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Engineered Biochar

Fundamentals, Preparation,
Characterization and Applications

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Engineered Biochar: Fundaments

Pristine Biochar and Engineered Biochar: Differences and Application

Monika Chhimwal, Diksha Pandey, and R. K. Srivastava

Abstract Biochar is carbon rich, porous substance produced under limited or no supply of oxygen. Pristine biochar is considered as a sustainable, beneficial, and low-cost product employed for soil conditioning, agricultural production, and pollutant removal. It is a promising product having a wide array of applications including catalytic reaction, carbon sequestration, pollution mitigation, and sustainable agriculture. The production of biochar is a sustainable practice to treat and valorize solid waste. Without any activation or modification, pristine biochar has lower surface area, porosity, and surface functional groups. To enhance the physicochemical and functional properties of pristine biochar, modification of biochar is done via physical, chemical, and biological methods. This chapter provides an overview of pristine biochar, including its production, modification, differences between pristine and engineered/modified biochar and multi-dimensional applications. Additionally this chapter covers knowledge gaps and perspectives in the domain of biochar technology and application.

Keywords Pyrolysis · Carbon sequestration · Biochar · Wastewater · Hydrochar

1 Introduction

Pristine biochar (PBC) is a carbonaceous material prepared by pyrolysis. Pyrolysis is the thermochemical conversion of raw materials at high temperature in oxygen-limited conditions. The raw materials needed to make biochar are a wide range of biomass-based wastes such as forest and crop residues, wood chips, sludge, municipal solid waste, sunflower husk, pelletized grape wine pressings, etc. (Lehmann et al. 2006; Colatoni et al. 2016).

The properties of biochar including its recalcitrant nature, surface area, porosity, varied functional groups, and the mineral content make it a suitable product for multi-dimensional applications such as pollutants removal, carbon sequestration,

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soil rehabilitation, wastewater purification, catalysis, reduction of greenhouse gases, geo-engineering, enhanced soil fertility, crop productivity, and sustainable energy production (Wang et al. 2017; Wani et al. 2021; Ramola et al. 2013). This product is well-liked in the wastewater treatment sector due to its significant adsorption properties for nitrogen, phosphorus, heavy metals, and other emerging contaminants (Chen et al. 2011 and Han et al. 2016). However, due to small particle size and low density, pristine biochar is hard to get separated from water (Tan et al. 2016). There is also a problem of low regeneration and potential adverse effects of spent pristine biochar disposal in the ambient environment. Characteristic properties of pristine biochar vary according to the type of raw materials used and the pyrolysis conditions operated during its preparation. Increase in textural properties such as pore volume and surface area occur when the pyrolysis temperature is optimum. These properties decline beyond the optimum temperature due to collapse of pores and structural deformation (Ramola et al. 2020a, 2021). Large surface area helps in the adsorption of heavy metals and other emerging contaminants. The surface area of pine needles pyrolyzed at 100 ℃ was 0.65 m^2g^{-1}, which increased to 112.4 $m^2\ g^{-1}$ at 400 ℃ (Chen et al. 2008). Ramola et al. (2020a) also reported increased surface area of biochar-bentonite and biochar-calcite composites at 500 ℃, i.e., 53.08 m^2g^{-1} and 32.29 m^2g^{-1}, respectively, that was maximum in comparison to the surface area of both biochar composites at 300 and 700 ℃. Surface area of some pristine biochar at different pyrolysis temperature is given in Table 1.

Table 1 Surface area of pristine biochar prepared at different pyrolysis temperature

Raw material	Temperature (℃)	Surface area ($m^2\ g^{-1}$)	Reference
Cottonseed hulls	350 650 800	4.7 ± (0.8) 34 ± (3) 322 ± (1)	Uchimiya et al. (2012)
Corn stover	350 600	293 527	Nguyen et al. (2009)
Soyabean stock	300 400 500 600 700	144.14 138.76 152.98 179.03 250.23	Kong et al. (2011)
Oakwood	350 600	450 642	Nguyen et al. (2011)
Wheat	300–400 500–700	200 300	Tang et al. (2013)

2 Production of Pristine Biochar

There are different methods for the production of biochar. The most common methods are pyrolysis, hydrothermal carbonization (HTC), and microwave carbonization (Table 2). These methods influence physical and chemical properties of biochar like yield, cation exchange capacity, specific surface area, functional groups, and ash content.

Pyrolysis is classified as either fast or slow pyrolysis based on the pyrolysis conditions. The temperature of 500 ℃, residence period of 2 s, and heat transfer rate of 300 ℃/min are the operational conditions for fast pyrolysis. The raw material decomposes very rapidly in fast pyrolysis because the temperature is high. Bio-oil (75 wt%), char (12 wt%), and gas (13 wt%) are the products of fast pyrolysis. Slow pyrolysis is operated at temperatures of 300–500 ℃, residence period of 5–30 min, and heat transfer rate of 5–20 ℃/min. Bio-oil (30–50 wt%), char (25–30 wt%), and gas (35 wt%) are produced via slow pyrolysis (Ramola et al. 2020b).

HTC system uses water medium for reaction under high pressure and temperature (Regmi et al. 2012; Zhang et al. 2013a, b). HTC provides significant advantages in conversion of biomass as it has high conversion efficiency, relatively low operational temperature, and no need of extensive energy for drying process (Sabio et al. 2016; Liu and Balasubramanian 2012b, a). The biochar produced by HTC is known as hydrochar. The fuel quality of hydrochar is similar to that of lignite (Liu et al. 2012) with high energy density.

Microwave pyrolysis is a comparatively modern pyrolysis technique that has several advantages over conventional techniques, including the ability to regulate the process along with power and cost reductions (Masek et al. 2013; Morgan et al. 2017). It tends to eliminate the drawbacks of traditional pyrolysis technologies, like

Table 2 Removal of different pollutants by biochar

Raw material	Pyrolysis temperature (°C)	Target contaminants	Maximum adsorption capacity	Reference
Bamboo, bagasse, peanut hull	600	Cd^{2+}, Pb^{2+}, Cu^{2+}	14.3 mg g[1]	Zhou et al. (2013)
Malt spent rootlets	300–900	Hg (II)	103 mg g[1]	Manariotis et al. (2015)
Sludge	400	As (II)	3.08–6.04 mgg[-1]	Wang et al. (2020)
Wheat straw	350–360	Cr (VI)	70.3 mg g[1]	Wang et al. (2020)
Bamboo	500	Quinolone	45.88 mg/g	Wang et al. (2015)
Sludge	700	Pentachlorophenol	47–50 mg/g	Devi et al. (2015)
Sludge	400	Atrazine	27.03 mol/g	Zhou et al. 2015

the need to shred raw material into smaller parts. Microwave modification is more adequate than traditional pyrolysis because it is fast and efficient, and it allows for homogeneous interior temperature distribution. As a result, it produces biochar with more surface area and functional groups than by traditional pyrolysis (Wang et al. 2009). It produces efficient biochar at a low temperature (300 ℃) while also enhancing soil water holding capacity (WHC) and cation exchange capacity (CEC) (Mohamed et al. 2016a, b).

3   Modified Biochar

Biochar engineering contributes to achieve enhanced properties of biochar for specific applications. This helps to modify the desired properties of biochar with improved efficiency. The physicochemical properties like specific area, pore structure, and surface functional groups can be enhanced by modification of biochar. Biochar engineering or modification is done via different physical, chemical, and biological methods for preparing activated or modified biochar (Ok et al. 2015;
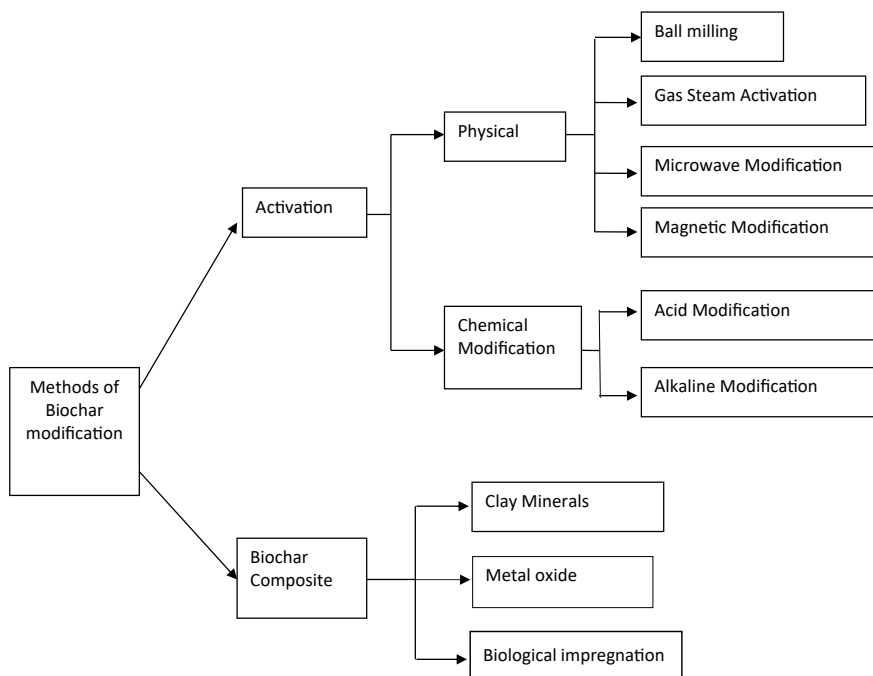
Fig. 1 Different biochar modification methods

Mohamed et al. 2016a, b; Rajapaksha et al. 2016; Yao et al. 2013). Figure 1 depicts different biochar modification methods.

3.1 Physical Modification

The most common methods for physical modification are ball milling, gas and steam activation, microwave modification, and magnetic modification. Physical modification contributes to improvement in pore structure and addition of oxygen containing functional groups. This modification also enhances micropores and mesopores in biochar with an improved surface area that provides enough space to adsorb organic pollutants, nutrient elements, and heavy metals (Wang et al. 2017).

3.1.1 Ball Milling Modification

The grinding of biochar particles through ball mill can improve the particle size and specific surface area that leads to more adsorption of organic and inorganic ions (Cai et al. 2016). Peterson et al. (2012) reported that using ball mill process, the surface area of corn- stover based biochar was improved 3.2 times and reached 194 m^2. The improvement of the functional groups in biochar can be achieved by adding chemicals during ball milling. Ball milling of biochar can also produce nano-sized biochar particles**.**

3.1.2 Gas/Steam Activation

Gas/steam such as water vapor, CO_2, and air can be employed for physical modification (Guo et al. 2009; Shim et al. 2015). This method improves the porosity formation in biochar by activating its carbon which leads to better surface area and surface reactivity, while removing incomplete combustible components. However, the gas/steam activation method decreases the availability of some functional groups on the biochar surface like COOH (carboxylic acid) that gets degraded in steam-based biochar activation process. COOH is considered as good adsorbent for heavy metals (Uchimiya et al. 2012). Due to its depletion during activation, the metal adsorption capacity of gas/steam engineered biochar is negatively impacted.

3.1.3 Microwave Modification

Microwave radiation with a frequency of 0.03–300 GHz may be utilized in a controlled environment to pyrolyze biochar at 200–300 ºC, yielding about 60% biochar (Tabatabaei et al. 2019). The microwave-modified biochar eliminates the need for biomass drying and shredding (Bhaskar and Pandey 2015). The biochar

produced via microwave modification possess additional functional groups and greater surface area than pristine biochar (Wang et al. 2017).

3.1.4 Magnetic Biochar Modification

The small particles size of biochar with low density makes its separation difficult from water and creates hurdle in the purification of water. It can also contribute in generation of secondary pollutants (Nguyen et al. 2013). Impregnation and co-precipitation pyrolysis are two common methods for magnetic modification (Yi et al. 2020). In impregnation method, biochar is impregnated with transitional metal salts. A magnetic biochar was made using Fe^{3+}/Fe^{2+} solution having 1.4%–80.6% of iron content (Mohan et al. 2014). This magnetized biochar has shown higher Pb^{2+} and Cd^{2+} removal capacities. The modified magnetic biochar has large number of carboxyl functional group on the surface which improves the adsorption capacity for heavy metal ions. Magnetic biochar can be derived through mixing of Fe^{2+}/Fe^{3+} ions into a solution of ammonia (Yu et al. 2013) while in case of co-precipitation ammonia and NaOH solution are used with constant stirring (Yi et al.2020).

