher sorption rate. Furthermore, biochar generated at temperature range (250°C–350°C) showed a very sluggish rate of sorption [115,116]. A group of researchers reported the effect of deashing treatment on biochar structure as well as its ability to bind phenanthrene (PHE) [117]. They also found that the hydrophobic impact of biochar was more apparent when it was produced at higher temperatures than when it was prepared at lower temperatures. Biochar generated at a high pyrolysis temperature, was found to have a larger carbonized fraction, which led to improved sorption of the comparatively hydrophobic trichloroethylene. Adsorption of methyl violet on biochar

occurred due to electrostatic attraction forces between dye and phenolic alcoholic groups [118–120].

Biochar has the ability to exchange its own cations (e.g., H<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup>) with heavy metals and, as a result, may establish a chemical bond with the heavy metals, allowing them to remain on its surface. There are two types of fractions that include exchangeable cations in biochar: H<sup>+</sup> ions derived from acidic functional groups like phenolic and carboxyl groups present in biochar, as well as alkaline minerals (e.g., K<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>O) produced during the manufacturing process (Fig. 5) [121]. However, the adsorption of heavy metals on biochar through cation exchange

Table 2  
Key factors governing biochar characteristics [94]

Factors			
Pyrolysis temperature		Type of feedstock	
Physical characteristics		Chemical characteristics	
At temperature (<400°C)	At temperature (600°C–900°C)	At temperature (<400°C)	At temperature (600°C–900°C)
Lower surface area	Higher surface area	Less carbon content	More carbon content
Suitable for controlling release of nutrients	Materials equivalent to activated carbon	Higher amount of N, S, K and P compounds	Lower extractable phenols, phosphorous, NH <sub>4</sub> <sup>+</sup> and NO <sub>3</sub> <sup>-</sup>
–	–	Lower pH and EC	Higher pH and EC

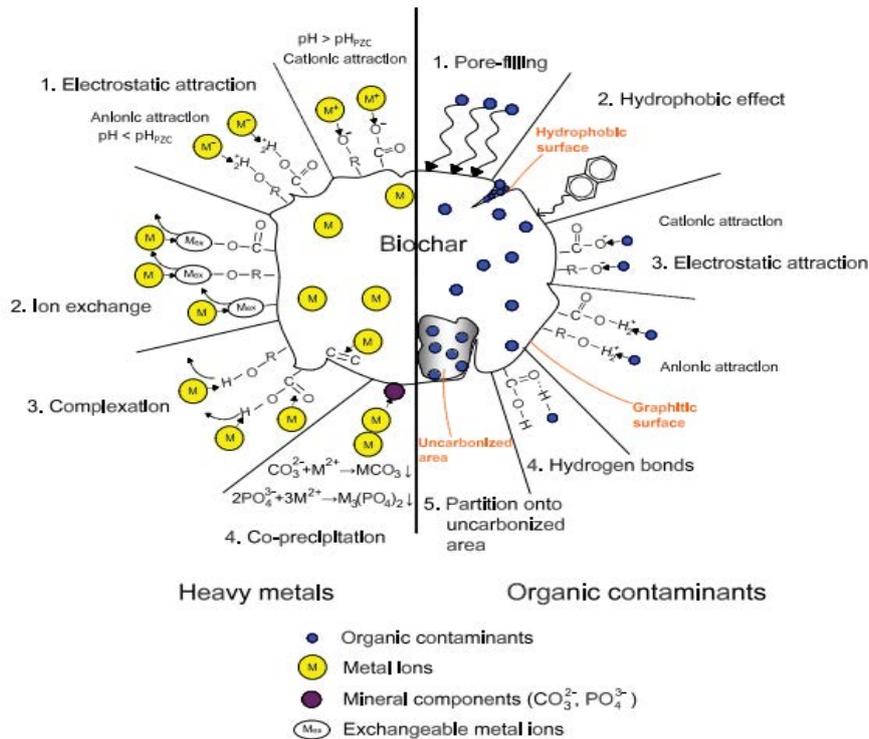


Fig. 4. Heavy metal and organic pollutant sorption processes on biochar [85].

may not be appropriate for the long-term immobilization of heavy metals in polluted soils.

#### 4. Biochar modification

Biochar is very effective in the remediation of a range of pollutants from aqueous solutions. The removal capacities of unmodified biochars were generally observed less than those of modified biochars [122]. Some studies suggested that there is a connection among surface area, functionality, and sorption capacity of biochar [123,124]. Micropores and mesopores in higher numbers provide a bigger surface area and a greater number of sorption sites, increasing the possibilities for the pollutants from aqueous environments to be adsorbed on biochar adsorbent surface. The modification of biochar is usually done in three steps: (i) in order to enhance surface area and porosity of biochar; (ii) to improve surface characteristics of biochar; and (iii) to integrate additional elements in the matrix of biochar to develop useful composites [125].

##### 4.1. Increase in surface area and porosity

A higher surface area of biochar provides more sorption sites, which increases the sorption capacity. A plethora of biochar modifying strategies have been developed in order to obtain this advantageous feature.

Physical modification of biochar typically involves the use of gases such as CO<sub>2</sub> [126] and steam [127]. Steam activation eliminates the incomplete combustion components and increases porosity, resulting in an increase in

the number of sorption sites. Poultry manure at 700°C was pyrolyzed by Lima and Marshall [128] to form biochar, which was then steamed at 800°C with different water flow rates and time durations. A study was conducted to determine the influence of treatment of CO<sub>2</sub> on biochars made from corn hulls, maize stover, and oak wood waste [129]. All prepared biochars displayed increased sorptive capacity due to their increased surface area and micropore volumes but it has no significant effect on the material’s functional groups [130]. Acidic or alkaline treatment of pine tree sawdust with diluted H<sub>3</sub>PO<sub>4</sub> prior pyrolyzing also increased surface area of biochar [131]. Biochar-KOH mixture pyrolyzed at 350°C–550°C, opened few closed pores and increased the range of smaller pores, thus enhancing the surface area and Cd sorption from the water through surface complexation [124]. One study reported that the increase in surface area via KOH modification, enhanced the sorption of oxyanions also [132]. Biochar treated with KOH improved its As(V) sorption capacity from 24–31 mg g<sup>-1</sup>, due to the increased surface area of the biochar [133]. The combination of solid NaOH with feedstock/biochar increased both the surface area as well as iodine sorption capacity [134]. Apart from physical, alkaline, and acidic modifications, outlined previously, few biochar composites have a higher surface area due to embedding specific components into the biochar matrix [125]. Chen et al. [135] noticed an increment in surface area and perviousness when montmorillonite was added to bamboo powder during pyrolysis, which led to improved NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> sorption capabilities of biochar adsorbent. The layered

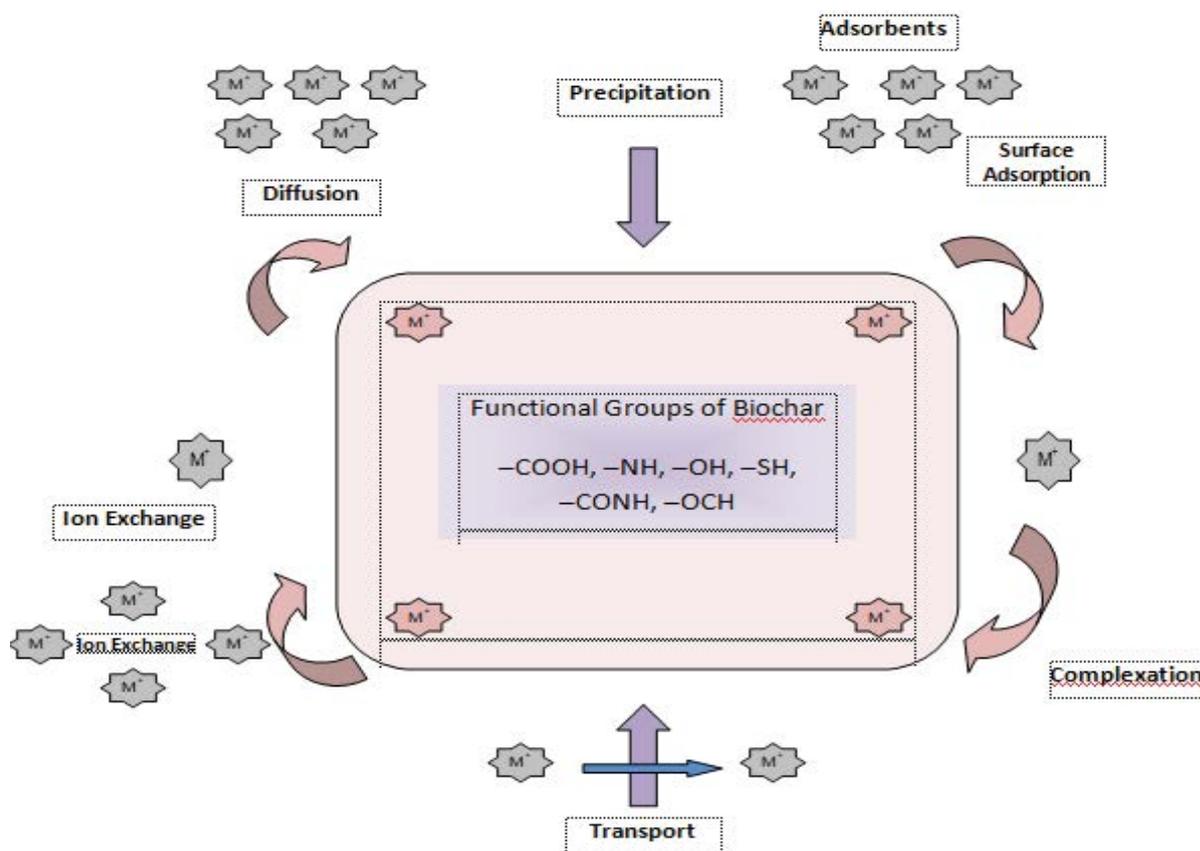


Fig. 5. Mechanism of biochar/biosorbent to remediate contaminants [111].