3.2 Chemical Modification

Biochar can be modified using acids and bases to increase surface area, micropores, cation exchange capacity, and functional group availability. Acid (H_2O_2, H_3PO_4, HNO_3, and HCl) and other chemical agents increase carboxyl groups and mineral composition of biochar. Various alkaline agents stimulate the functional groups and promote electrostatic interaction at biochar surface that enhance the adsorption capacity for heavy metals (Mahmoud et al. 2012; Jingchun et al. 2013). Organic compounds, clays metal oxides can also be impregnated on biochar for chemical modification. Modified corncob biochar coated with magnesium salts resulted in positive surface charge of biochar that further enhanced the adsorption of phosphate ion with maximum adsorption capacity of 319.63 mg/g (Sizmur et al. 2017).

3.2.1 Chemical Coating

The surface area can be improved by coating nanoparticles or metal oxides on the surface of biochar during pyrolysis to produce biochar-based nano composite. The chemical impregnated biochar results in improved surface area, pore size, functional group, catalytic efficiency, and more active sites for binding (Kazemi et al. 2020).

$-OH$ and $-CH$ are very important surface functional groups that help in adsorption of heavy metals. When the pristine biochar is modified by HNO_3 or NH_3, a new amino functional group gets attached to the biochar surface and the modified biochar becomes more efficient to remove heavy metals. Biochar derived from cactus fibers

and modified through HNO_3 had more adsorption sites and surface carboxylic group (Qian et al. 2013).

Song et al. (2014) used $KMnO_4$ for pyrolysis of corn straw at 600° C. This modified biochar showed increased O/C ratio and oxygen in Mn-OH and Mn-O structure which was effective for Cu^{2+} adsorption in comparison to pristine biochar. A corn straw-based biomass was dipped into $FeCl_3.6H_2O$ solution before slow pyrolysis at 600 ℃ for 1 h. The resultant modified biochar had more functional groups, higher stability, larger surface area (He et al. 2018) and improved As (V) adsorption capacity up to 400 times.

Similar approach of biochar activation was adopted by Shen et al. (2019), where corncob biomass was treated with $MgCl_2$ before pyrolysis to get MgO plated biochar. This modified biochar had 380 time more surface area as compared to pristine biochar. Biochar derived from spruced wood when impregnated with $AlCl_3/FeCl_3$ solution and pyrolyzed at 650 °C for 1 h, removed fluoride ion with adsorption capacity of 13.6 mg/g (Tchomgui et al. 2010).

3.3 Biochar-Based Composite

3.3.1 Clay Coating

Clay has well-defined surface chemistry, large particle size, and surface area (Yao et al. 2014), which can efficiently adsorb inorganic and organic pollutants like dyes, heavy metals, etc. Bentonite, montmorillonite, and kaolinite are used as adsorbents for pollutant removal. Yao et al. (2014) pretreated the biomass with kaolinite and montmorillonite and the mixture was pyrolyzed at 600 ℃, for 60 min. The adsorption capacity of modified biochar increased by five times for methylene dye compared to unmodified biochar due to more ion exchange and electrostatic attraction. Takaya et al. (2016) also used clay-coated biochar for the recovery of phosphate from wastewater. The oak wood-based biochar was impregnated with magnesium by treating with $MgCl_2.6H_2O$ before pyrolysis at 600 ℃ for 60 min. The modified biochar efficiently removed phosphate in comparison to pristine biochar. Ramola et al. (2020a) prepared different biochar clay mineral composites with spent waste, bentonite, and calcite as raw materials. They observed an increased surface area, porosity, and adsorption capacity of biochar composites for Pb in comparison to pristine biochar. Similarly, a novel rice husk biochar-calcite composite (BRH-C) was prepared for efficient removal of phosphate at low concentration. The optimum pyrolysis conditions for preparation of BRH-C were 700 °C (temperature), 2.3 h (time), and rice husk-calcite ratio of 4.2:1 (w/w). BRH-C removed better phosphate than rice husk biochar or calcite alone, suggesting synergistic effects of both rice husk biochar and calcite as a composite. Calcite also altered the yield and textural properties of BRH-C and added characteristics calcite functional groups and minerals (Ramola et al. 2021).

3.3.2 Biological Impregnation

The small size of microorganisms makes them penetrable in minute pores of biochar, where these organisms develop a biofilm. The rigid pore structure of biochar prevents microorganisms to be washed out. The presence of these microorganisms inside the inert biochar modifies it through biofilm generation and colonization. It has been well known that microorganisms are excellent in the degradation of organic matter and adsorption of heavy metal (Hamedi et al. 2015). Biochar activated with microbial film sourced from the mining field, reported naphthenic acid degradation and removal of heavy metal at the same time from wastewater (Frankel et al. 2016). Another study by Dalahmeh et al. (2018) investigated that biofilm activated biochar, degraded pharmaceutically active compounds like caffein, carbamazepine, and ranitidine from sewage. It was observed that activated biochar degraded >90% carbamazepine in comparison to 7% in sand active biofilm during 154 days.

3.3.3 Biomass Composite Formation with Metal Oxide

Nano metal oxide and hydroxide-biochar can be produced through enrichment of targeted element by bioaccumulation, post pyrolysis nanoparticle impregnation, and biomass treatment by metal salt. The biomass activation through this way increases the active adsorption site for inorganic and organic contaminants and surface area (Tan et al. 2016). Post pyrolysis metal oxide impregnation of nanoparticle could be achieved through conventional impregnation, evaporative, and heat treatment method.

4 Applications of Biochar

The properties of biochar make it a dynamic substance for its multi-dimensional use (Fig. 2). Although pristine biochar and engineered biochar both are efficient in removing the contaminants, still the improved performance of engineered biomass have been reported in the various study.

4.1 *Biochar for Soil Conditioning and Carbon Sequestration*

Biochar is resistant to decay so it can stay in the soil for longer time. Biochar application in soil enhances the soil stability to act as carbon sink. The co-dopped activated biochar is also reported to enhance the carbon sequestration (Mašek et al. 2019). Biochar also reduces nitrous oxide, carbon dioxide, and methane from agricultural land. Different concentrations of biochar ranging from 2 to 60% (w/w) can reduce the emission of nitrous oxide higher than 20% (w/w) (Rawat et al. 2019).

Fig. 2 Application of biochar
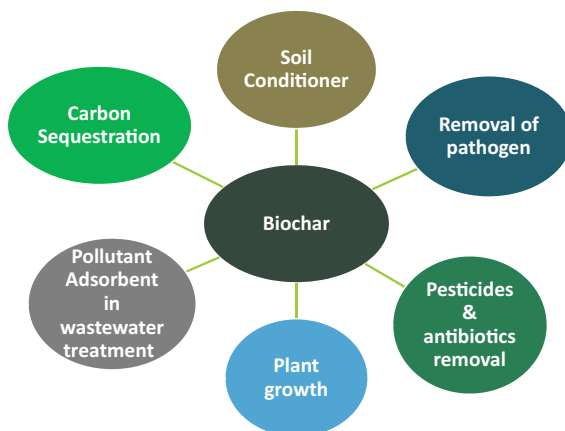
It also increases the water holding capacity, cation exchange capacity, total nitrogen, and phosphorous (Lehmann et al. 2003). Plant response toward the uptake of nutrients, and the availability of nutrients like zinc, phosphorous, and potassium increased with the use of biochar in soil. In comparison to pristine biochar, biochar dopped with nutrients like Ca, Mg, and K on its surface promotes more soil fertility by immobilizing and releasing the nutrients simultaneously (Igalavithana et al. 2017). Acidic and alkaline biochar are also used for the treatment of soil.

Biochar provides medium for the growth of mycorrhiza that provides the suitable conditions for colonization of plant roots. Biochar can affect the growth of fungi by changing the properties of soil. It has also been reported that biochar improves the nitrogen fixation in *Phaseolus vulgaris* (Rondon et al. 2007). Biochar also protects fungal hyphae and beneficial microbes from attacks of mites, protozoans, and nematodes (Rawat et al. 2019). Biochar amended soil can suppress the growth of pathogen through its antagonist effect and with indirect interaction through induction of systemic resistance in plants. Biochar triggers the induction of system plant defense only for leaves diseases such as powdery mildew in strawberry, gray mold in tomato, and foliar blight in soybean (Jaiswal et al. 2020). There are many studies that report use of biochar to control the pathogen in soil. It can resist the growth of soil borne as well as air borne pathogen that causes powdery mildew (Bananomi et al. 2015). The biochar prepared from citrus wood can control the gray mold (*Botrytis cinerea*) on tomato and pepper (Rawat et al. 2019). Similarly, biochar obtained from the grounded hardwood prevents the root lesion (causal organism *Fusarium oxysporum*) in asparagus (Elmer et al. 2011).

4.2 Biochar for Remediation of Pollutants from Aqueous Medium

Biochar has a good adsorption capacity for different pollutants (Table 2). Biochar derived from the switchgrass was used for the removal of metribuzin herbicide as well as antibiotics like tetracycline and sulfonamide. Electron donor–acceptor interactions and specific functional groups at the surface of biochar enhanced the removal of pollutants (Peiris et al. 2017). Sulfamethoxazole (SMX) is a sulfonamide antibiotic used for animals and humans. This antibiotic was adsorbed by the digested bagasse biochar and adsorption process was governed by π-π interaction. The biochar made up of rapeseed straw, peanut at 350 °**C** showed maximum adsorption capacity toward the removal of methyl violet, i.e., 123.5–195.4 mg/g. Electrostatic interaction was reported as the main mechanism behind this removal. Several studies reported that the performance of biochar for pollutants removal depends on the polarity index, the quantity of functional groups, and aromaticity index (Braghiroli et al. 2018; Cha et al. 2016).

Ca-Mg loaded biochar enriched with nano- CaO and MgO particles had more organic functional groups and increased surface area as compared to pristine biochar that resulted in more adsorption of phosphate ions with adsorption capacity of 294.22, 315.33, and 326.63 mg/g respectively (Fang et al. 2015).

Inyang et al. (2012) revealed that biochar made from anaerobic digestion of sugar beetroot at 600 °C can remove Ni (II), Pb (II), Cd (II), and Cu (II) effectively up to 97%. Wheat straw-based biochar when pyrolyzed at 200 °C, can remove Cr (VI) with a maximum adsorption capacity of 35.78 mg/g. There are four mechanisms that work behind the adsorption of heavy metals: the electrostatic attraction between biochar surface and heavy metals, complexation with a surface functional group or π electron-rich domain, exchange of ion between the surface of biochar and heavy metals, and process of co-precipitation to form insoluble compounds (Wang et al. 2020; Ramola et al. 2020b).

Pristine biochar is very effective in adsorbing the inorganic ions. The exhausted nitrogen and phosphorus laden biochar can further be recycled and reapplied for soil conditioning. A study on bamboo biochar reveals that biochar has adsorption capacity of 6.4 mM/g for NH_4^+ ion from wastewater. At high pH (pH > pH PZC) biochar easily adsorbs the NH_4^+ ions through electrostatic force (Viglasova et al. 2018).

For removal of phosphate ions from the wastewater, the sludge derived, and walnut derived biochar was used, and it was found that there was an electrostatic attraction between phosphate and biochar surface (Ajmal et al. 2020). Rice husk is an abundantly available agricultural waste with a global annual production of approximately 1.2 Giga tonne (Costa and Paranhos 2018). Optimized, ecofriendly, and cost-effective rice husk biochar-calcite composite was used to remove phosphate from the aqueous solution. Results demonstrate efficient removal of phosphate (87.3%) in comparison to pristine biochar (Ramola et al. 2021).

A biochar from maize straw at 300, 500, and 700 °C was studied for the removal of thiacloprid. The process of adsorption occurred through pore filling hydrophobic interaction as well as π-π interaction. Similar study was done with pyrolyzed swine manure biochar for understanding the adsorption mechanism for imidacloprid (Wang et al. 2020).

Antibiotics are sometimes difficult to degrade in environment. Biochar can be an effective adsorbent that can reduce the toxicity of antibiotics. Sulfonamides (SAs) and Tetracyclines (TCs) are the most commonly used antibiotics in agricultural fields. Their excessive amount is harmful for the environment. Adsorption mechanism of pristine biochar for the removal of SAs has been done by Peris et al. (2017). They found that biochar prepared at high temperature makes a strong π-π electron donor-acceptor bond between the arene ring on SAs and surface of biochar.

4.3 Biochar Application for Removal of the Pathogen

Urban storm water is highly contaminated with pathogens. There is a need to decontaminate this water before its confluence into surface water. The mechanism which works behind the removal of pathogens is filtration of large size pathogen and adsorption of negatively charged cell of bacteria. Biochar can act as filtration layer for microorganism. The size of biochar particles is crucial to act as a filtration layer. The minimum particle size of 1.4 mm has the capacity to remove atleast 1 log 10 CFU of microorganism from the wastewater. Studies show that biochar can filter >1 log 10 CFU of *Saccharomyces cerevisiae* from a diluted wastewater (Perez-Mercado et al. 2019).

5 Factors Affecting Adsorption by Biochar

Biochar has stacked layers of graphene and aromatic structure that are interconnected to one another (Conte et al. 2021). This makes biochar armored with rich pore structure and large surface area. Different mechanisms involved in the removal of pollutants from aqueous solution by biochar may work solely or side by side with one another depending upon the properties of biochar and pollutants. The main mechanisms involved in the adsorption process are cation exchange, electrostatic interactions, precipitation, complexation, and chemical reduction (Ramola et al. 2020b). Some of the factors that affect the removal mechanisms are discussed as follow.

5.1   pH

The pH of solution affects the charge present at the surface of biochar. The value of pH, where the net charge at the surface of biochar is zero is called as zeta potential (pH_{PZC}). When the value of pH is less than pH_{PZC}, biochar surface is positively charged and it can bind anionic form of metals like $HAsO_4^{2-}$ and $HCrO_4^{2-}$. When the value of pH is greater than pH_{PZC} the biochar becomes negatively charged and binds with cations like Hg^{2+}, Cd^{2+}, and Pb^{2+} (Li et al. 2017).

5.2   Functional Groups Present in Biochar

The carboxylic (COOH) and phenolic (OH) group of biochar gravitate the sorption of methyl violet on biochar (Xu et al. 2011). It has been reported that the graphitization degree of biochar and electron donor–acceptor (EDA) interaction between electron acceptors and electron donor of graphite surface magnifies the sorption rate of sulfonamides (SAs) on different surfaces of biochar (Xie et al. 2014). Phenolic group (−OH) and methine group (−CH) also play vital role in adsorption of heavy metals.

5.3   Minerals in Biochar

Different minerals at the surface of biochar increase their adsorption efficiency. It has been reported that minerals like CO_3^- (carbonate), HCO_3^- (bicarbonate), and $H_2PO_4^-$ (dihydrogen phosphate ion) adsorb Pb (II) at the surface of digested cow dung biochar through surface precipitation. When Pb (II) reacts with CO_3^-, HCO_3^-, and $H_2PO_4^-$, it forms $PbCO_3$ (lead carbonate), $Pb_5(PO_4)_3X$ (X can be ions of fluoride, chloride, bromine, etc.) and $Pb(CO_3)_2$ (Lead II carbonate) (Inyang et al. 2012). Similarly, the addition of bentonite (montmorillonite and quartz) and calcite in a cigarette waste biochar composite was found to increase the removal of Pb from aqueous solution by acting as a catalyst and altering the physicochemical properties, textural properties, and functional properties of the biochar composite (Ramola et al. 2020a). Addition of calcite in rice husk biochar demonstrated higher phosphate removal in comparison to pristine biochar without any calcite addition. Calcite changed the physicochemical and functional properties of biochar and removed phosphate via pore filling, electrostatic interaction, and precipitation working simultaneously side by side (Ramola et al. 2021).

6 Conclusion and Recommendation for Future Direction

Biochar is a renewable, cost-effective, ecofriendly, and sustainable product. Pristine biochar is easy to prepare, but its wide application is still in the testing stage. Although a broad range of raw materials are available for biochar preparation, but a thorough comprehension of the production and modifications are required for its specific applications. Biochar is gaining popularity as an adsorbent for removing pollutants from air, water, and soil. Organic pollutants are removed by hydrophobic, electrostatic attraction/repulsion via—electron donor–acceptor and partitioning between biochar and pollutant, whereas inorganic pollutants are removed via ion exchange, surface-complexation, precipitation, and ionic interactions. Despite the fact that modified biochar is more efficient than pristine biochar, appropriate biochar activation and modification methods are still not fully understood. Since the engineered biochar production is more expensive than pristine biochar, more research is required to explore the engineered biochar manufacturing methods and its cost-effectiveness. Currently, wide range of research is being conducted on pristine and engineered biochar, with most of the work being done in the laboratory only. There are limited reports on the effectiveness of modified biochar in a wide range of applications. To determine its fate and contribution for a sustainable environment, a thorough examination of the raw materials, engineering process, pyrolysis temperature, collection, and recycling of modified biochar is required.

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Waste to Wealth: Types of Raw Materials for Preparation of Biochar and Their Characteristics

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Abstract Biochar is carbonaceous material prepared from thermo-chemical conversion of biomass-based raw materials. These include agro-waste, forestry waste, animal manure, sewage sludge, and municipal waste. Different pyrolysis conditions and raw materials alter the properties of biochar such as pH, surface area, porosity, cation exchange capacity, nutrient availability, and water holding capacity. These physico-chemical properties further influence the functional properties of biochar for its different applications. In the present chapter, role of different raw materials used for the preparation of biochar, their effects on the properties, and characterization of biochar are discussed.

1 Introduction

Industrialization and urbanization are the need of today's world which are very important for the sustenance of human beings on earth (Rajaeifar et al. 2019). The problems associated with rapid industrial development are air pollution especially the release of polyaromatic hydrocarbons (PAHs) (Kumar et al. 2021a), water pollution including surface water and groundwater (Bolan et al. 2022), generation of sludge and

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lignocellulosic waste (Kumar and Thakur 2018; Kumar et al. 2021c), soil pollution due to release of organic and inorganic pollutants (Zhou et al. 2022; Sarkar et al. 2021), carbon dioxide emissions leading to climate change (Kumar et al. 2018; Thakur et al. 2018). To remediate these pollutants, various techniques have been adopted recently to reduce the pollutants load and simultaneously generate value-added products (Bhujbal et al. 2022; Gupta et al. 2022; Maddalwar et al. 2021).

Lignocellulosic biomass is considered as one of the potential raw materials for generation of heat via direct burning, but simultaneously it produces gaseous pollutants such as greenhouse gases, trace gases, aerosols, particulate matter (PM2.5 and PM10), polycyclic aromatic hydrocarbons (PAH), and non-methane hydrocarbon compounds (NMHCs) (Mishra et al. 2020; Prabha et al. 2021, Ramola et al. 2020a). Thermochemical conversion of biomass to biochar is one of the possible strategies to manage environmental waste such as lignocellulosic (Kumar et al. 2021b; Fuke et al. 2021; Ramola et al. 2020a), municipal waste (Mishra et al. 2021), and algal waste (Kumar et al. 2020a).

Biochar has large surface area, small bulk density, strong adsorption capacity, high stability, and diverse structural properties (Bolan et al. 2021; Lyu et al. 2016). Production of biochar is also environmentally and economically feasible (Kumar et al. 2020b; Ahmad et al. 2014; Ramola et al. 2021a). It is of multifaced utility as has been used for adsorption and treatment of varied pollutants from water such as polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), dyes, pharmaceuticals, nutrients, pesticides, and trace metals (Kumar et al. 2020c; Yao et al. 2012; Wathukarage et al. 2019; Ramola et al. 2020b, 2021a, b).

The major raw materials for the production of biochar are biomass-based wastes. The choice of raw material for the preparation of biochar is also a key component in characterizing and classifying the biochar. Biomass is referred as an organic, complex biological material derived from living organisms. It is categorized as woody biomass and non-woody biomass (Tomczyk et al. 2020). The woody biomass comprises natural biomass residues obtained from forestry and trees that have high calorific value, low moisture content, high bulk density, and low ash. Non-woody biomass comprises mainly agricultural wastes, especially crop residue, animal wastes, industrial solid, and urban wastes that have high moisture content, low calorific value, high ash content, and low bulk density (Jafri et al. 2018). The moisture content in these raw materials is prominently responsible for the biochar formation. If the moisture content is more in raw material, then it not only reduces the calorific value but also requires more energy for pyrolysis and hence inhibits the biochar formation. Therefore, for production of efficient and economically viable biochar, the moisture content should be low (Tripathi et al. 2016).

Different types of wastes produced as agricultural by-products and crops residues including wood wastes are characterized as efficient raw material for the production of biochar (Lyu et al. 2020). The conversion of raw material to biochar is carried out by thermo-chemical processes which usually includes pyrolysis, gasification, and hydrothermal carbonization (Wang et al. 2018; Ramola et al. 2020a). The biomass contains different constitutes like lignin, cellulose, and hemicellulose which is responsible for the different amount of biochar produced during pyrolysis

(Xie et al. 2015). The selection of raw material biomass affects the overall yield, content, and structure of biochar. Generally, for high biochar yield, a high lignin containing raw material is preferred. On comparing the yield of biochar from different raw materials, the animal-based biomass shows the best results because of its high inorganic components that prevent the loss of volatile substances which is responsible for the mesoporous structure within the biochar (Pan et al. 2020). The activation and adsorption properties of biochar depend on the elemental content present in it that forms the relation between nitrogen and double bond oxygen holding functional group of biochar on its surface (Rajapaksha et al. 2016). This elemental content changes at high pyrolysis temperature that results in increase of aromatic properties which mainly increase the carbon (C) content and decrease the polarity due to the decrease in the content of hydrogen (H) and oxygen (O). In general, biochar prepared using wood waste, sewage sludge and livestock manure have high C and O content in comparison to other raw materials (Pan et al. 2020).

2 Biochar Characterization

Characterization of biochar is done to understand the properties of biochar for its use in various purposes. In this context, on November 2015, International Biochar Initiative (IBI) has issued guidelines for defining biochar properties to be used in soil. Similarly, the European Biochar Foundation (EBC) has issued guidelines for production of biochar as agricultural amendment. These guidelines mostly focus on the production of biochar and its properties according to the need without compromising its utilities (Igalavithana et al. 2017). To evaluate various properties of biochar, generally five preferable characterization methods have been reported such as physico-chemical, surface, molecular, proximate, and ultimate analysis (Fig. 1).

3 Classification of Biochar

Unlike characterization, the classification of biochar is also related with the selection of biomass and its constituents. Classification can be carried out on a different basis, but majorly the carbon content is accepted prominently. On the basis of carbon content, the biochar is classified into three groups, i.e., biochar with high carbon content (BHC), biochar with medium carbon content (BMC), and biochar with low carbon content (BLC) (Hu et al. 2021).

BHC is produced from unprocessed raw materials like bamboo, wood, grass, and agricultural residues. BHC has carbon content >75% and higher ash content, which illustrate its impact on soil improvement and yield of plant biomass. Whereas the biochar having low ash content shows high porosity and increased carbon stability in the soil. It is suitable for the remediation of contaminated land and also as a supplement to animal feed (Hu et al. 2021). BMC is composed of mixture of unprocessed
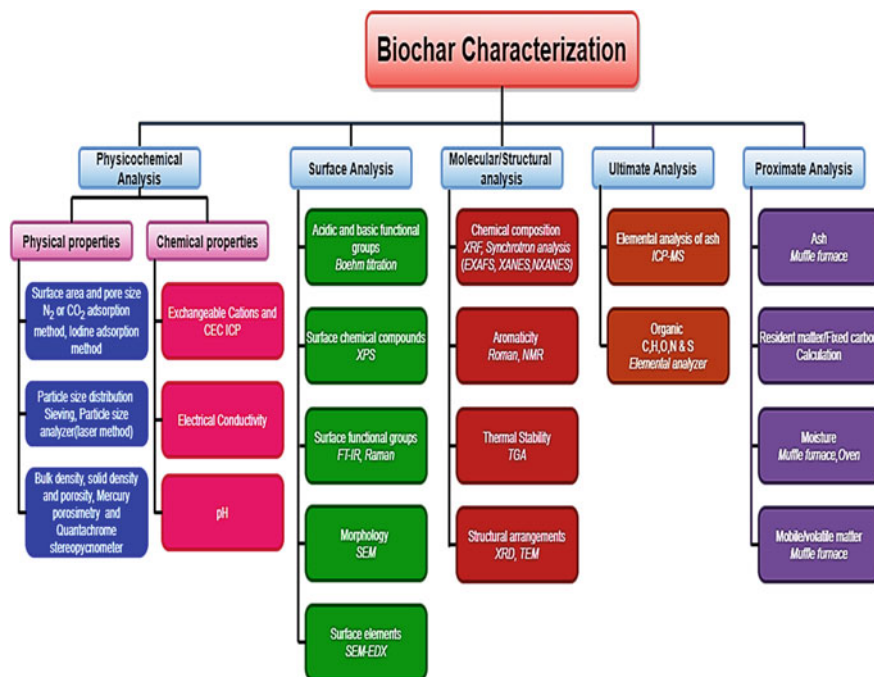
Fig. 1 Schematic representation of biochar characterization methods

raw materials (wood, bamboo, and mineral mixtures) and agricultural crops residues. This has moderate carbon content (approximately 55%) and used mainly as additive in livestock manure processing and bioenergy production (Hu et al. 2021). BLC is prepared by sludge, food waste, crop residue, manure, and wood mineral mixtures. This has < 30% of carbon content which can be used (post balancing the elemental concentration and adjustment of pH) as a major source of micro and macronutrients for agricultural crops and plants (Ghosh et al. 2016).