surface of clay modified biochar was investigated using SEM technique, and the morphology of the surface was found to be similar to that of regular clay structures [136].

#### 4.2. Enhancement in positive charge on biochar surface

Biochar is having negatively charged surface and high pH value, which makes it a suitable sorbent for metal cations and an ineffective sorbent for oxygen containing anions like  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{AsO}_4^{3-}$ . So, biochar is frequently utilized as a framework for embedding metal oxides with positive charges. Hydrogen oxyanions with a negative charge can be removed from water using composites [125].

In order to ensure that metals are dispersed equally over the biochar surface, several procedures for creating biochar-metal oxide composites have been designed. In this process, biochar plays a significant role because it acts as a pervious carbon support, allowing the metal oxides to get precipitated and enhance both their surface charge and their surface area. When it comes to metal attachment, the most often used methods in which biochar and raw materials are immersed in solutions of metal chlorides or nitrates ( $\text{FeCl}_3$ ,  $\text{MgCl}_2$ , and  $\text{Fe}(\text{NO}_3)_3$ ) [125]. After being heated at  $50^\circ\text{C}$ – $300^\circ\text{C}$  in the presence of air, the nitrates or chlorides are driven out in the form of  $\text{Cl}_2$ ,  $\text{NO}_2$ , and  $\text{NO}_3$  gases, respectively, while the metal cations get converted into respective metal oxides [137]. Zhang et al. [138] employed

a variety of biomass wastes to prepare biochar-MgO composites, which they achieved by mixing feedstock materials with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solution followed by pyrolyzing the resulting mixes. The SEM imaging revealed that MgO particles on the biochar surface were equally spread, as demonstrated by experimental results. The presence of a positively charged magnesium oxide (MgO) layer on top of the biochar improved the sorption ability for phosphorus and nitrogen from sewage to 835 and 95  $\text{mg g}^{-1}$ , respectively. They were able to prepare biochar/MgAl-layered double hydroxides after mixing cotton stalks with  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solutions, and then drying the resulting product [138].

Magnesium, aluminium, and manganese oxides are embedded into the surface of biochar to form composites that are used in the construction of bridges and other structures. These composites have the potential to improve the sorption of metal ions as well as oxyanions in aqueous solutions [139]. An experiment was conducted to optimize the impacts of magnesium modification on sorption ability of metal cations in aqueous solutions. As part of this investigation, they investigated the lead (Pb) sorption on biochar formed from cypress sawdust and treated with  $\text{MgCl}_2$ . It was found that the modified biochar showed higher sorption capacity than the raw material significantly, by around 7.4 fold. Generally, the sorption of anions containing oxygen is caused by electrostatic attraction in biochar matrix on biochar-metal oxide composites, whereas the sorption

of metal ions is attributed either to co-precipitation in lattice of metal oxides or to chemical sorption on functional groups having  $O_2$  on biochar matrix [140]. Rajapaksha et al. [141] discovered that the majority of metal oxide modifications reduced surface area due to pore clogging with the precipitates of metal oxides. The modifications ultimately increased sorption ability due to formulation of pH-dependent bonds with positively charged functional groups on biochar surfaces [141].

#### 4.3. Increase in oxygen-containing functional groups on biochar surface

There is a range of functional groups on biochar surface, including carboxyl, hydroxyl, and phenolic groups, as well as additional functional groups that are capable of readily reacting with contaminants chemically and removing them from aqueous medium. Acidic treatment not only increases the amounts of oxygen-containing functional groups on biochar surface but also improves the potential of biochar surface to chemically interact with positively charged contaminants by selective sorption [142,143].  $HNO_3$  was used to modify cactus fibre biochar in order to enhance the number of carboxylic groups on the surface available as sorption sites for the metal cations ( $Pb^{2+}$  and  $Cu^{2+}$ ). According to this result, the sorption capacity observed at pH 6.5 was an order of magnitude higher than the sorption capacity seen at pH 3, suggesting that the sorption capacity is chemically induced on oxygen-containing functional groups and pH-dependent. In rice straw biochar, the O/C ratio was found to be more in the final product after being treated with a mixture of  $H_2SO_4$  and  $HNO_3$ , indicating that the structure of biochar was enriched with oxygen-containing functional groups [142]. Due to high costs of biochar modification using strong acids on a larger scale application, as well as the environmental concerns associated with the disposal of modification agents, scientists have been working towards the development of more affordable and environmentally friendly oxidants to modify biochar. Song et al. [144] pyrolyzed corn straw at 600°C and then added the biochar to a  $KMnO_4$  solution. XPS investigations of MnOx-biochar revealed that the increased oxygen concentration was concentrated primarily in Mn-OH and Mn-O structures, which accounted for increase in  $Cu^{2+}$  sorption ability of biochar (from 19.6 to 160.3  $mg\ g^{-1}$ ) [144]. An increase in number of oxygen-containing functional groups on the biochar surface has also been observed after treatment with  $H_2O_2$  [145]. Cation exchange occurred on the modified biochar surface as a consequence of increased number of oxygen-containing functional groups. The cation exchangeability of the modified biochar surface was nearly twice that of the unmodified one [146–148].

#### 4.4. Biochar magnetization

Magnetization of biochar opens up new possibilities. With magnetic biochar, the problem of biochar separation from aqueous solutions can be handled easily. Approximately 69.6% of all magnetic biochar production processes involve impregnation–pyrolysis and co-precipitation [149]. This method involves impregnating the

biochar suspension with a transition metal salt solution, then pyrolyzing the resultant product. Magnetic biochar (chemical co-precipitation of biochar with magnetite) was prepared by using  $Fe^{3+}/Fe^{2+}$  solution (1.4%–80.6%) in this manner [91] which showed greater sorption capacity for  $Pb^{2+}$  and  $Cd^{2+}$  from solutions. Microwave heating is used extensively in magnetic biochar production, in addition to pyrolysis. Biochars were treated with HCl following the pyrolysis at temperature of 500°C and microwave heating in inert environment. The magnetic biochar has more carboxyl active functional groups at the surface, making it more negatively charged, improving heavy metal ion sorption rate and capacity. Aside from surface functional groups, magnetic components such as  $Fe_2O_3$ ,  $Fe_3O_4$ , and FeO also help in the improvement of sorption ability.  $Fe_3O_4$  acts as an active chemical sorption or reduction site for  $Cr^{6+}$  [150]. The process of pyrolysis transformed the magnetite ( $Fe_3O_4$ ) in magnetic biochar into iron oxide (FeO). The removal effect can be enhanced by introducing metals like Zn, Cu, and Mn, etc. The magnetic properties of magnetic biochar are primarily influenced by the type of magnetic species and the dosage of transition metal salt [151,152].

#### 4.5. Biofilm formation on biochar surface

Biochar's high surface area, porosity, and inertness make it an ideal scaffold for biofilm colonization and growth. The bacteria adhere to the biochar surface by secreting different chemical substances, and create an extracellular biofilm, which increases their survivability compared to the traditional separate microbial treatment [153]. Biochar's surface functional groups and pervious structure help in binding of pollutants in biotic systems, while microbes help break down refractory chemicals through metabolism [154]. It is becoming more common to utilize biotic biochar in both water and wastewater treatment as an outcome of synergistic elimination impact it provides.