On the basis of requirement and availability of biomass, the biochar can be produced via various methods such as pyrolysis, hydrothermal carbonization, gasification, etc. (Kumar et al. 2020b, c; Ramola et al. 2020a). Due to an increase in pyrolysis temperature carbon graphitization takes place in the layers of biochar which is associated with deoxygenation and dehydration of biochar and it progressively results in the atomic H/C ratio and O/ C ratio of the biochar (Bogusz et al. 2015; Li et al. 2017). Different instruments are used for comprehensive structural and functional characterization of biochar which includes high-resolution transmission electron microscopy (HR-TEM) (Santhosh et al. 2020), X-ray diffraction (XRD) (Shaaban et al. 2013), Raman spectroscopy (Xu et al. 2020), energy-dispersive X-ray (EDX) spectroscopy (Ma et al. 2016), Fourier transform infrared spectroscopy (FTIR) (Singh et al. 2016), field-emission scanning electron microscopy (FE-SEM)

(Ma et al. 2016), inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Pourret and Houben 2018). BET is extremely helpful for the textural analysis of biochar (Zhu et al. 2018). Carbon nanostructure can be characterized by high-resolution transmission electron microscopy (HR-TEM) and XRD (Martin et al. 2019). The degree of weight gain and loss of the biomass raw material is determined by an analytical method popularly known as Differential thermal gravimetric analysis (DTGA) (El-Sayed and Mostafa 2014; Ramola et al. 2020b).

4 Raw Materials for the Preparation of Biochar

The type of raw material plays a vital role in the determination of the biochar properties (Amonette and Joseph 2009). Cellulose and hemicellulose contribute in producing bio-oil whereas, lignin contributes in producing high yield of biochar (Kan et al. 2016). Gymnosperms plants contain 47–50% carbon content whereas, angiosperm plants contain comparatively high cellulose to lignin ratio and they both are suitable as raw material for biochar (Pandey 1999). Residues from mill and forests are also proved to be potential raw materials for the production of biochar. Residues from agricultural lignocellulosic biomass are also used for biochar production for example sorghum (Kotaiah Naik et al. 2017), corn stover (Zhu et al. 2015), sugarcane bagasse, bamboo, rice husk (Ramola et al. 2014, 2021a, b), wheat straw (Junna et al. 2014), forest residues thinning (Puettmann et al. 2020), cardboard waste (Ghorbel et al. 2015), paper waste and paper mill sludge (Yoon et al. 2017), switchgrass (Koide et al. 2018), paper mill waste (Van Zwieten et al. 2010), logging residues (Campbell et al. 2018), municipal solid waste (Jayawardhana et al. 2016), wastewater organic sludge (Bolognesi et al. 2021), energy crops (Blanco-Canqui 2016), banana peduncle (Karim et al. 2014), and aquatic biomass (Mokrzycki et al. 2021).

4.1 Effect of Type of Raw Material on Biochar Properties

Plant biomass used as raw material for biochar preparation is composed of hemi-cellulose, cellulose, and lignin. The relative amount of these compounds in the raw biomass determines the extent of chemical, physical, and structural changes in the biochar during pyrolysis. Weight loss at low temperature is due to the evaporation of water. These components are gradually pyrolyzed with the increase of temperature. The major decomposition process occurs between 200 and 500 °C. Hemicelluloses degradation happens in the low temperature range from 200 to 260 °C, whereas cellulose degradation occurs between 240 and 350 °C. Lignin is much more recalcitrant (degradation between 250 to 500 °C) than hemicellulose and cellulose during pyrolysis (Lehmann and Joseph 2015; Fan et al. 2017; Wani et al. 2021). It has been reported in most of the studies that the biochar derived from herbaceous biomass for example grass, corn stover, sugar bagasse, hydrophytic weeds, and wheat straws

showed appreciably high content of inorganic elements than the biochar obtained from woody biomass (Bakshi et al. 2020). The biochar derived from microalgae was found to have highest fixed carbon, i.e., 24.8% followed by Camellia oleifera shells (21.95%) and pruned plum (21.07%) (Voca et al. 2016; Fan et al. 2017; Hossain et al. 2017).

4.1.1 Effect of Raw Material on Surface Area and Porosity

Similar to pyrolysis temperature, the properties of biochar are also equally affected by the composition of raw material. Ippolito et al. (2015) have described the selection of raw material as the most important influence on final biochar properties. Biochar prepared from lignin rich biomass is porous with large surface area, high aromatic organic components, and low ash content. Thermal cracking which contributes to surface area expansion occurs frequently in wood biochar as a result of unequal shrinkage of interior parts and exterior surfaces of the inflexible wood masses. During the pyrolysis, micro-molecule organic compounds are increasingly lost which create voids within the biochar matrix and consequently increases overall surface area and pore volume (Quicker and Weber 2016). Whereas, biochar from manures/biosolids has low surface area due to deformation, structural cracking, or micropore blockage (Ahmad et al. 2014), along with less distinct porous structures in the raw material itself as compared to wood-based biochar (Ippolito et al. 2015). The herbaceous raw material contains high percentage of silica components that often produce porous biochar with high ash composition. Animal manures as starting raw material are not very porous but it is shown that their porosity improves through pyrolysis (Yavari et al. 2015).

In general, for biochar production, a biomass with high lignin content yields macroporous structure, whereas biomass with high cellulose content yield microporous structures (Li et al. 2017). Another, important factor that can further deteriorate the surface area and pore volume is prolonged pyrolysis time which can cause melting, shrinkage, and elemental realignment. This destruction may be more pronounced for softwood biomass, resulting in a reduced adsorption capacity (Yavari et al. 2015; Ramola et al. 2021a). Biochar also tends to show different surface functionalities in relevance with hydrophobicity and hydrophilicity in correspondence with basic and acidic environmental conditions. The biochar contains stable and unstable C composition which is also responsible for surface chemistry and the varied heterogenous nature of biochar (Batista et al. 2018).

Surface chemistry plays a very integral role in influencing the surface behaviour of biochar in different environments for example it shows hydrophilic functionalities in an acidic environment and hydrophobic functionalities in basic environment (Ebrahimzadeh Omran et al. 2020). The studies were done on pine wood biochar and rice husk biochar showed that adsorption of Pb by pinewood biochar showed effective adsorption than rice husk biochar (Liu and Zhang 2009). During pyrolysis the dehydration of the biochar takes place which simultaneously increases the pore space in the biochar. The pore size in biochar is highly variable and is classified as

nanopore, micropore, and macropore, i.e., <0.9, <2 nm, >50 nm, respectively (Li et al. 2017). The preparation of biochar is the most important factor, as the activation process (chemical and physical activation process) used during biochar formation enhances the surface area and porosity of the biochar (Kim et al. 2012; Ramola et al. 2021a).

4.1.2 Effect of Raw Material on Cation Exchange Capacity and pH

In comparison to woody biomass, the biochar prepared from non-woody biomass such as crop waste, grasses, and manures has more CEC and pH. During pyrolysis, formation of oxygenated surface and inorganic functional groups take place, which increases the CEC (Briggs et al. 2012). The treatment of soil with woodchip biochar results in higher saturated hydraulic conductivities than manure-based biochar (Zhu et al. 2015).

The biochemical composition and structure of seaweeds are significantly different from lingo-cellulosic biomass. The seaweed-derived biochar is generally characterized by high yield, nutrient content, and CEC but relatively low organic carbon content and surface area (Roberts et al. 2015). It has been now well-established fact that the O/C ratio is directly proportional to the CEC value of the biochar (Huff et al. 2018). The highest cation exchange capacity is reported in the biochar produced at low pyrolysis temperature. The average obtained CEC at the pH range from 1.5 to 7.5 at 250 °C for grass, oak, and pine is reported to be 51.9 ± 15.3 mol C/kg. Pyrolysis done at 600 °C gives the CEC value in the range of 21.0 ± 17.2 mol C/kg (Mukherjee et al. 2011; Zhou et al. 2018).

The biochar produced from hydrothermal carbonization process leads to the production of organic acids and hence, results in the decrease of pH of the hydro chars (acidic hydro chars) (Quicker and Weber 2016). After pyrolysis, the ash content is increased significantly this results in increase in pH which get enhanced with the increase in degree of carbonization process (Ippolito et al. 2015). The studies done on spelt, nut shells, sewage sludge, grass, miscanthus, manure, and bamboo biochar had pH in the range of 10–12. The pH can also be increased by increasing the residence time for the first 5–10 min of hydrothermal carbonization (Conti et al. 2014).

4.1.3 Effect of Raw Material on Nutrients of Biochar

In general, wood-based biochar contain more C and lower plant available nutrients, manure-based biochar contains less C and more plant available nutrients whereas grass-based biochar typically falls somewhere in between woody and manure biochar (Ippolito et al. 2015). Less than 0.002% of the total N, 2.2% of the total P and 17% of the total K present would be supplied by hardwood biochar, whereas the biochar from

soft wood can supply 27% and 6% of the total P and K present (Dieguez-Alonso et al. 2018; Ippolito et al. 2015). The biochar derived from the animal materials has high amount of trace elements such as magnesium, potassium, calcium, and phosphorus than the biochar derived from plant materials. The comparative studies between wheat straw and pig manure biochar showed that biochar derived from pig manure contains calcium and magnesium in considerable amounts whereas, the biochar derived from wheat straw did not contain these elements in a mentionable amount when elemental studies were done by Xu et al. (2014).

5 Conclusion

As there is a tremendous increase in urbanization and industrialization, huge quantity of solid waste is generated that causes threat to human health as well as environment. In India, about 75–80% of the municipal waste gets collected and out of this only 22–28% is processed and treated whereas the remaining waste is disposed off indiscriminately at dump yards. It is projected that by the year 2031, the MSW generation shall increase to 165 million tonnes and to 436 million tonnes by 2050. One most prominent solution to this increasing problem is to convert the solid waste in biochar. Different raw materials and pyrolysis conditions affect the chemical and physical properties of biochar along with their bulk properties. The increase in the pyrolysis temperature results in the increase in surface area, elemental content, pore size, carbon mass fraction, micropore volume, carbon stability, and fixed carbon. Maximum efficiency can be obtained by optimizing activation of biochar and its properties. Standard characterization techniques can also be used for more insights into the properties of biochar. Some specific points also need to be addressed for example the combined modification methods for different biochar, the determination of the stability of different biochar produced from different raw materials, and final fate of biochar in the environment.

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Biochar Preparation by Different Thermo-Chemical Conversion Processes

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Abstract Conversion of biomass into char has been practiced for centuries and millennia as a way to produce charcoal for cooking or smelting of metals. This relied on simple production processes with low efficiency and poor productivity until the end of the nineteenth century when industrial charcoal production was established. Today, a diverse range of technologies for thermo-chemical conversion of biomass exists, all of which have the potential to produce biochar. In the past decade, a number of designs specifically aimed at biochar production emerged at small and medium scale, driven by the growing interest in biochar as means for atmospheric carbon removal and sequestration. This chapter provides a brief overview of the different approaches to biochar production, identifying key opportunities and challenges, as well as future directions for research, development, and deployment.

Keywords Pyrolysis · Biochar · Gasification · Hydrothermal carbonization · Biomass

1 Introduction

The term biochar and the whole research field are only just over a decade old, but the basic technology for biochar production has been known and used for millennia. Simple charcoal burning processes and dry distillation of wood were the first applications of pyrolysis for thermal decomposition of biomass aimed at production of solid and liquid products, namely, charcoal as a fuel and organic chemicals for wood preservation, respectively. While there has been a vast number of different designs in different geographic locations and at different times, what all of these approaches had in common was the use of predominantly woody biomass that was converted in a batch (rather than on a continuous basis) into the final product(s) by heating in absence or in restricted presence of air.

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One of the earliest pieces of evidence, of using produced biochar, is found in Terra Preta (TP) of Amazon Basin in South America. TP or the dark earth soils are fertile-rich carbon layers of soil that remain interspersed with relatively infertile Amazonion ferrisols**.** Fertile TP are believed to be intentional/unintentional anthropogenic efforts that gave rise to accumulation of large amount of plants and animal debris, ashes, bonfire residues, and several elements (Costa and Kem 1999). There are other well-documented examples of production and application of biochar in agriculture. For example, rice husk charcoal has most likely been used since the beginning of rice cultivation in Asia (Ogawa and Okimori 2010). The liquid product of this charring method was used for a variety of purposes, including the preservation, house painting, caulking for sealing wood barrels, shipbuilding, and attaching arrowheads to spear shafts (Gabhane et al. 2020).