Biochar with biofilm promotes the biodegradation of organic pollutants [125]. A researchers' group investigated the usage of biochar-biofilm filters to remove pollutants from drugs wastewater. These biofilters outperformed sand filters in the treatment of carbamazepine by over 98% over a 22-week period [155]. Overall, modification strategies should be chosen based on the target contaminant's properties and removal process. These procedures increase the porosity of biochar, making it an excellent sorbent for pollutants whose sorption requires pore-filling, such as heavy metals. Acids and oxidants improve the cation exchangeability of oxygen-containing functional groups on biochar surface, allowing for ion exchange-dependent sorption of the heavy metal cations and  $NH_4^+$  ions on biochar surface. Biochar with alkaline modification has strong aromaticity, enhancing EDA interaction and sorption for dyes and antibiotics. It also reduces the O/C ratio, enhancing the hydrophobicity of biochar [156]. The sorption of negatively charged oxygenated anions like  $PO_4^{3-}$ ,  $NO_3^-$ , and  $AsO_4^{3-}$  is made possible by metal oxides with positive charges buried in biochar. Additionally, metal oxides enhance the number of active functional sites in biochar, significantly associated with its catalytic action. Amino-rich compounds, in addition to assimilation of nitrogen, function as active sites [157]. Also, biochar

Table 3  
Biochar prepared from diverse feedstocks for removal of various pollutants from water and wastewater

Contaminant	Biomass feedstock	Procurement method	Highest removal ability	References
Heavy metals	As(III)	Jute stick	Dried, mixed in phosphoric acid, pyrolysis temp. 475°C under inert atmosphere with drying after washing	0.093 mg g <sup>-1</sup> [158]
	As(III)	Straw	Pyrolysis temp. 350°C, mixing in KOH, drying, further pyrolysis at 800°C, mixing with HCl, with drying after washing	2.6 mg g <sup>-1</sup> [159]
	As(III)	Jute stick	Drying, pyrolysis at 400°C, steam activation at 800°C, washing, drying	0.073 mg g <sup>-1</sup> [158]
	As(V)	Mung bean husk	Washed, dried, pyrolyzed at 550°C, activated using steam at 650°C	0.36 mg g <sup>-1</sup> [160]
	As(V)	Pine wood shavings	Milling, pyrolysis at 250°C, 550°C under less O <sub>2</sub> environment followed by steam activation at 800°C	0.001 mg g <sup>-1</sup> [161]
	As(V)	Coal blending	Coal pulverization, forming briquettes, grinding, pyrolyzed at 630°C under inert atmosphere, steam activation at 950°C	0.68–0.71 mg g <sup>-1</sup> [162]
	As(III)	Coal blending	Coal pulverization, forming briquettes, grinding, pyrolyzed at 630°C under inert atmosphere, steam activation at 950°C	0.68–0.71 mg g <sup>-1</sup> [162]
	Cu(II)	Bamboo, peanut hull, hickory wood, bagasse	Pyrolyzed at 600°C followed by the chitosan adaptation	14.3 mg g <sup>-1</sup> for Pb <sup>2+</sup> [163]
	Cd(II)	Bamboo, peanut hull, hickory wood, bagasse	Pyrolyzed at 600°C followed by the chitosan adaptation	14.3 mg g <sup>-1</sup> for Pb <sup>2+</sup> [163]
	Pb(II)	Bamboo, peanut hull, hickory wood, bagasse	Pyrolyzed at 600°C followed by the chitosan adaptation	14.3 mg g <sup>-1</sup> for Pb <sup>2+</sup> [163]
Dyes	Cr <sup>6+</sup>	Waste glue residue	ZnCl <sub>2</sub> modification	325.5 mg g <sup>-1</sup> [164]
	Hg(II)	Malt spent rootlet	Pyrolysis at 850°C for 1 h	103 mg g <sup>-1</sup> [165]
	Hg(II)	Malt spent rootlets	Pyrolysis temp. ranged between 300°C–900°C	130 mg g <sup>-1</sup> for MSR750 [166]
	Ni(II)	Lotus stalks	Pyrolysis at 300°C, 350°C, and 400°C in the presence of zinc borate as flame retardant	61.7 mg g <sup>-1</sup> for 0.5 g ZB [167]
	Acid red	Rice husk, coir pith	After placing the biomass in a muffle furnace at 700°C for 5 h to prepare charcoal, it was added to a Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O solution and agitated for 30 min in a sonicator. Washed using distilled water, dried in oven at 105°C for 24 h, and calcined at 500°C for 4 h in a muffle furnace	97.6% [168]
	Hydroquinone	Sewage sludge	12 min microwave-assisted pyrolysis at 500°C, 980 W for 1 h	1,218.3 to 1,202.1 mg g <sup>-1</sup> [169]
	Lanasyne	Bamboo cane	H <sub>3</sub> PO <sub>4</sub> modification afterward pyrolysis at 400°C, 500°C, and 600°C	2.6 and 103 mg g <sup>-1</sup> [170]
	Orange and Lanasyne Gray	Bamboo cane	H <sub>3</sub> PO <sub>4</sub> modification afterward pyrolysis at 400°C, 500°C, and 600°C	2.6 and 103 mg g <sup>-1</sup> [170]
	Methyl orange	Biochar	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O disseminated in ethane-1,2-diol; KBr/KCl was dissolved in distilled water; biochar in distilled water was merged in the Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O solution; mixed solution was stirred for 12 h and dried at 60°C	80% [171]
	Orange G	Sugarcane residues	Sugarcane residue was impregnated with FeSO <sub>4</sub> ·7H <sub>2</sub> O solution and agitated for 24 h at 60°C; put in covered crucibles and pyrolyzed in muffle with N <sub>2</sub> atmosphere for 4 h at 600°C	99.7% [172]
Reactive Red 141	Orange II	Corn biomass	Pyrolyzed at 400°C for 3 h in a N <sub>2</sub> atmosphere (80 mL min <sup>-1</sup> ); ball milled for 1 h; heated in tube furnace at 800°C for 2 h in inert atmosphere	Nearly 100% [173]
	Reactive Red 141	Pecan nutshells	Pyrolysis at 800°C for 1 h	130 mg g <sup>-1</sup> [174]

(Continued)

Table 3 Continued

Contaminant	Biomass feedstock	Procurement method	Highest removal ability	References
1,3-Dichloro- propene	Rice husk	Rice husks were loaded in porcelain crucibles and pyrolyzed for 4 h in a muffle furnace. Pyrolyzed at temperatures ranging from 300°C to 400°C, 500°C to 600°C, and 700°C	~90%	[175]
Dibromochloro- propane	Almond shells	Pyrolysis at 650°C for 1 h followed by steam activation at 800°C	102 mg g <sup>-1</sup>	[176]
Diethyl phthalate	Pine needles, wheat/ maize straw	Feedstocks were put in a pot of ceramic; a muffle furnace was used to reduce the amount of oxygen in the atmosphere; and the feedstocks were pyrolyzed for 6 h at 300°C, 400°C, and 500°C, respectively.	Nearly 100%	[177]
Phenols, PAHs and other organics	Orange peel	Pyrolysis for 6 h at 150°C–700°C	Naphthalene 80.8 mg g <sup>-1</sup> , 1-naphthol 186.5 mg g <sup>-1</sup> 23.5 mg g <sup>-1</sup> 70%–100%	[178] [179] [180]
Phenanthrene	Malt spent rootlets	Pyrolyzed at 800°C for 1 h		
Polychlori- nated biphe- nyls	Pine needles	Placed in ceramic pot and compacted without headspace, then covered for pyrolysis in a muffle furnace at temperatures of 300°C, 400°C, 500°C, 600°C, and 700°C under O <sub>2</sub> -limited conditions for 1, 2, 4, 6, 8, and 12 h		
Thiacloprid	Maize straw and pig manure	Pyrolysis at 300°C, 500°C, and 700°C for 4 h	Approx. 8.1 mg g <sup>-1</sup>	[181]
Trichloroeth- ylene	Rice hull	Pyrolyzed in muffle furnace for 6 h at 350°C in an oxygen-deficient environ- ment; biochar dissolved in FeSO <sub>4</sub> ·7H <sub>2</sub> O solution with a pH of 5.0; N <sub>2</sub> purged for 1 h; dropwise addition of NaBH <sub>4</sub>	66.8%–99.4%	[182]
Atrazine and simazine	Maple, elm oak wood chips and barks	Pyrolysis at 450°C for 1 h	243–1,066 mg g <sup>-1</sup> for simazine 51–1,158 mg g <sup>-1</sup> for atrazine	[121]
Pesticides	Broiler litter	Pyrolysis at 650°C for 1 h followed by steam activation at 800°C	About 83.3 mg g <sup>-1</sup> for BL700 with steam activation	[183]

(Continued)