The traditional methods of biochar production involved burning of piled wood with limited air in a closed soil pit. Another method involved burning of biomass in open space followed by immediate covering of the half-burned biomass with soil (Gabhane et al. 2020). Until the end of nineteenth century, biochar was prepared by handmade reactors. These reactors were traditional in their make containing clay, bricks, and metal such as clay burner, brick kilns, firebrick pits, and iron retorts. With modernization came the application of steel ovens which increased the production and improved the quality of biochar with better chances of recovery of volatile compounds and bio-oil (Emrich 1985; Reilly 1925).

One of the differences between the traditional processes and modern biochar production is the range of raw materials used. While traditional charcoal production or dry distillation required lump wood, modern biochar production can utilize a wider range of raw materials unsuitable for traditional processes, such as agricultural residues (e.g., straws and husks), but also materials not available in the past (e.g., sewage sludge and anaerobic digestate).

When heated in the absence of air, biomass cannot ignite and burn, releasing gaseous products of combustion. Instead, it undergoes thermal decomposition of the organic constituents. In the first step, biomass loses its moisture at temperatures up to approx. 150 °C, this is then followed by a volatilization of the most labile biomass components, such as extractives, and gradual decomposition of the key biomass constituents, i.e., hemicellulose, cellulose, and lignin. The least thermally stable component of biomass is hemicellulose that starts decomposing already at 250 °C and its peak decomposition rate is achieved at around 325 °C. This is followed by the decomposition of cellulose that starts at temperatures around 350 °C and peaks at 425 °C. The most thermally stable of the three organic components of biomass is lignin with a wide decomposition temperature ranging between 300 and 800 °C. The exact decomposition behavior of any biomass is therefore influenced by the proportion of the key organic constituents, as well as their specific characteristics, such as lignin type that differs with biomass type. In addition, inorganic constituents in biomass (ash) also play an important role in its thermal decomposition, catalyzing certain reactions that can either enhance or suppress biochar formation, depending

on the nature of the minerals and the process conditions. Therefore, a good understanding and careful selection of biomass raw materials is important for production of engineered biochar (Wani et al. 2021).

The thermo-chemical decomposition of biomass yields three co-products: solid biochar, liquids, and gases. The relative yields depend on the type of the process used, with gasification yielding most gas products, fast pyrolysis most liquid products, and slow pyrolysis and hydrothermal carbonization yielding most biochar (Ramola et al. 2020). As alluded to in the previous paragraph, the yield and properties of the products are also dependent on the biomass raw material as well as specific process conditions, such as temperature and residence time which vary within certain characteristic operational envelope for each of the main process, and will be further discussed in corresponding subsequent sections of the chapter dedicated to individual technologies.

Traditionally, biochar would either be the main target product of a biomass conversion process, such as in charcoal production by slow pyrolysis, or a by-product of a process aimed at production of liquid or gaseous products, e.g., fast pyrolysis or gasification. Another approach to biochar production is that of a biorefinery, producing a range of solid, liquid, and gaseous co-products, thus maximizing the efficiency of biomass utilization.

2 Biomass Pyrolysis

2.1 Overview of the Pyrolysis Process

The term "pyrolysis" is derived from two words, pyro, a prefix based on Greek "pyr", meaning "fire" and lysis "a process of disintegration or dissolution". It is a process where in the absence of oxygen carbon-based organic matter decomposes because of heating to high temperatures, typically above 300 °C, yielding a wide range of solid, liquid, and gaseous co-products. The process involves a series of complex reactions involving bond breakages, resulting in a release of gaseous and volatile compounds with smaller molecular numbers, as well as formation of new bonds during condensation reactions resulting in formation of large aromatic carbon structures within biochar and heavy tar components. In most pyrolysis processes, there are two stages of pyrolysis. During primary pyrolysis, biomass decomposes into primary products that are released into the environment of the reactor where they are likely to undergo further reactions as part of the secondary pyrolysis process. The secondary pyrolysis process involves reactions of primary pyrolysis products with each other in the gas phase, as well as between the gas and solid phase (biochar), typically reducing the yield of liquid co-products, and increasing the yield of char and gases. The extent of the secondary pyrolysis reactions can be controlled by the design of the process, based on requirements.

2.2 Slow Pyrolysis

Traditional charcoal production processes are a typical example of slow pyrolysis, with very low heating rates, typically around 100 °C/h or even lower, and long residence times, in the order of hours or even days. This provides sufficient time for larger biomass particles to get heated throughout and undergo pyrolysis, thus making it suitable for conversion of lump wood and similar biomass raw material. Slow pyrolysis is typically carried out in batch units, such as earth mounds, brick kilns, or steel retorts of different designs. The operation involves loading of biomass into the unit, sealing of the processing unit, to avoid ingress of air and therefore combustion of the biomass, followed by heating. Heating can be supplied either externally, typically using a fire around the steel retort that heats the vessel and its content, or internally, where some air is allowed into the unit at the start of operation, providing sufficient oxygen for combustion of a fraction of the biomass batch, which then provides the energy needed to drive the pyrolysis of the remaining biomass once the air supply is stopped. Pyrolysis units with internal heat supply yield less biochar per unit of raw material inputs and some of the raw material is combusted at the start of the operation. On the other hand, retorts with external heat supply can utilize other sources of heat, such as combustion of agricultural residues and waste, as well as residual process heat, e.g., from combustion of pyrolysis vapors, or another combustion unit or high-temperature industrial process. As a result, retorts typically provide higher biochar yields as none of the feedstock in the retort is combusted.

There are many different designs of batch slow pyrolysis processes, ranging from the traditional charcoal burning kilns to modern steel retorts. Examples, detailed descriptions, and discussion can be found elsewhere (Emrich 1985).

Slow pyrolysis is typically carried out in individual batch units processing one batch at a time, especially for kilns. For larger operations, several units can be operated simultaneously, with each unit being at a different stages of the cycle, thus approximating a continuous production as at any point in time there is a unit that has completed the charring process and can be emptied and re-loaded. Such operations offer higher efficiency due to minimal or no downtime irrespective of whether kilns or retorts are used. When using retorts, a further improvement can be achieved by interlinking the units and staging their operation in such a way that the gas produced during pyrolysis in one unit can be used to heat up another unit that has just been loaded with new raw material, and thus initiate the pyrolysis process. In this way, the consumption of external fuel can be considerably reduced, and the efficiency of the overall operation can be improved. The number of individual units required for such semi-continuous operation depends on the duration of the pyrolysis step as well as other key steps in the process, such as charging and discharging of the units, which are related to the size of the units. The larger the number of units in the sequence, the closer the process approximates a continuous pyrolysis unit. The batch-wise nature of operation means that opportunities for process automation in many designs are limited, certainly for kilns) and as a result the operations can be

very labor intensive, often involving working in hazardous conditions (presence of fine dust, volatile organic compounds, toxic gases, etc.).

A special type of a slow pyrolysis process is the so-called flaming pyrolysis or flame-curtain pyrolysis. It owes its name to the fact that volatiles released from biomass during the process are allowed to react with air and therefore burn and form flames above the solid biomass and biochar. By controlling the flow of air, it is possible to minimize combustion of the solid biochar and restrict it only to the combustion of volatiles which in turn provides the heat needed for the pyrolysis process. This process, due to its simplicity and low costs, is typically used in rural areas for a small-scale biochar production (Cornelissen et al. 2016), but larger industrial units utilizing the flame-curtain pyrolysis principle are now available on the market.

2.3 Intermediate Pyrolysis

There is no clear boundary between slow pyrolysis and intermediate pyrolysis, but a notional divide can be drawn based on achieved heating rate and mean residence time of solids in the pyrolysis reactor. Intermediate pyrolysis units would typically achieve biomass heating rates in the order of 100 °C/min or higher and mean residence time of solids in the pyrolysis zone in the order of minutes to tens of minutes. To meet these criteria, biomass needs to be reduced in size to allow fast enough heating of the entire particle so that the desired level of conversion is achieved within the residence time in the pyrolysis zone. Particle sizes between a few millimeters and tens of millimeters are most commonly used. Intermediate pyrolysis is typically carried out in continuous pyrolysis units where an uninterrupted stream of biomass is fed into the pyrolysis reactor and a stream of products is recovered from the reactor also on a continuous basis. This makes intermediate pyrolysis technologically a more complex process, both in terms of equipment and operation. On the other hand, the continuous processing units offer higher efficiency and better product quality control and offer the potential for a high degree of automation, reducing labor requirements and improving working conditions.

There are three major types of processes in this category, the rotary kiln, auger reactor, and vertical moving bed reactor. The main difference among these is the way in which material is moved through the pyrolysis zone, and a large number of variations in their basic design exists, distinguishing units offered by different manufacturers. Each of the different types of units offers certain advantages for biochar production, but also has its constraints and limitations.

The rotary kiln is a design commonly used in the processing industry, e.g., driers, cement kilns, waste processing, etc., at a range of scales, from small units processing a few hundreds of tons of material per year to units processing hundreds of thousands of tons of material per year. This technology is very flexible in terms of biomass raw material type and particle size, and can easily handle particles smaller than a millimeter as well as particles several centimeters in size. In its simplest form, rotary kilns consist of a rotating steel cylinder that is heated internally or externally by hot

gases from combustion of auxiliary fuel. The rotary kiln reactor axis is inclined at a slight angle to encourage material flowing from the entry point toward the exit. The way particles move inside the rotary kiln and therefore their residence time in the reaction zone are dependent on a number of parameters, such as the particle shape and size, the material density, speed of rotation of the kiln, the angle of incline, etc. More complex rotary kiln designs can include various additional features inside the rotating cylinder, such as baffles and paddles (in drum pyrolizers) that adjust the way material flows inside the reactor with the aim to improve heat transfer, modify residence time, etc. Detailed discussion of the mechanisms and implications for design of rotary kilns is beyond the scope of this chapter and more details can be found elsewhere (Boateng 2015).

The auger reactor, also called the screw reactor, is another common design in the processing industry, mostly used in units on small-to-medium scale. The reactor consists of a stationary steel outer tube containing an auger that moves material forward as it rotates. When used for pyrolysis, the heat needed for the process is supplied either externally through the reactor wall or, in some cases, internally from the heated auger inside the reactor. Augers of different designs with constant or variable pitch can be used, depending on the material being processed, the desired heating rate and residence time, etc. Some designs utilize twin or even multiple interlocking augers to achieve desired processing conditions. Individual auger pyrolysis reactors can also be stacked to achieve a longer overall residence time without the need for a long single reactor. This stacking also allows for use of different processing conditions in each of the stages which can be advantageous for some types of biomass and biochar. Auger reactors are most often used for small-to-medium size pyrolysis units as further scale-up is complicated by mechanical issues related to operation of moving internal parts (auger) in a high-temperature environment with small clearances.

The third type of process, vertical moving bed reactors (Zhang et al. 2018), often does not have any moving mechanical parts in the reactor itself and the material fed at the top of the reactor moves downward through the reactor just by the force of gravity, with the speed of movement controlled by the discharge rate of the biochar at the bottom of the reactor. This design allows for a considerable scale-up and offers flexibility in terms of biomass used and processing conditions required. One particular challenge associated with this type of reactor is ensuring that all the particles move through the reactor in a similar way without creation of hot or cold spots as this would result in increased heterogeneity in the biochar quality. It is therefore important to design the reactor for a specific type of raw material and ensure that the raw material and its particle size and shape is within the scope of the particular design. Some smaller unit designs, such as the multiple-hearth reactor, include mechanical moving parts in form of trays that distribute biomass in the reactor among a number of trays spaced vertically along the reactor axis, with biomass cascading down from the top of the reactor. This design allows for uniform distribution of the material through the reactor and good interaction with hot gases in the reactor.

2.4   Fast Pyrolysis

Unlike slow pyrolysis technology and to some extent intermediate pyrolysis technology that have been in use for over a century in industrial installations, fast pyrolysis technology was developed in the second half of twentieth century with the aim to maximize the production of liquid biofuels from lignocellulosic biomass. This preferential production of liquid products requires rapid heating of biomass followed by rapid quenching of the volatile products (Bridgwater 2012). Typical fast pyrolysis reactors operate with heating rates of several hundred °C s^{-1} and at temperatures between 400 and 600 °C. Such fast heating is achieved by using small biomass particle size, typically less than 2 mm in reactors with high heat and mass transfer rates. Under such conditions, bio-oil yields of 40–75 wt% can be obtained, depending on the type of biomass used. The need for very fast heating places special requirements on the reactor that has to allow for rapid heat transfer into the biochar particles. This is achieved by a close contact of small biomass particles with a heat carrier, such as hot sand in a fluidized bed reactor or a screw reactor, or a hot metal surface in an ablative reactor or a screw reactor (Bridgwater 2012).