Table 3 Continued

Contaminant	Biomass feedstock	Procurement method	Highest removal ability	References
Antibiotics	Rice straw	Biochar was pyrolyzed at 450°C for 12 h; 10 mmol Co(NO <sub>3</sub> ) <sub>2</sub> dissolved in 9 mL H <sub>2</sub> O and 36 mL DMF; 5 mL ammonia was added; the mixture was treated at 180°C for 10 h in a teflon-lined stainless steel autoclave; the mixture was calcined at 350°C for 2 h	~90%	[184]
Fluoroquinolone antibiotic (Ofloxacin)	Potato stems and leaves	Magnetization and humic acid-coating	8.4 mg g <sup>-1</sup> for ENR, 10.0 mg g <sup>-1</sup> for NOR, 11.5 mg g <sup>-1</sup> for CIP	[185]
Sulfamethoxazole	Spent malt rootlets	Placed in custom-made quartz vessels and heated to 900°C	Nearly 100%	[186]
Tetracycline	Saw dust	FeCl <sub>3</sub> ·6H <sub>2</sub> O and ZnCl <sub>2</sub> solution doped at 100°C then calcined at 600°C for 2 h	Above 89% after 3 cycles	[185]
Indicator organisms and pathogens	Wood chips	Pyrolysis with steam activation	3.62 ± 0.27 log units of bacteria removed	[187]
Fecal indicator bacteria	Rice husk	Pyrolysis	3.9 log units of bacteria removed	[188]
NH <sub>4</sub> <sup>+</sup>	Bamboo	Pyrolysis at 370°C	6.4 mM g <sup>-1</sup>	[189]
NO <sub>3</sub> <sup>-</sup>	Bamboo	Pyrolysis (460°C) in clay suspension	5–9 mg g <sup>-1</sup>	[190]
PO <sub>4</sub> <sup>3-</sup>	Sewage sludge and walnut shell	Two feedstocks pyrolyzed at 600°C for 3 h	303.5 mg g <sup>-1</sup> of biochar of sewage sludge	[191]
<i>Saccharomyces cerevisiae</i>	Hardwood	Pyrolysis	>1 log <sub>10</sub> CFU of bacteria removed	[192]
Inorganic ions	Spruce wood	Pyrolysis at 650°C for 1 h after being impregnated with AlCl <sub>3</sub> /FeCl <sub>3</sub> solution	13.6 mg g <sup>-1</sup>	[193]
	Wood and rice husks	Magnetic modification and co-precipitation of Fe <sup>2+</sup> /Fe <sup>3+</sup> ions	25–28 mg g <sup>-1</sup>	[194]

combined with biofilm can be used to degrade some harmful organic pollutants to lessen their toxicity.

## 5. Biochar in water treatment

To accomplish “Sustainable Development Goal, that is, to ensure accessibility and sustainable management of water and sanitation for all by 2030”, the conversion of current research approaches into frugal and practical solutions is a mandate response since millions of people have insufficient access to safe and clean drinking water.

### 5.1. Biochar adsorbents

Biochar has witnessed good sorption capacity for removal of contaminants from aqueous medium. The treatment of water with biochar observed comparable merits to current low-cost processes since it has the potential to remove all the physical, chemical, and biological impurities. It does not generate carcinogenic by-products and hence, maintains the organoleptic attributes of water. Linear material flows into close looped material cycles via integrating biochar in water treatment and sanitation systems' transformation. According to the published studies, biochar may be used directly for water as well as wastewater treatment as an adsorbent for pollutants removal, or it has the potential to be used in built wetlands and to improve the water holding capacity of soil. On the subject of biochar's ability to remove various contaminants from water and wastewater, Table 3 is a collection of the sources cited in this section.

#### 5.1.1. Heavy metal cations

Rapid industrialization is the most significant route of water pollution. The volumes and varieties of industrial wastewater are constantly increasing. Biochar is emerging as a new strategy for removing a variety of toxins from industrial effluent, including heavy metals. The removal of heavy metal cations such as  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{6+}$  and  $\text{Ni}^{2+}$  has garnered a great deal of interest due to the negative consequences that they should have if discharged into the nature. Batch sorption tests showed that biochar treated with chitosan had a high level of elimination efficiency for the heavy metals as  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  from solutions [163].

$\text{ZnCl}_2$  modified glue residue biochar was developed and employed for the sorption of  $\text{Cr}^{6+}$ . The highest sorptive capacity was  $325.5 \text{ mg g}^{-1}$  [164]. A researchers' group remediated  $\text{Hg}(\text{II})$  ions by using biochar made from malt spent rootlets (MSR) from aqueous medium. After 24-h time of contact with  $1 \text{ g L}^{-1}$  biochar, the removal effectiveness reached up to 100%, with a utmost sorption capacity of  $103 \text{ mg g}^{-1}$  for  $\text{Hg}(\text{II})$  ions [165,166]. Zinc borate (ZB) was used as a flame retardant in the preparation of lotus stalks (LS) biochar for the treatment of nickel. Comparing the sorption of  $\text{Ni}(\text{II})$  on LS biochar with and without ZB, LS biochar sorptive capacity for  $\text{Ni}(\text{II})$  was increased from 3 to 10 times [167].

#### 5.1.2. Organic contaminants

The use of pesticides brings economic benefits in agro-economic production through controlling pests. However, an

extreme usage of pesticides results in lethal effects in non-target animals, as well as damage to ecological equilibrium and human health. When it comes to pesticide contamination remediation, biochar is used as a specialized rehabilitation technique [195]. Biochar was generated by pyrolyzing swine dung at  $600^\circ\text{C}$  in order to use it as a sorbent for the insecticide imidacloprid [107]. The development of maize straw biochar at temperatures ranging from  $300^\circ\text{C}$  to  $500^\circ\text{C}$  was carried out in order to examine thiacloprid sorption. According to the findings, sorption was caused due to pore filling and hydrophobic interactions [181]. Valili et al. [179] pyrolyzed MSR biochar at  $800^\circ\text{C}$ , which showed a considerable increase in phenanthrene (PHE) sorption capacity, which was 2 orders of magnitude more than that of raw material [179]. Biochar produced from sewage sludge via pyrolysis at  $500^\circ\text{C}$ , followed by the treatment with HCl, was tested for adsorption of hydroquinone and  $1,218.3 \text{ mg g}^{-1}$  sorption capacity was observed by Reis et al. [169]. The sorption was significantly influenced by EDA interactions.

Biochar sorption is the most widely used approach for the treatment of dye-based wastewater. Two dyes, that is, Lanasyn Orange and Lanasyn Gray, often used in dyeing of carpets, were mostly sorbed on nanoporous biochar generated from bamboo [170]. The primary sorption mechanism was pore filling, and the sorptive capacities of the two dyes were  $2.6$  and  $103 \text{ mg g}^{-1}$ . The higher surface area ( $2,130 \text{ m}^2 \text{ g}^{-1}$ ) of biochar, as well as its huge pore volume ( $2.7 \text{ cm}^3 \text{ g}^{-1}$ ), have been linked to the higher sorption capacity of this biochar material [170]. Biochar made from pecan nutshells was used to remove Reactive Red 141 (dye) from aqueous medium. In addition to being low-cost and environmentally friendly, biochar has the potential to serve as an alternative for other traditional sorbents [174]. Qiu et al. [196] developed biochar for the removal of reactive brilliant blue and Rhodamine B from aqueous medium. The electrostatic interaction between Rhodamine B and biochar, as well as Rhodamine B protonation, cause the biochar to have a clear adsorption effect on Rhodamine B. Fan et al. [197] prepared biochar from municipal sludge to remove methylene blue (MB), which was confirmed by a pseudo-second-order model (upto 100% adsorption). MB removal efficiency was observed 60% still after three cycles using biochar.

#### 5.1.3. Inorganic ions

The sorption of  $\text{NH}_4^+$  by hydrous bamboo biochar has been investigated with a sorptive capacity of  $6.4 \text{ mM g}^{-1}$ , which was found to be higher than expected [189,198]. Hu et al. [199] studied  $\text{NH}_4^+$  sorption and observed that pH had an effect on  $\text{NH}_4^+$  sorptive capacity through modifying the surface charge of biochar (negative when  $\text{pH} > \text{pH}_{\text{pZC}}$ ) [199]. Ion exchange with anionic functional groups such as  $-\text{OH}$  and  $-\text{COOH}$  was found to be a significant contributing factor to  $\text{NH}_4^+$  sorption. The bamboo-based biochar/montmorillonite composite was prepared and tested for nitrate removal and finally concluded that this biochar can be effectively employed in the treatment of industrial effluents comprising anionic pollutants like nitrates ( $\text{NO}_3^-$ ) [190].

A biochar produced from walnut shells and sewage sludge was found to be effective at absorbing  $\text{PO}_4^{3-}$ . Out of all the biochars tested, the sewage sludge-based biochar

having the highest sorptive capacity ( $303.5 \text{ mg g}^{-1}$ ) was the most effective choice for  $\text{PO}_4^{3-}$  sorption. They compared the removal of metal after magnetic alteration to biochars before and after the removal of  $\text{PO}_4^{3-}$  ions from wastewater. Magnetic biochar showed twice the sorption ability ( $25\text{--}28 \text{ mg g}^{-1}$ ) of unmodified biochar ( $12\text{--}15 \text{ mg g}^{-1}$ ). The sorption of the original biochar was mostly dependent on electrostatic attraction, whereas the sorption of the magnetic biochar was primarily dependent on surface precipitation and complexation [191].

With its strong electronegative character and small ion size,  $\text{F}^-$  possesses a strong attraction towards metal ions such as  $\text{Al}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Fe}^{3+}$  [200], which makes it a good candidate for electrostatic attraction. The highest  $\text{F}^-$  removal capacity of Al-modified spruce wood biochar was found to be  $13.6 \text{ mg g}^{-1}$  in one study [193].

### 5.2. Biochar composites

To enhance arsenic (As) immobilization, Fan et al. [201] used one-pot pyrolysis of sawdust and  $\text{Fe}_2\text{O}_3$  mixture to embed nZVI on BC. The mobility of As in soil reduced as compared to the pristine BC treatment. This may have happened due to As adsorption and co-precipitation on the surface of BC caused by nZVI corrosion formation ( $\text{FeOOH}$ ). Furthermore, following adsorption by nZVI-BC, the majority of As(V) was reduced to As(III) [201]. The highest adsorption capacity improved from  $75.8$  to  $127 \text{ mg g}^{-1}$  when Zhang et al. [202] employed chitosan-modified magnetic BC to improve  $\text{Cr}^{6+}$  removal from aqueous solution. Fe–O stretching was detected on magnetic BC (MBC) and chitosan-modified MBC (CMBC) as compared with regular BC, and when combined with XRD spectra, it was observed that  $\text{Fe}_3\text{O}_4$  was successfully loaded on BC. When FTIR spectra were analyzed and compared before and after the reaction, the C=O, C–O, Fe(III)–O, and H–O all altered, indicating that they all took part in the reaction. At one end, the aforementioned group can aid in the reduction of  $\text{Cr}^{6+}$  by donating electrons while on the other hand, can form a complex with  $\text{Cr}^{6+}$  and the CMBC/MBC surface group. Furthermore, electron-donating can deliver electrons to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , and subsequently  $\text{Fe}^{2+}$  as a reductant reduced  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  indirectly

[202]. Gao et al. [203] prepared BC by co-pyrolyzing rape straw and  $\text{KH}_2\text{PO}_4$ , which demonstrated a high immobilization capability for heavy metals such as Cd, Pb, and Cu. This might be due to heavy metals directly complexing and precipitating with phosphate and  $-\text{OH}$  on BC surface, or by raising pH and available P of soil. Inorganic contaminants were removed at a maximum rate of  $31$  to  $904 \text{ mg g}^{-1}$  by BC-based composites. Biochar-based composites combine the benefits of BC with the benefits of other materials, resulting in a significant increase in removal efficiency [203]. Tan et al. [204] produced BC following modification with  $\text{Na}_2\text{S}$  and  $\text{KOH}$  for Hg(II) adsorption. The rates of adsorption rose by  $76.95\%$  and  $32.12\%$ , respectively. The rise in specific surface area from  $32.85 \text{ m}^2 \text{ g}^{-1}$  (pristine BC) to  $55.58 \text{ m}^2 \text{ g}^{-1}$  ( $\text{Na}_2\text{S@BC}$ ) or  $59.23 \text{ m}^2 \text{ g}^{-1}$  ( $\text{KOH@BC}$ ) may be attributed to the removal of coal tar accumulated in pores. Another effective technique to boost the Hg(II) removal rate is to use  $\text{Na}_2\text{S@BC}$  to form HgS precipitates with Hg(II) [204]. Li et al. [205] made  $\text{KMnO}_4$ -modified BC and used it to remove U(VI). Through coordination and Lewis acid–base interaction, the rise in oxygen containing functional groups and the creation of  $\text{MnO}_2$  nanoparticles produced by the modification of  $\text{KMnO}_4$  significantly improved the U(VI) adsorption capacity [205]. Wang et al. [206] impregnated the BC with  $3.65\%$  Mn to improve lead removal. At pH 5.0, the rate of lead removal rose from  $6.4\%$  to  $98.9\%$ . The rise in hydroxyl groups and the decrease in  $\text{pH}_{\text{PZC}}$  was attributed to this enhanced lead removal. At  $298 \text{ K}$ , the maximal adsorption capacity of modified BC was five times that of pristine BC, with a faster adsorption rate [206]. Fan et al. [207] pyrolyzed rice straw at various temperatures to see if BC could remove common antibiotics like tetracycline (TC). Due to its wide specific surface area, abundant aromatic structure, and rich graphite carbon, BC produced at a higher temperature might have a maximum adsorption capacity of  $50.72 \text{ mg g}^{-1}$  [207]. Liu et al. [208] modified biochar using chitosan and  $\text{FeS}_x$  for tetracycline removal, and the maximum capacity of tetracycline removal by biochar and modified biochar were  $51.78$  and  $193.01 \text{ mg g}^{-1}$ , respectively [208]. Taha et al. [209] utilized rice straw as biomass, then processed it with phosphoric acid to produce TBC for pesticide removal in water. Surprisingly, within  $10 \text{ min}$ , the residual pesticide concentration was

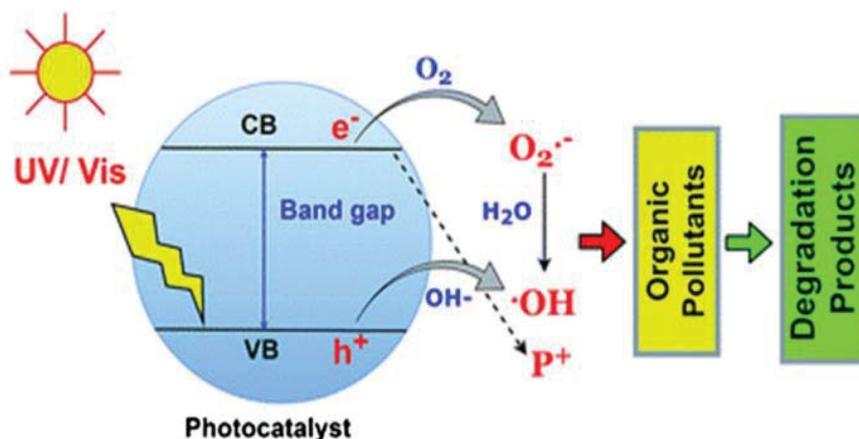


Fig. 6. Fundamentals of photodegradation of organic pollutants by reactive oxygen species (ROS) [214].

less than the maximum permissible limit in drinking water ( $0.1 \mu\text{g L}^{-1}$ ). Furthermore, at pH 7.0, all pesticides (except oxamyl) could be eliminated in 2 h [209]. Biochar is rich in aromatic structure, and it exhibited good performance in removal of hydrophobic organic pollutants [210].

### 5.3. Biochar photocatalysts

This section focuses on recent advances in wastewater treatment using biochar-based photocatalysts (BCPs). The diverse synthetic modes like sol–gel, calcination, hydrothermal/solvothermal, ultrasound, and in situ, can all be used to combine semiconductors within a biochar matrix. Apart from well-known adsorptive properties of biochar, it may also decrease the band gap, ease electron transport, inhibit electron-hole charge recombinations, and lessen semiconductor photocorrosion, etc. [211].

BCPs can be employed in a variety of applications. The removal of organic contaminants from wastewater is one of the most promising uses of BCPs due to large surface area and highly oxidative reactive species, which boosts the adsorption capacity during photodegradation. According to Lisowski et al. [212], the formation of highly reactive species such as OH and  $\text{O}_2^-$  and  $\text{h}^+$  significantly mineralized methanol into methyl formate and carbon dioxide in a reactor loaded with soft-wood pellets-TiO<sub>2</sub>. Furthermore, they suggested that TiO<sub>2</sub> supported by biochar may act as electrodes as well as for water splitting during hydrogen generation. Matos [213] studied the efficiencies of biochar assisted Au-TiO<sub>2</sub> for the degradation of organic contaminants. This is due to the presence of oxygen-containing groups on the biochar surface, which inhibit photo-generated charge recombination and hence aid in the breakdown of contaminants. BCPs, when compared to commercial nanoparticles, exhibited a high level of stability. The incorporation of nanoparticles into biochar matrix can: enhance physicochemical properties of nanoparticles; shuttle electrons through a graphene-like skeleton; increase in availability of active sites; act as electron reservoir which conducts away the electron from the  $\text{e}^-/\text{h}^+$ ; reduce the bandgap energy by carbon or other non-metal doping (impurities or dangling bonds)improving the charge separation. As a result, it performs well in terms of organic pollutant breakdown and adsorption in aqueous solution. However, some aspects of the development of highly efficient BCPs must be investigated in future researches, such as heating/operating conditions; use of different biomasses and nanoparticles; biomass to nanoparticles ratio, and use of other waste materials such as manure and sewer sludge composite with nanoparticles [214]. A pictorial representation depicting fundamentals of photodegradation of organic pollutants by reactive oxygen species (ROS) is included in Fig. 6 [214].