Besides the fast heating, it is also critical to minimize contact time between released volatiles that are very reactive and biochar in the reactor as this would enhance secondary pyrolysis reactions, reducing the yield of liquid products and increasing formation of biochar and pyrolysis gases. The vapors are therefore quickly removed from the hot reaction zone and are quenched and separated from the gas stream in a set of condensers. The produced biochar is often used as a source of energy to power the process, but in principle can be collected and used if another source of heat is available. The typical yield of biochar from a fast pyrolysis process is in the range of 10–25 wt%. Due to the nature of the fast pyrolysis process, biochar obtained from fast pyrolysis has different properties compared to biochar from slow or intermediate pyrolysis (Bruun et al. 2012).

2.5   Microwave Pyrolysis

All the processes discussed so far relied on heat transfer by convection and conduction, and to a small extent radiation, between a high-temperature heat source or carrier and biomass particles. In these processes, heat is transferred from the surface of a particle (that is in contact with the heat source) toward its center. In this situation, volatiles released during the heating travel in the opposite direction, passing through the hot partially or even completely pyrolyzed particle layer on their way to the surface, undergoing secondary reactions along the path. However, there is also another class of processes that utilize microwave radiation as a means for heating biomass particles from within. This type of heating is also referred to as volumetric heating, as particles heat up initially on the inside of the particles, and the heat then propagates toward the surface. As a result, volatiles released inside the particles travel

through a yet unreacted biomass at lower temperatures and therefore do not react as extensively as in case of conventional heating (Mašek et al. 2013).

Microwave heating can be adopted to different reactor designs mentioned in previous sections depending on specific requirements, and both batch and continuous processing units have been developed at a range of scales. Unlike processing using conventional heating provided by combustion of part of the pyrolysis gas and vapors, microwave reactors require electricity as the main source of energy. This presents some advantages as well as challenges. The challenges are related to the cost of electricity and its carbon and environmental footprint. As mentioned earlier, units utilizing conventional heating can use pyrolysis co-products to supply most if not all the energy required by the pyrolysis process without the need for external energy sources (except for small amounts of electricity for auxiliary systems). Microwave pyrolysis units cannot easily do this as it would require electricity generation from the co-products, and while this is feasible, it involves additional equipment and therefore costs. Therefore, the electricity would be most likely sourced from the grid, or alternatively other local sources, such as renewable energy installations. Where electricity comes from a grid with high emission factors, this has a negative impact on the overall carbon balance of the process. On the other hand, where renewable energy with low emission factors is used, this has a significant positive impact on the carbon balance (Gronnow et al. 2013). The advantages of microwave pyrolysis relate to a large extent to the easy control of the process, where the amount of power and its delivery to different parts of the unit can be easily controlled and monitored, unlike heating using hot combustion gases, offering flexibility in terms of processing conditions.

3 Biomass Gasification

The primary objective of biomass gasification is to produce gas rich in combustible gases, such as H_2, CO, CH_4, etc., depending on the intended use of the gas, such as chemical synthesis or combustion for heat and power. As a result, the process is designed, and is operated in a way that minimizes production of solid carbonaceous residues. Nevertheless, there are technical and economic limits to the extent to which all the solid carbon can be converted into gas and in practice gasifiers produce a solid residue (typical yield from a few percent to over 10 wt%) with considerable carbon content as well as high mineral content. The yields depend on the biomass raw material used as well as the gasification technology. There are many gasifier designs, but the most common ones include downdraft gasifier, updraft gasifier, and fluidized bed gasifier, with the first two being more commonly used for small-to-medium-scale gasification plants and fluidized bed mainly for large-scale plants (Sikarwar et al. 2016).

Gasification chars, although clearly distinct from chars obtained by pyrolysis, can be considered biochar as they offer carbon sequestration potential when not combusted. The differences between gasification char and pyrolysis char are both

physical and chemical, and stem from the very different processing environments (Fryda and Visser 2015). Gasification units typically operate at much higher temperatures compared to pyrolysis units, with temperatures often above 1000 °C. In addition, the presence of a gasification agent, such as CO_2 or H_2O at the high temperatures, results in dramatic loss of solid carbon and only the least reactive carbon is retained in the solid residue together with a large fraction of ash, originating from the mineral matter in biochar. As a result of the high ash content, the pH of gasification char tends to be higher than that of pyrolysis biochar. In addition, contamination with hydrocarbons (tars) can be an issue in gasification chars, depending on the gasifier type, but also importantly on the way biochar is separated and recovered from the reactor (Rogovska et al. 2012). To obtain biochar with minimum tar contamination, it is necessary to ensure that biochar and the product gas containing tars are not in contact at temperatures where the tar could condense on the biochar or inside its pores.

Due to the relative widespread use of small-scale biomass gasification units, these should not be overlooked as a potential source of biochar, despite the comparatively low yield and specific challenges related to biochar properties and potential contamination. Solutions to these potential problems exist and can be deployed. In many contexts, gasification may be preferred to pyrolysis, due to the higher yield of energy-rich gases that can be used for electricity generation in off-grid locations. It is also possible to tune the process to some extent to yield more or less biochar, depending on the demand (the same is true for pyrolysis).

4 Biomass Hydrothermal Carbonization (HTC)

Hydrothermal carbonization is a thermo-chemical conversion process undertaken in an aqueous environment, and thus is clearly distinct form pyrolysis and gasification that are carried out in gaseous environment. Typical processing temperatures are lower than in gasification, or even pyrolysis, at around 200–400 °C, but the pressure in the reactor is much higher so that water is in critical or even supercritical state, making it much more reactive than under ambient condition. Due to the need for aqueous reaction environment, the HTC process does not require pre-drying of biomass feedstock as is often required for pyrolysis and gasification. Therefore, biomass with high moisture content, such as sludges and slurries, can be used effectively in the process for production of solid carbon products, often referred to as hydrochar.

The distinction between biochar and hydrochar in terms of terminology is based on the difference in the chemical and physical properties of the two materials (Zhang et al. 2019; Kambo and Dutta 2015). Biochar produced by pyrolysis tends to be much more stable than hydrochar, and therefore more suitable for long-term carbon sequestration (Gronwald et al. 2016). However, subsequent thermal treatment of hydrochar can increase its degree of carbonization and yield a material with a higher stability (Liu et al. 2018).

5   Conclusion and Prospects

5.1   An Overview of the Current Status of Biochar Production

In the past decade, a significant progress has been made in research, development, and demonstration of biochar production. It is now possible to buy on the market several different technologies specifically developed for biochar production, and while maturity of many of these is still relatively low, it is likely to improve dramatically with increased number of users, and units produced. This development in technology has seen a shift from biochar production using traditional methods toward more mechanized processes with higher efficiency and lower environmental footprint. While most biochar production technologies at present are at small-to-medium scale, future increased demand for biochar as a method of carbon sequestration, but also as a material with numerous beneficial applications is likely to lead to establishment of larger production facilities associated with industries where large quantities of biomass are available and that would benefit from integration with biochar production in terms of material and energy flows as well as carbon footprint. Potential examples include bioethanol plants, palm oil mills, and other biorefineries where residues, such as empty fruit bunches, sugarcane trash and bagasse, lignin, etc. could be used as feedstock for biochar production, instead of being incinerated. The biochar could then be used within the supply chain back on plantations or fields, storing carbon, and ameliorating soil.

While the basics of biochar production are well understood, there is a pressing need to optimize biochar production processes to maximize their efficiency and to deliver quality biochar (with minimum contamination) at acceptable cost, across different scales. Further research and development is also needed on production of engineered biochar with properties tuned and enhanced for different specific applications. This requires collaboration between scientists from different disciplines, engineers, and industry, due to the complex mechanisms involved in biochar formation and interactions between biochar and its surroundings. Therefore, we are likely to see a further acceleration in applied research related to use of biochar in a growing range of applications, and production of optimized biochar using different processing conditions, pre-treatment, post-treatment, and additives, as could be observed in the literature already (Panahi et al. 2020; Awasthi 2022). There is also a need for fundamental research to underpin the different applications and importantly to provide further insights into the longevity of biochar carbon storage in different environments to enable its full implementation on carbon markets.

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Engineered Biochar: Preparation and Characterization

Physical Treatment for Biochar Modification: Opportunities, Limitations and Advantages

Prathmesh Anerao, Gaurav Salwatkar, Manish Kumar, Ashok Pandey, and Lal Singh

Abstract Biochar is a thermo-chemically synthesized/fabricated product of biomass. Recently, biochar applications have spanned into various disciplines such as environmental remediation, water purification, catalysis, tissue engineering, additive in organic waste compost, electrode material and modifier, etc. Modification of biochar is done for specific applications. It brings out the activation of the raw biochar through physical and chemical treatments. Physical modification is frequently done to achieve the superior quality of biochar. In recent years, the application of physical modification method has gained attention as a cost-effective and greener method. The current chapter comprehensively describes the recent developments in physical treatment processes of biochar, opportunities, challenges along with future prospects.

Keywords Biochar · Biomass · Physical activation · Pyrolysis · Environmental remediation

1 Introduction

Rapid upsurge in urbanization and industrialization led to the adaptation of chemical-based agricultural-crop production since green revolution (Mishra et al. 2020). This has caused increased heavy metals, persistent organic pollutants (POPs) and pesticides into the environment and food chain (Bolan et al. 2022; Nie et al. 2020; Sun et al. 2020). For the safety of human health, food chain and environment, the World Health Organization (WHO) has raised it as a matter of serious public concern (WHO 2017). The depletion of soil fertility and productivity is caused due to use of agrochemical products in farming (Maddalwar et al. 2021; Lal 2015). Soil pollution

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has also caused decreased soil organic matter (SOM), imbalanced nutrient avail-ability, increase global soil acidity by 30% and soil salinization by 20% (Agegnehu et al. 2017). This concern of soil nutrient depletion is directly associated with the world's food insecurity. Therefore, many conventional methods are being used for the remediation of these agrochemicals for quick and better productivity. Methods like ion exchange, chemical precipitation and adsorption are used for the removal of chemical residues from the soil but they are neither so effective nor very econom-ical (Kumar et al. 2021a; Oliveira et al. 2017). Furthermore, conventional sustainable agricultural amendments like composts and manure utilization are frequently used to improve the productivity. However, long-term application of these has led to increase in ammonia and methane level in soil which led to the upsurge of serious problems like contamination of groundwater and, emission of greenhouse gases (GHGs) (Awasthi et al. 2019). In this case, there is a need for the development of more sustainable and improved agricultural systems which would be utilized for uplifting the rural economies and also establish the proper global agriculture management (Kumar et al. 2021c; Kammann et al. 2015).

Recently application of biochar as adsorbents, additives and soil amendments has gained attention due to its green and cost-effective nature (Kumar et al. 2021b; Mishra et al. 2021; Ramola et al. 2013). Biochar is a porous carbonaceous material produced by thermochemical conversion of biomass (Bolan et al. 2021; Kumar et al. 2020b). In this process the carbon-rich biomass (raw material) is thermochemically decomposed in no or less oxygen environment. Woody biomass (Fuke et al. 2021), cattle residues, manures (Mishra et al. 2021), agriculture waste (Ramola et al. 2021), algae (Kumar et al. 2020a), sewage sludge (Kumar et al. 2020b) and municipal wastes (Kumar et al. 2020c) are generally used as raw material for synthesis of biochar. The chemical composition of biochar depends on the pyrolysis temperature and the type of raw material used (Bolan et al. 2021; Ramola et al. 2020). The reaction atmosphere (either oxidative or reductive), heating rate and duration are also few factors which play major role in the properties and further application of biochar (Mandal et al. 2021). Thermal treatment of biomass at high temperature produces biochar along with biofuels and syngas as by-products. In thermal treatment (<400 °C), chemical changes occur in the plant biomass for attaining structural stability which can be identified and confirmed by Fourier Transform Infrared (FTIR), thermal or elemental analyser Nuclear Magnetic Resonance (NMR), etc. (Qian et al. 2019; Mandal et al. 2021). To improve the efficiency of pristine biochar, post modification is desirable.

The activated biochar produced post modification (either physical or chemical) is efficient, cost-effective, eco-friendly adsorbent and its production could counterbal-ance the emission of greenhouse gases because of its ability to store carbon in stable form (Xiang et al. 2020; Bolan et al. 2021). There are several modification/treatments method of biochar such as physical, chemical and biological (Kumar et al. 2020b; Yang et al. 2019). However, application of physical treatment of biochar is considered as most effective and economical. The present chapter provides a comprehensive state of the arts related to physical modification technologies of biochar for its sustainable application. Furthermore, this chapter discusses the opportunities and challenges

associated with physical modification methods of biochar along with prospects for future research.