A brief discussion on TiO<sub>2</sub>-BCPs, g-C<sub>3</sub>N<sub>4</sub>-BCPs, Bismuth-BCPs, CQD-BCPs, ZnO-BCPs is given below:

#### 5.3.1. TiO<sub>2</sub>-BCPs

Due to its benefits of strong photo-activity, moderate pricing, non-toxicity, cheap cost, and good chemical stability, TiO<sub>2</sub> has become the most widely used photocatalyst in the field of water treatment in recent decades. However,

TiO<sub>2</sub> faces the issues of low response of visible light sensitivity and significant high charge recombination. Zhang et al. [215] used the sol–gel technique to prepare reed straw biochar-based TiO<sub>2</sub>. The combination of TiO<sub>2</sub> and biochar reduced  $\text{e}^-/\text{h}^+$  pair recombination and increased photocatalytic degradation efficiency. When compared to pure TiO<sub>2</sub> (58.47%), the sulfamethoxazole elimination rate was higher (91.27%). Furthermore, the BC-TiO<sub>2</sub> produced was effectively used in real water with a 65.70% removal rate. Lu et al. [216] used a direct hydrolysis technique and pyrolysis of discarded walnut shells to make a variety of TiO<sub>2</sub>-BCPs photocatalysts for the elimination of methyl orange. The catalyst with a weight ratio of BC/Ti (0.2/1) exhibited maximum decolorization efficiency of 92.45% and mineralization efficiency of 76.56% after recycling 5 times. Lisowski et al. [212] followed an ultrasound-assisted route to develop TiO<sub>2</sub>-based wood and straw-derived biochar photocatalysts. The plate-like particle structure of the developed photocatalysts via pyrolyzing at 700°C was quite helpful for light usage and electron–hole separation. The band gap energy ( $E_g$ ) of TiO<sub>2</sub>-BCP ranged between 2.12–2.50 eV through Kubelka–Munk function, depending on the biomass feedstocks and temperatures [211].

#### 5.3.2. Bi-BCPs

The remarkable photo-oxidation ability, unique electronic structure, and toxin-free features of Bi-BCPs have piqued interest in wastewater treatment. Zhu et al. [217] developed Bi-BCPs for effective estrone decomposition. They discovered that  $K_{\text{obs}}$  value was more than 20 times that of pristine Bi/Bi<sub>2</sub>O<sub>3</sub>. The OH• radicals produced by the synergistic impact between biochar and Bi/Bi<sub>2</sub>O<sub>3</sub> were responsible for the improved outcome. Li et al. [218] developed Bi<sub>2</sub>O<sub>3</sub>/ZnAl-LDH-BC that demonstrated efficient photocatalytic degradation of contaminants when exposed to visible light.  $E_g$  of Bi-BCPs was lower (2.42) as compared with Bi<sub>2</sub>O<sub>3</sub> and ZnAl-LDH (2.75 and 2.9, respectively), due to synergistic effects amongst precursors. Kumar et al. [219] observed the 97.4% removal of methylparaben in 2 h under sunlight using BC-Fe<sub>3</sub>O<sub>4</sub>-BiVO<sub>4</sub>. The inclusion of biochar resulted in a large surface area, which facilitated degradation of contaminants through radical attack and expedited the radical generation. Gao et al. [220] used corn cob char to make BC/Fe<sub>3</sub>O<sub>4</sub>/Bi<sub>2</sub>O<sub>3</sub> photocatalyst via solvothermal method. The higher visible-light absorption was observed by Li et al. [221] due to the unique biochar-based heterojunction structure. Bismuth oxyhalides (BiOX) showed better photocatalytic activity than anatase TiO<sub>2</sub> which was attributed to specific layered structure interleaved with [Bi<sub>2</sub>O<sub>2</sub>] slabs and double halogen atoms slabs [222]. Li et al. [223] used a one-step hydrolysis approach to produce a magnetic Fe<sub>3</sub>O<sub>4</sub>/BiOBr/BC (reed straw) composite with visible-light responsiveness. Because of the increased separation of  $\text{e}^-/\text{h}^+$  pairs, BCPs had improved photocatalytic activity for carbamazepine removal (95.51%) [211].

#### 5.3.3. g-C<sub>3</sub>N<sub>4</sub>-BCPs

Schottky junction formed by g-C<sub>3</sub>N<sub>4</sub> and highly conductive carbon materials improved charge separation

[224,211]. Kumar et al. [225] developed a range of g-C<sub>3</sub>N<sub>4</sub> photocatalysts based on biochar for wastewater treatment. For methylparaben and 2-chlorophenol photodegradation under solar light, BC supported g-C<sub>3</sub>N<sub>4</sub>/FeVO<sub>4</sub> was developed which demonstrated outstanding photocatalytic activity, with removal rates of 98.4% for methylparaben and 90.7% for 2-chlorophenol. Zheng et al. [226] used one-pot pyrolysis to make BC-based g-C<sub>3</sub>N<sub>4</sub> with varied mass ratios. Biochar's capacity can be increased by modifying it with g-C<sub>3</sub>N<sub>4</sub>. Under natural circumstances, BC100 (100 (urea):1 (biomass)) removed 100% of RR120 by adsorption and photocatalytic destruction. Kumar et al. [227] formulated a BC-based g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> heterojunction which exhibited higher removal rate of 99.3% for pesticide paraquat under visible radiation, than 92.1% under sun light. Biochar enhanced charge separation, quantum efficiency, and free radical production due to an increase in visible spectrum absorption. To remove Cr<sup>6+</sup> from wastewater, Li et al. [228] followed a two-step calcination approach to create biochar-based g-C<sub>3</sub>N<sub>4</sub> nanosheets composites. Because of the excellent thermal stability, photogenerated electrons, and wide specific surface area, graphitized BCPs may totally degrade Cr<sup>6+</sup> and total chromium. Zhang et al. [229] pyrolyzed kapok fibre to prepare biochar modified graphitic carbon nitride BCPs which narrowed the band gap, extended light absorption, and raised photocatalytic activity by facilitating electron transport [211].

Because of its metal-free composition, adjustable electronic band gap (2.7 eV), excellent thermal stability (600°C in air), and nontoxicity, g-C<sub>3</sub>N<sub>4</sub> is an emerging material for the degradation of pollutants [230]. Like a composite material of g-C<sub>3</sub>N<sub>4</sub> from melamine and alum sludge developed by Kim et al. [231], sludge as a supporting matrix of g-C<sub>3</sub>N<sub>4</sub> can boost its photocatalysis and adsorption capability. Alum sludge and melamine were combined in various mass ratios during synthesis, and heated in a muffle furnace under nitrogen environments at 550°C for 4 h. It is worth mentioning that g-C<sub>3</sub>N<sub>4</sub> photocatalysts cannot adsorb any arsenic species; but, the resultant composite may photocatalytically oxidize As(III) to As(V) as well as adsorbing arsenic under the light [231,232].

#### 5.3.4. CQDs-BCPs

Carbon quantum dots (CQDs) have emerged as a potentially cheaper and more ecological alternative to conventional unsustainable materials [233]. It takes into account the excellent benefits of tunability, biocompatibility, and stability [234]. The structural stability and photocatalytic activity of CQDs can be improved through photoluminescence, electron transport, and electron reservoir features. The preparation approach employed for CQDs by Briscoe et al. [233], principally incorporated top-down and bottom-up routes. Larger carbon structures are broken down into smaller portions in a top-down approach. The bottom-up technique involved developing CQDs from molecular precursors. When biomass precursors are utilized to make CQDs, the latter technique has the benefit of being more sustainable and biocompatible. The addition of biochar-based CQDs (BCQDs) to a semiconductor might alter the band structure and increase light absorption [235].

Using the solvothermal technique, Yao et al. [236] created a BCQDs modified flower-like BiOI composite. The primary active species for MB photodegradation were identified to be •O<sub>2</sub><sup>-</sup> and h<sup>+</sup>. The BCQDs worked as electron acceptors, allowing electron-hole pairs to be separated even more easily. Wang et al. [237] used hydrothermal treatment of bamboo powder to make BCQDs and BCQDs/Ag/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. They claimed that the use of BCQDs facilitated photoelectron production and transport. In addition, BCQDs served as an electron reservoir, enhancing photocatalytic activity [211].

#### 5.3.5. ZnO-BCPs

Aside from TiO<sub>2</sub>, ZnO is also commonly employed in photocatalysis [238]. For the photoreduction of Cr<sup>6+</sup>, Ramya et al. [239] used tannery sludge activated carbon (SBAC) supported ZnO nanocomposites (ZnO-SBAC). Its photocatalytic performance is dependent on the ratios of raw materials, just as other biomass carbon-supported ZnO catalysts, such as the jute fibre carbon-based ZnO. In the same way, ZnO-SBAC relied on it. The composite with a weight ratio of 2:3, had the lowest band gap energy of 2.96 eV and the highest photocatalytic activity among all the prepared weight ratios of ZnO to SBAC, where the introduction of sludge activated carbon prevented the e<sup>-</sup>/h<sup>+</sup> recombination process by trapping the photogenerated electrons. Loading ZnO on rectorite/sludge-derived biochar (ZnO@RSDBC) yielded a new core-shell structure photocatalyst with enhanced photocatalytic activity due to formation of a heterogeneous interface [232,240].

#### 5.4. New strategies of biochar-based materials in water treatment

Sludge biochar-based catalysts presented heterogeneous advanced oxidation for pollutants due to their efficient and cost-effective characteristics. They've become more important in real-world wastewater treatment, such as biologically pre-treated coal gasification wastewater and refinery wastewater. The sludge biochar-based catalysts not only improved the removal capacities for harmful contaminants, but they also increased profitability. Sludge biochar-based catalysts might be improved by using less expensive dopants like transitional metals (Fe, Mn) and adopting a promising processing method like slow pyrolysis. They are, however, nonetheless dealing with a decrease in active areas, such as metal leaching. This proclivity can be considerably minimized by raising the pH of the aqueous phase. A large variety of sludge biochar-based catalysts have been developed, and they function well across a wide pH range. More significantly, the problem of becoming oxidized must be resolved as soon as possible. In the heterogeneous advanced oxidation of wastewater, more efforts are required in future to enhance the antioxidant properties of sludge biochar-based catalysts [232].

Bioremediation is generally considered as one of the most ecologically benign, adaptable, and environmentally friendly technologies for removing contaminants, with several advantages. Although microorganisms are inefficient in removing high-concentration pollutants and compete with native microorganisms [241]. Many studies have used biochar as a carrier for promoting microbial degradation, and immobilization has been considered as an effective

strategy to overcome such hurdles. Attachment or adsorption on a solid surface, encapsulation inside a porous matrix, aggregation via flocculation and crosslinking are all the pathways for immobilizing microbial cells onto biochar [242]. Because of the easy and moderate immobilization process, sodium alginate is often employed in immobilizing microbial cells. Pino et al. [243] investigated free and immobilized microbial cells (on biochar and alginate) to observe whether they may improve phytoremediation of pollutants in the soil. The elimination of the PCB congener by biochar-immobilized microorganisms was up to 30.3% after 60 d of plant development, which was more effective than alginate-immobilized cells (6.8%) and free cells (<5%). Chen et al. [244] investigated free and immobilized microbial cells (on BC and fresh plant residues) to improve phytoremediation of polycyclic aromatic hydrocarbons (PAHs) pollutants in water. Immobilized bacteria with plant residues removed 85%–93% and 94%–98% of phenanthrene and pyrene from water, respectively, which was lower than immobilized bacteria with biochar (92%–100% for phenanthrene and 96%–100% for pyrene), which can be assigned to biochar's strong affinity for PAHs. Phosphate-solubilizing bacteria (PSB) were shown to be capable of both phosphate and lead immobilization. Although when it was introduced to soil for direct competition with indigenous microbes, could not be able to multiply rapidly. Zhang et al. [245] immobilized PSB on cow dung biochar to improve PSB growth and reproduction, fastens the phosphorus dissolution and lead immobilization [246].

Biofiltration (BF) employing biochar-based biofilters is a clean method commonly utilized to treat a range of pollutants due to cost-effective and easy availability. The biofilter is a solid surface that supports the development of plants and contaminant-degrading organisms [247]. Biofilter beds containing biochar as a carbon source not only improved the efficiency of biological treatment systems, but also increased the rate at which contaminants were removed. Baltrenas et al. [248] investigated the removal of xylene using a birch wood biochar-based filtration bed, and observed 86% removal efficiency of biofilter for xylene. Biochar effectively increased microorganism growth and reproduction, with colony-forming units reaching  $10^7$ – $10^{10}$  CFU/g for yeast,  $10^7$ – $10^9$  CFU/g for fungi, and  $10^8$ – $10^{10}$  CFU/g for bacteria. Thus, inoculated bacteria in a BC-based biofilter can play an important role in removing acetone, xylene, and ammonia from the air. Deepa et al. [249] used biochar as the primary material in their biofilter bed medium to remove  $\text{Cr}^{6+}$ , with a maximum removal rate of 99.99%. BC's carboxyl, hydroxyl, and carbonyl groups can help in removal of  $\text{Cr}^{6+}$  by releasing negatively charged ions like carbonates and hydroxides, which can lead to heavy metal ions precipitation. Prado et al. [250] employed biochar as a bed material in the construction of wastewater treatment biofilters with an removal efficiency and degradation rate of 92% and  $185 \text{ g-COD m}^3 \text{ d}^{-1}$ . The increased biodegradation efficiency was ascribed to the electroconductivity of the material, found to be 6.6 times greater than inert gravel [246].

Because of biochar's low density and tiny particle size, it is difficult to extract biochar from water, which limits its applicability. To meet with the challenges, researchers toiled hard to mix biochar with a polymeric matrix to

create a new class of membranes known as biochar-based 2D membranes. Mixed matrix membrane (MMM) consisted of continuous polymer phase (such as glassy, rubbery) and was evenly dispersed with filler particles [251]. Biochar was easier to be assembled into a 2D membrane through mutual interactions in comparison to other adsorbents [252]. Incorporating biochar into matrix membranes is a viable technique for not only increasing adsorption capacity and lowering costs, but also overcoming the above-mentioned limitations. Using casting and electrospinning methods, the BC-based 2D membrane could be readily constructed using biochar and polymer. He et al. [253] developed a biochar-based membrane for the treatment of copper and lead-contaminated wastewater by casting biochar particles into polysulfone (PSF). Compared to a pure PSF membrane, the biochar-based membrane was more hydrophilic with greater water flux. For copper and lead, the maximal adsorption capabilities were 90.36% and 90.16%, respectively. After four cycles, the adsorption capacity for copper and lead could still be 87.4% and 86.83%, respectively. It has been established that embedding biochar particles in PSF did not block adsorption sites of biochar. Another popular polymer in biochar-based membranes is polyvinylidene fluoride (PVDF). Ghaffar et al. [254] created a biochar-based membrane by casting a combination of BC and PVDF into a porous structure with high mechanical strength, equally scattered BC particles on the surface and cross-section of the membrane. This membrane showed a remarkable capability for adsorption of Rhodamine B dye ( $187 \text{ mg g}^{-1}$ ). Furthermore, these membranes can be effectively recovered from water, indicating a promising future for environmental remediation applications [246].

As small biochar particles (mm to cm) limit the application of biochar in water treatment, the biochar-based membrane may overcome the limitation of biochar materials in recycling and secondary pollution. 3D biochar-based macrostructure, a hierarchical porous-structured carbonaceous hydrogel or aerogel exhibited good performances to be used as biochar applications. Aerogels and hydrogels are two types of gels that are classified according to their compounded media (water or air) [255]. Because of the limitations of industrial supercritical drying, traditional aerogels lack mechanical stability and are expensive on a wide scale usage. This drawback might be overcome by coating polymers on 3D networks. Wang et al. [256] synthesized a carbonaceous aerogel from biomass and modified it with polydimethylsiloxane (PDMS) to achieve outstanding separation and collection of oil and organic solvent from water. Furthermore, this carbonaceous aerogel is small and portable, making it useful in unwanted circumstances like organic solvent leaks and tanker spillage. A novel type of carbonaceous hydrogel has been developed utilizing a one-step approach including hydrothermal carbonization (HTC). This approach is a template-directed carbonization-activation process with significant benefits such as facile and exact control of structural parameters and mechanical strength, extreme flexibility, high chemical reactivity [246]. Liu et al. [257] synthesized a 3D porous biochar aerogel with high porosity and surface area ( $2,607 \text{ m}^2 \text{ g}^{-1}$ ) using a one-step direct carbonization-activation technique. The  $\pi$ - $\pi$ /n- $\pi$  EDA interactions, pore-filling effect, and

electrostatic interactions supported the 90% removal of phenicol antibiotics (PABs) using 3D porous biochar aerogel within 10 min only. Zhang et al. [258] prepared carbonaceous hydrogel utilizing waste soybean dreg which demonstrated a high and quick adsorption capacity for Zn(II), Fe(III), Cu(II), and Cr(III), respectively, of 121.2, 78.5, 75.4, and 41.7 mg g<sup>-1</sup>. The removal rate reached 88.6%, 81.9%, 84.4%, and 75.1% of the amount of equilibrium adsorption in the first two minutes. To summarize, the high adsorption capacity, recycling efficiency, and porous structure of the 3D biochar-based macrostructure made it a great choice for eliminating organic contaminants and heavy metals. Apart from decontamination, 3D biochar-based macrostructures may also be used in energy storage and electrochemical catalytic activities [246].