2 Biochar Activation/Treatment

The pristine biochar does not have prominent physico-chemical and functional properties like surface functional group, surface area, porosity, cation exchange capacity and adsorption capacity in comparison to modified or engineered biochar. These properties can be enhanced by the treatment or activation of biochar that is performed in three ways i.e., physical, chemical and biological (Xiao et al. 2020) (Fig. 1). The activation of biochar improves the efficacy of biochar by improving the content of surface functional groups and removing the undesirable material from it (Huang et al. 2020). In comparison to other activation methods, physical activation is considered as more feasible and sustainable due to simpler process and effectiveness (Kumar et al. 2020b, c).

3 Physical Modification of Biochar

Due to high pyrolytic temperature in oxidative environment, the biomass losses more volatiles and gases and clogs the pores of end products (Liu et al. 2015). Therefore, to remove these carbon portions, and also increase the surface properties of biochar, various physical activation methods are applied (Sakhiya et al. 2020). Physical activation includes a sequence of process which is simplified into two steps i.e., activation and carbonization (Sakhiya et al. 2020). In post pyrolysis (partial carbonization), the raw biochar is activated and carbonized with the help of thermal treatment and gasification using inert gas like H_2 or He, oxidizing medium like oxygen, steam and carbon dioxide. Apart from these, some other methods of the physical activations are also used such as microwave, plasma treatment, ultrasound and electrochemical (Sajjadi et al. 2019).

3.1 Physical Modification Type I—Gaseous Activation

In this process the biochar is exposed to oxidizing agents like steam, oxygen, ozone and carbon dioxide for a desired volume at 700 °C or above. These agents actually penetrate into the internal structure of biochar and widen the opening of inaccessible pores (Sajjadi et al. 2019).
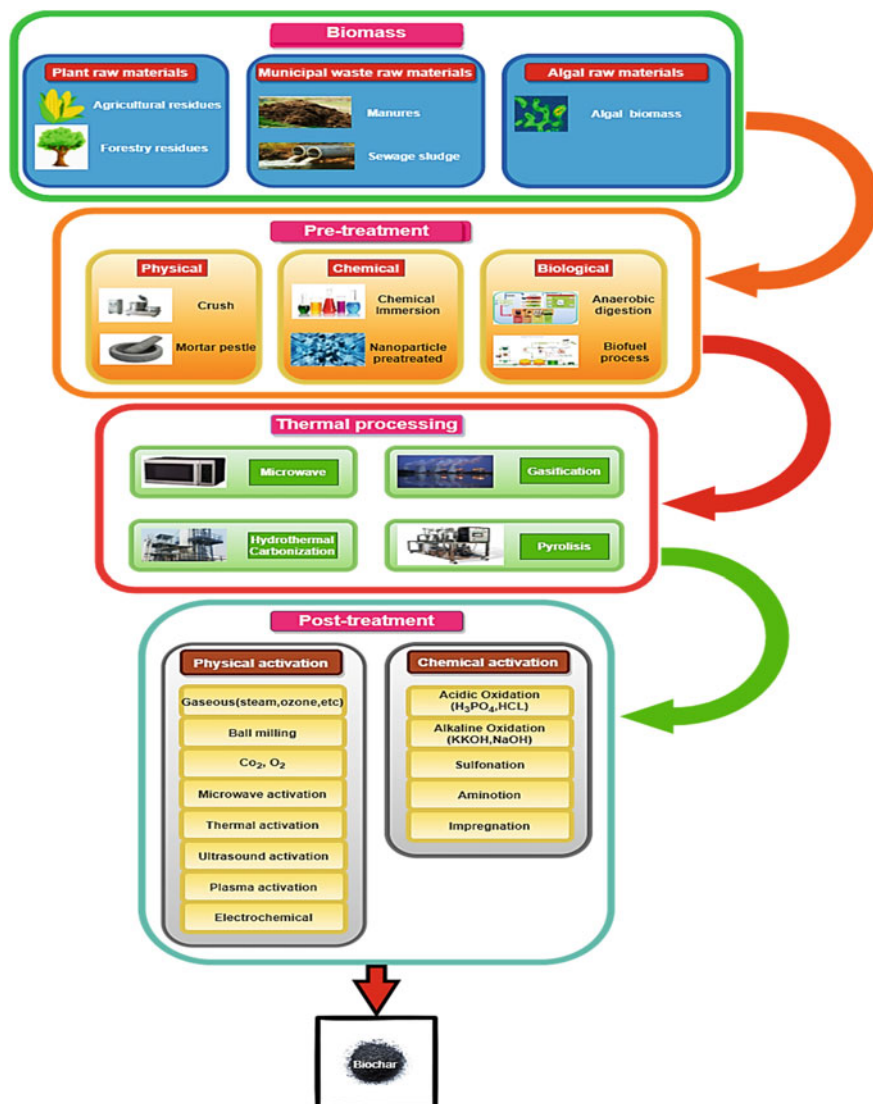
Fig. 1 Schematic representation of biochar tailoring and activation methods

Steam Activation

The depletion of carbon due to the reactions of water–gas shift is correlated with the pore formation in physical activation. The mechanism of steam activation takes place by three crucial steps i.e., diffusion, chemisorption and gas shift reactions (Cha et al. 2016). In the diffusion process, the water molecules get diffused into the pores and get chemisorbed in the carbon active sites with the formation of oxygen surface complex. This is followed by the decomposition of oxygen surface complex by carbon monoxide (CO) which increase the gasification rate by the production

of CO_2. The active states of carbon react with hydrogen and get deactivated. This gasification of carbon through water leads to the formation of micropores in biochar (Sajjadi et al. 2019; Akhil et al. 2021).

A study was done by Shim et al. (2015) to evaluate the physicochemical properties, toxicity and steam activation effect on biochar produced from *Miscanthus sacchariflorus*. The surface area of biochar was found to be less in comparison with the activated biochar, however, no significant difference was observed in the sorption capacities. A comparative model was developed which demonstrates that the steam-activated biochar dominates over the raw biochar in terms of efficiency, acute toxicity and the adsorption efficiency. Similar study was done by Lou et al. (2016) on pine sawdust biochar prepared at 300–550 °C and designed especially for efficient adsorption of phosphate. The results showed removal of phosphate up to 4%, without affecting the pH and other properties of biochar. Another study was carried out by Rajapaksha et al. (2015) for the removal of sulfamethazine (SMT) from the water with the help of steam-activated biochar prepared from invasive plant *Sicyos angulatus L.* The adsorption capacities of conventional and steam-activated biochar were compared and the results showed enhanced sorption capacity of 37.7 mg/g at pH 3, that was 55% more in comparison to pristine biochar (Table 1).

Carbon dioxide activation

CO_2 can be used as an alternative for biomass pyrolysis and activation. Biochar pyrolyzed under CO_2 has more O and N. High rate of carbonization refers to the low H/C ratio and high O/C ratio which shows high hydrophilic nature of biochar

Table 1 Application of steam-activated biochar in removal of environmental pollutants

Raw material	Pyrolysis temperature (°C)	Steam activation temperature (°C)	Contaminant adsorb	Adsorption capacity (mg/g)	References
Bur cucumber plant	700	700	Sulfamethazine	37.7	Rajapaksha et al. (2015)
Tea waste	300	700	Sulfamethazine	2.79	Rajapaksha et al. (2015)
Giant Miscanthus	500	600	Copper	15.4	Shim et al. (2015)
Mung bean husk	550	650	Ranitidine hypochlorite solution	12	Mondal et al. (2016)
Rise husk	700	700	Glyphosate sorption	123.3	Herath et al. (2016)
Softwood	500	800	Copper, Zinc nitrite, Phenol	1.22	Han et al. (2017)
Peanut hulls	500	850	–	19.2	Girgis et al. (2011)

Table 2 Burn off and ash content of biochar feedstock by CO_2 activation

Raw material	Pyrolysis temperature (°C)	CO_2 activation temperature (°C)	Burn off (%)	Ash (%)	References
Oak	500	800	67.1	7.1	Lee et al. (2017)
Peat	–	650	–	73.5	Veksha et al. (2016)
Aspen wood	600	780	76	–	Veksha et al. (2016)
Oil palm shell	400	600	–	23	Abioye and Ani (2015)
Willow tree	700	800	–	11.3	Kołtowski et al. (2017a, b)
Oak	500	700	31.8	–	Shajjadi et al. (2019)
Corn hulls	500	700	32.3	–	Zhang et al. (2004)

(Tian et al. 2017). The CO_2-activated biochar has proven to be potential adsorbent for pollutants and other applications such as soil amendment. The mechanism of biochar (C) activation with CO_2 is done by Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$). Here, the dissociation of CO_2 takes place on carbon surface to form surface oxide which is desorbed from the surface due to the developed pore and the gaseous product CO is adsorbed on carbon active sites and reverts back to the gasification reaction (Lee et al. 2017). These CO_2-activated biochar adsorbents have ability to trap CO_2 and utilize it for enhancing physicochemical properties like microporosity, specific surface area, hydrophobicity and aromaticity. Research by Pallarés et al. (2018) showed the activation of barely straw biochar by two methods: steam and CO_2. Significant increase in the final biochar yield by 43% was observed that proved that the CO_2-activated biochar has much efficacy than the steam activation. Moreover, biochar raw material at different CO_2 activation temperature produces various burn off and ash content as depicted in Table 2.

3.2 Physical Modification Type II—Ozone (O_3) Activation

O_3 has been extensively used in the activation of biochar for oxidizing the carbonaceous materials, as it attacks on both edge carbon atoms and basal plane carbon atoms present in the biochar (Jimenez-Cordero et al. 2015). This is a two-stage process i.e., fast gasification which is followed by the slow surface functionalization. The gasification stage involves the first-order reaction rate, implying that O_3 attack on site-specific graphite that leads to the disappearance of O_3. From the Fourier-transform infrared spectroscopy (FTIR) analysis, the surface oxides which is formed during

reaction are identified, which also includes further detection of aldehydes, ketones, carboxyl, diketones and cyclic carbonyl (carbonates and lactones) present at the edges of carbons graphite. This process increases the acidic oxygen functional groups and oxidation level on the biochar surface. This two-stage activation i.e., gasification and surface functionalization using O_3 profoundly impact the adsorption capacity of activated carbon (Sajjadi et al. 2019). The ozone activation of biochar creates the acidic oxygen functional groups which enhance the cation exchange capacity of soil. O_3 exposure for 10 min on the high internal surface area of biochar could create sufficient amount of surface oxides i.e. about 20–30% of the total biochar mass.

In a study conducted by El-Nemr et al. (2020) the effectiveness of ozone-modified biochar and unmodified biochar derived from the biomass of *Pisum sativum* peel waste was investigated for removal of copper (II) from aqueous media. Here the activation/modification of biochar was carried out by ozone followed by labelled ammonium hydroxide as Pea-B and Pea-BO-NH$_2$. The results showed increased adsorption capacities of activated biochar up to 156.25 mg/g. Further characterization of this activated biochar revealed that the amino groups formed in the modified biochar result in the increased adsorption rate. Similarly, in another study by Jimenez-Cordero et al. (2015), biochar was oxidized in presence of O_3 and then in inert atmosphere it was subjected to desorption of O_2 group at high temperature. High burning off of the biomass due to the high oxidation temperature leads to increase in the number of activation cycle which results in the activation of carbon micropores up to $0.52 \text{cm}^3/\text{g}$.

3.3 *Physical Modification Type III—Thermal Activation*

The decomposition of biomass at high temperature in less oxygen environment is known as thermal decomposition. This process involves various phenomena like decomposition, followed by transformation and biomass molecular structural rearrangement (Dodevski et al. 2017). In this process first the dehydration of biomass occurs at low temperature between 100 and 200 °C, after this the temperature increases gradually that leads to decomposition of organic molecules such as cellulose, hemicellulose and lignin. The complete degradation of all biopolymers and aromatic molecules takes place by the rising temperature. Furthermore, these aromatic ring structure stacks up at high temperature and develops a significant quantity of amorphous and crystalline matters on the biochar surface (Kleber et al., 2015). To remove these stacks and improve the efficiency of biochar, the thermal treatment of biochar occurs at very high temperature (600–1500 °C) for 1–2 h. This treatment removes the hydrogen and oxygen atoms with the release of gas which tends to reduce the biochar yield (Sajjadi et al. 2019) (Table 3).