## 6. Challenges and future directions

A huge number of hazardous chemicals, including PAHs, dioxins, and acrolein, are generated during biochar production. The physicochemical properties of biochar, as well as its biological toxicity, are affected by different production techniques. The pyrolysis temperature and biomass type had an effect on PAH concentrations in biochar. The biological toxicity of biochar generated at low temperatures was found to be enhanced. The concentration of PAH in conventional biochar was 0.07–4 µg g<sup>-1</sup>. When biochar was generated from paper mill sludge and wood, it showed 17–27 µg g<sup>-1</sup> PAH, which was found to be significantly high. Toxic dioxin and furan like PCDD and PCDF concentrations, were much lower at 700°C than at 300°C. According to one study, biochar may have deleterious effects on fibroblasts due to particle properties/size and dosage influencing biochar toxicity. Pristine biochars may contain potentially harmful components such as heavy metals and metalloids. The amounts of heavy metals in biochar may vary depending on the biomasses used as feedstocks. For instance, biochar generated from sludges and animal manures was high in heavy metals such as Cd, Pb, Mn, Cu, Ni, Zn, and Cr, when compared to green waste. Furthermore, long-term use of biochar may result in the release of internal harmful substances as a result of aging and degenerative processes, resulting in secondary pollution of aquatic ecosystems. Thus, to minimize detrimental effects of biochar on the environment, potential risk factors should be addressed before preparation and utilization of biochar. Short-term simulation studies cannot ensure the safety of long-term water treatment applications. Long-term water experiments and risk assessments are essential for biochar usage in environmental remediation/clean up because the addition of biochar to the soil may modify soil pH, influencing the ability of microorganisms. BC can also generate free radicals, which can impede germination, halt growth, damage plasma membranes, and ROS generated by free radicals may induce oxidative stress and cellular toxicity. 20% of studies suggested that biochar-soil incorporation exhibited a negative impression on yield/growth. Aside from biochar, the potential risks linked with modifying agents cannot be ignored. Biochar was significantly found toxic to *D. magna* after steam activation. Furthermore, certain composite materials may include NaOH, KOH, HCl, and H<sub>2</sub>SO<sub>4</sub>, which

will change the pH of BC, altering the soil or water environment and influencing organism growth and reproduction. Although biochar-based composites can improve pollutant removal efficiency, but little is known about their durability and biological toxicity. As a result, before proceeding with practical applications, it was necessary to thoroughly assess the stability and biological effects of biochar-based composites in water/soil environments in order to avoid toxic substances shedding from the composites, which could cause secondary environmental contamination and biological damage. Biochar-based composites combine the advantages of biochar with nanomaterials, however potential risks and environmental harm must be considered. Nonetheless, pristine biochar has certain limits in its ability to selectively adsorb high concentration pollutants. To compensate for this limitation, biochar-based composite materials were created by combining functional components, magnetic compounds, and nanoparticles. New tactics for novel biochar-based materials such as 2D membranes, 3D carbonaceous hydrogels/aerogels, or immobilized microorganisms on it have been explored for better removal of pollutants. However, the usage of biochar particles and biochar-based composites unavoidably results in the emission of tiny particles into the environment, which can cause biological toxicity and harm to human and environmental health [246].

Despite the excellent developments and performances of BCPs in pollutant degradation from aqueous environments, there are certain limitations and knowledge gaps. ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> showed toxicity towards microorganisms. The majority of research on photocatalytic wastewater treatment using BCPs focused on single organic or inorganic substances. Real wastewater, on the other hand, frequently contains many types of contaminants. During the removal process, there may be competitive adsorption or photocatalysis among different materials. As a result, more research into the effectiveness of BCPs in treating real wastewater is required. The reuse of BCPs from slurry systems is still a challenge, which restricts their utilization. Magnetic separation using an external magnetic field in the water treatment process is one possible technique to solve this problem. More study is needed to determine how to recover BCPs efficiently on a commercial level. Regardless of its benefits, certain hazardous waste biomass, such as sewage sludge and municipal waste, may emit harmful organic or inorganic chemicals during the pyrolysis process, posing environmental and health dangers. More study on the long-term effects and security of wastewater treatment applications of BCPs is needed. So far, major studies have been conducted in a static environment, which are commonly used to evaluate the photocatalytic activity of novel catalysts. Photocatalysis in dynamic environments may show different behaviours, which require more research investigations [211].

Adsorption processes include various mechanisms, and many influencing parameters, such as biochar features (structure, pores, surface charge, functional groups, etc.), adsorbate qualities (molar size, mole weight, logK<sub>ow</sub>, etc.), and experimental conditions such as solution pH, contact time, adsorbent dose, temperature, etc., can all contribute to adsorption capacity. Due to a lack of plentiful evaluation of materials or sophisticated measurements, several proposed basic assumption models or multiple experiments

are unable to elucidate adsorption mechanisms in a better way. This study proposed a data-based model for predicting biochar adsorption performance accurately without experimentations, which may be proven highly useful in terms of biochar water/wastewater treatment. A robust Cubist model was developed, quite helpful for designers and operations managers in visualizing or predicting the  $Q_e$  of a given biochar with no additional lab-scale studies, less time duration, and good generalizability. If we already know the influence concentration of pharmaceuticals, this approach is incredibly useful to obtain biochar dosage precision for applying in real-world investigations. The findings also showed that adsorbent efficacy may be improved by modifying the structure of the biochars rather than the functional groups, most likely by increasing the pyrolyzing temperatures. Because the accuracy and generality of prediction models are based on data quality and the selection of suitable algorithms, future research should focus on collecting and mining pharmaceuticals adsorption data on biochars. Since, there is a strong relationship between the algorithm and the data set, a trial and error strategy in exploring for the optimized machine learning (ML) algorithm is also required to implement to the specific dataset of adsorption before training and tuning any final algorithm extensively. However, predictions obtained from ML-based models may be difficult for environmental researchers and water sector operators to implement and comprehend. Therefore, a user-friendly web user interface/open source software/information is greatly required for further prediction research. Data dimension reduction is also needed to save computer time and resources while enhancing model accuracy. Finally, for practical investigations employing biochars on real water bodies, the influence of several ubiquitous organic competitors such as amino acids, proteins, humic compounds, and saccharides on the adsorptive sites with pharmaceuticals should be addressed [259].

## 7. Conclusions

Biochar is a promising tool to address challenges due to environmental pollution, resource conservation, and linear economy. It is a well-recognized renewable resource in remediation of pollutants from aqueous, soil, and gaseous medium. It is especially effective at removing heavy metals, organic pollutants, dyes, medicines, pesticides, and other impurities from aqueous environments. The characteristics and sorption capacity of biochar is strongly influenced by the pyrolyzing temperatures and the feedstock used. The usage of biochar as sorbents is continuously increasing, as evidenced by published research, but more exploration is required, particularly in column sorption and effective effluent clean-up comprising multi-contaminants. This paper provides an in-depth assessment of the widespread use of biochar in the treatment of water and wastewater to remove prevalent organic, inorganic, and several other emerging pollutants. This work evaluated the numerous ways for obtaining biochar from diverse feedstocks, which may serve as a foundation for future research into the sorption behaviour of biochar. Based on the processes, the emphasis has been given on the modification of biochar in order to enhance its performance, with

the aim of increasing porosity or surface sorption sites, as well as the surface area of biochar. Future researches are required for identifying new modes of activation, adsorption and desorption mechanisms of different types of pollutants for treating wastewater in an efficient manner for field-scale applications. The mechanism of pollutant removal is directly linked to the interaction between biochar and pollutants. Removal of contamination may occur through physisorption (electrostatic attraction/repulsion, H-bonding, pore-filling, diffusion, and hydrophobic) or chemisorption (electrophilic interaction) mechanisms in presence of different functional groups such as COOH, OH, etc. Other removal mechanisms may include partitioning, chemical transformation, and biodegradation. The key experimental factors which affect biochar-pollutant interactions are feedstock used, pH, temperature, concentration of pollutant, and dose of applied biochar. For assessment and evaluation of economic advantages and environmental impacts, life-cycle analysis and recycling studies of biochar must be performed. The potential risks of biochar and biochar-based materials to the environment should not be ignored prior to biochar applications like their stability, biological toxicity. Field trials and exclusion of unnecessary contaminants during preparation processes of biochar must be explored. This article summarized state-of-art information that would be quite helpful in finding new opportunities in the field of biochar research.

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