Table 3 Removal of various contaminants via thermal activated biochar

Biochar raw material	Pyrolysis temperature (°C)	Thermal activation temperature (°C)	Contaminants adsorb	Removal efficiency (%)/adsorption capacity (mg/g)	References
Aspen wood	600	780	Molybdenum (Mo)	93.46%	Veksha et al. (2016)
Willow tree	700	900	Polyaromatic hydrocarbons (PAH)	85.12 mg/g	Kołtowski et al. (2017b)
Coconut	650	800	Polyaromatic hydrocarbons (PAH)	83.4%	Kołtowski et al. (2017b)
Poplar wood	550	750	Organic compounds	83.7%	de Caprariis et al. (2017)
Bamboo chips	700	700	1-Butyl-3-methylimidazolium hexafluorophosphate	0.513 mmol/g	Yu et al. (2016)
Corn straw	500	800	Mercury (Hg^{2+})	1.19 mg/g	Tan et al. (2017)

3.4 Physical Modification Type IV—Microwave Activation

The electromagnetic waves of frequency from 300 MHz to 300 GHz having wavelength of 1 m to 1 mm is termed as microwave (Huang et al. 2016). The major benefit of using microwave as activating agent is that it provides uniform and quick internal heating with the help of three mechanisms i.e., ionic conduction, dipole polarization and the interfacial polarization. Here the heat is provided under temperature gradient via dielectric heating which evenly heats the entire volume of material within limited temperature in defined duration, unlike the other conventional method where heat is transferred from surface to the material causing variation of temperature and conduction phenomena (Wang et al. 2018). This procedure of microwave heating generates tiny microplasma spots, found throughout the reaction mixture which results in enhancing the process of chemical reaction and its local temperature, leading to the activation of biochar. This is majorly utilized in the industry for large-scale production. For proper valorization and energy recovery from the biomass, the conventional methods for pyrolysis and activation would not provide appropriate results but the use of process like vacuum pyrolysis, solar pyrolysis and microwave pyrolysis gives rise to the biomass recycling. In microwave activated pyrolysis the solid biochar is produced as the main product which is significantly used for remediation of environmental pollutants (Foong et al. 2020; Wahi et al. 2017) (Table 4).

Table 4 Application of microwave activated biochar in removal of various pollutants

Raw material	Pyrolysis temperature (°C)	Microwave activation temperature (°C)	Contaminants adsorb	Adsorption capacity (mg/g)	References
Prosopis juliflora	500–600	600	Remazol Brilliant Blue R (RBBR)	83.3	Nair and Vinu (2016)
Peanut hull	500	300–500	RBBR	149.3	Zhong et al. (2012)
Risk husk	700	600	Methylene Blue (MB)	441.52	Foo and Hameed (2011)
Orange peel	700	600	MB	379.63	Foo and Hameed (2011)
Pistachio shell	–	600	MB	296.57	Foo and Hameed (2011)
Cotton stalk	–	680	MB	294.12	Deng et al. (2010)
Pulp mill sludge	400	1200	–	285.7	Namazi et al. (2016)

3.5 Physical Modification Type V—Ultrasound Activation

Sonication has been used widely for the enhancement of mixing and reducing the mass transfer of solid–liquid interactions. The leaching of various minerals like Na, K, S, O, Cl, Fe and Al from carbonaceous material results in the swelling of biochar and improvement in the internal surface area. This action increases the adsorption capacity via modifying the biochar external and internal properties (Kleber et al. 2015). Under the ultrasound irradiation of 1 atm at 65 °C of CO_2/H_2O-based system, the exfoliation of graphite oxide clusters, leaching of minerals, reductive CO_2 fixation and hydrogenation takes place. This ultrasonic treatment induces physical and chemical changes in biochar like water splitting, carboxylation, leaching, hydrogenation and swelling. Ultrasound-treated biochar has higher heating values, reaction rate and high internal surface area (Mulabagal et al. 2015). This method proves to be more effective and efficient as compared to conventional methods because of the much lower energy requirement for activation with increase in carbon content of biochar.

A study was carried out by Nguyen et al. (2021) on biochar generated by the biomass of water bamboo husk (*Zizania latifolia)* pyrolyzed at 600 °C and then activated using ultrasound activation. The ultrasound irradiation improved the reaction rate up to 80% i.e., the reaction gets completed in 4 h by this method instead of conventional method which took around 24 h. In a study Peter et al. (2020) state that the ultrasound-assisted pre-treatment was efficient in the activation and regeneration

of biochar. When the ultrasound of 40 kHz was provided to the pre-treated samples of biochar, the adsorption capacity was increased up to 0.65 mg/g from the conventional technique (0.3 mg/g). The thermodynamic studies state that the ultrasound plays an important role in enhancing the surface area of biochar which results in improved adsorption rate of heavy metals.

3.6 Physical Modification Type VI—Plasma Activation

Like solid, liquid and gas, plasma is the fourth state of matter. It is produced by the electric discharge and does not occur naturally. The voltage and electric current affect the charged as well as neutral particle in the plasma which further affects ionization density and temperature of plasma particles (Karim et al. 2017). This system is classified on the basis of thermodynamic equilibrium state and plasma generation method. Depending upon the application, the thermal plasma reactors have been designed using various equilibrium plasma techniques. These require power levels from 100 W to 10 MW. This is best method for execution of gasification and pyrolysis. On comparing with conventional heating furnaces, the plasma reactor promotes fast reaction rate, high energy density and low formation of tarry compounds. This has a greater advantage of quick start up and shut down which reduce time utilized under pre- and post-process and has benefits like rapid cooling and heating, etc. (Niu et al. 2017). In this process of plasma activation high-energy electron is emitted by the plasma that is responsible for breaking the surface chemical bonds and also expanding the surfaces which directly relates to the adsorption rate of the process. This provides large output in limited time duration with low consumption of resources (Karim et al. 2017).

In a recent study, Zhang et al. (2019a) used plasma treatment technique for the removal of mercury from the biochar. Here, hydrogen sulfide (H_2S) plasma modification was utilized for enhancing biochar productivity for the removal of mercury (Hg). The biochar obtained from wheat straw was utilized and modified using sulphur and carboxyl containing functional groups which form mercury sulfide (HgS) and mercury oxide (HgO) and remove Hg in the form of their sulphides and oxides. For better adsorption, low temperature is preferred which controls the physical and chemical adsorption. This has increased the efficiency of biochar from 26.4% to 95.5%. Similarly, another study was conducted by Wang et al. (2018) for the removal of Hg from non-thermal plasma modification using chlorine active sites. Here various biochar was prepared using rice straws, corn, wheat, black bean, millet, etc. via pyrolysis in high pure nitrogen at 600 °C, where non-thermal plasma modification by chlorine increased the HgO removal efficiently from 8.0% to 80%, which proves the efficiency of plasma treatment.

3.7 Physical Modification Type VII—Electrochemical Modification

The electric field modification can be utilized for enhancement of physicochemical properties of biochar. The electric current is applied accordingly for the enhancement of physical properties like porosity and surface area of biochar. Mostly an aluminium-based electrode in the presence of H_2SO_4 and NaOH solution for limited time period is applied in electrochemical modification of biochar where the acid generates the hypochlorite ions in the presence of NaCl solution and post this electrochemical process the pyrolysis is performed (Jung et al. 2015). These oxidants have the ability of improving the porosity and morphology of biochar. The factors like pH, electrode, and solution play a key role in determining the efficiency of this process. This electrochemical-based system improves porosity and surface area resulting in higher rate of adsorption (Sajjadi et al. 2019).

Moreover, biochar-based energy storage and conversion device is gaining attention these days (Kumar et al. 2020c; Cheng et al. 2017). A study was carried out for electrochemical modification and one-step pyrolysis for preparation of iron-based biochar composite using $FeCl_3$ pre-treated corn straw biomass. This process generates the graphite electrode and developed a sustainable Fe_3O_4 based magnetic adsorbent. These Fe_3O_4 nanoparticles were crystalline having uniform dispersion forming rod-like structure of biochar. This modification contributes to the Pb adsorption and also effectively work on the magnetic waste water treatment by biochar adsorbent (Yang et al. 2019).

4 Limitations of Physical Modifications

Physical modification has several advantages over chemical modification as it does not use toxic chemicals which can affect human health as well as cause environmental pollution. Apart from the benefits, physical modifications consume a huge amount of energy which can directly affect the cost involved in the production of biochar. Also, these approaches make biochar production process non-greener. Moreover, this could make biochar activation process non-compatible and non-economical at commercial scale (Sajjadi et al. 2019).

5 Conclusions and Future Prospects

Currently, diverse applications of biochar are gaining global attention. Biochar has been proved as an environment-friendly, cost-effective, thermochemical product of biomass. Biochar is thoroughly applied as adsorbent for the removal of contaminants from wastewater. It also acts as a good carbon storage material in the soil. However, to

improve the efficiency of biochar, physical modification is desirable. Therefore, this chapter discussed most prominent physical treatment methods which are required for various purposes and be effectively executed.

To achieve the growing demands of biochar application, further studies and developments are required for the commercial advancement in biochar production as current technologies are only favourable for small-scale production of biochar i.e., up to few tons per day. These low productions are unable to fulfil the demand and also lack in proper utilization of by-products of pyrolysis like tar and non-condensable gas. Similarly, the reaction conditions need to be controlled and optimized to increase the production efficiency of biochar and also make the production process more environment-friendly. The modification of biochar in the coming future should be designed according to its targeted applications like to understand the productivity on various agroecosystems and conducting field experiment for monitoring the long-term effects on soil properties. In the future, the biochar should be modified to have long-lasting effect on immobilization of contaminants and increased reusability.

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Chemical Treatments for Biochar Modification: Opportunities, Limitations and Advantages

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Abstract The biochar can be utilized as an efficient adsorbent for contaminated soil and water. However, the practical implementation of biochar in immobilization and removal of contaminants need some modifications. So, recently focus has shifted on production process modification to alter the original structure and surface characteristics in order to achieve high remediation efficacy and to preserve the environment. The application-oriented or outcome-based modified/synthesized biochar is generally termed as engineered/designer biochar. Chemical modifications like acid treatment, base treatment, amination, surfactant modification, impregnation of mineral sorbents and magnetic modification are commonly done as biochar modification methods. In general, the modification methods are widely adapted to obtain enhanced sorption capacity of modified biochar and its practical implementation in environmental remediation. The selection and performance of the modification process depend on contamination type (i.e., inorganic/organic, polar/nonpolar, anionic/cationic, hydrophilic/hydrophobic), land type (industrial/farming), environmental conditions and the objective of remediation. This chapter evaluates and summarizes biochar modification methods, process mechanisms, and their contaminant remediation efficacy in soil and water.

1 Introduction

Biochar is a stable carbon-rich by-product of biomass carbonization in an oxygen-restricted environment (Lehmann and Joseph 2009; Ramola et al. 2014). Biochar applications include C sequestration (Kuzyakov et al. 2009; Woolf et al. 2010),

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adsorption of greenhouse gases (Singh et al. 2010), soil remediation, (Ahmad et al. 2014; Mohan et al. 2014b) soil fertilization (Chan et al. 2007, 2008) and geo-engineering (Wani et al. 2021). The chemical and physical properties of biochar are generally influenced by raw material and pyrolysis conditions i.e., pyrolysis temperature, residence time, heating rate and reactor type. Biochar offers its own set of benefits, including a high carbon content, high cation exchange capacity, broad surface area and structural stability (Rizwan et al. 2016). Biochar dispenses promising adsorption ability allowing it to remove heavy metals and organic contaminants. Physiochemical parameters such as surface area, pore size distribution, functional groups and cation exchange capacity, varying with the preparation settings, determine the adsorption capacity of biochar (Ahmad et al. 2012; Mohan et al. 2014a, b; Gai et al. 2014). Due to the increased micro-pore volume caused by the elimination of volatile organic compounds, biochar generated at high temperatures has a greater surface area and higher carbon content (Chen et al. 2008). However, as temperature rises, biochar yield declines (Xu et al. 2015). This necessitates the formulation of an optimal strategy in terms of biochar yield and adsorption capacity.

The complexity and heterogeneous nature of the chemical and physical composition of biochar make it an excellent sorbent for contaminants (Park et al. 2015; Vithanage et al. 2015a). In spite of the significant contribution of biochar in environmental remediation, the extensive focus of researchers has been witnessed recently on biochar modification. This modification includes altering the surface characteristics and novel structure in order to increase sorption properties for environmental applications (Ok et al. 2015). It is important and necessary to review the scientific research literature on engineered biochar and its after-effects for the ease of future process design and increasing efficacy. It also paved the way for extensive use of modified biochar for environmental benefits and remediation. This article offers a comprehensive summary and critical assessment of the process mechanisms, principles and applications of numerous chemically engineered biochar in view of up-to-date suitable peer-reviewed research work.

2 Chemical Modification of Biochar

The properties of biochar mainly depend on the type of raw material and the thermal profile of the production process. After the pyrolysis process, the developed biochar requires some application-specific modifications in the properties of biochar. The modification of biochar is performed to increase the surface area, introduce the oxygen-containing functional groups and enhance the adsorption capacity and catalytic performance. There are several chemical methods for modification of biochar which includes mainly acidic modifications, alkaline modifications, oxidizing agent modifications, metal salts modification and impregnation of graphene. Different chemical treatments for biochar modifications are depicted in Fig. 1.
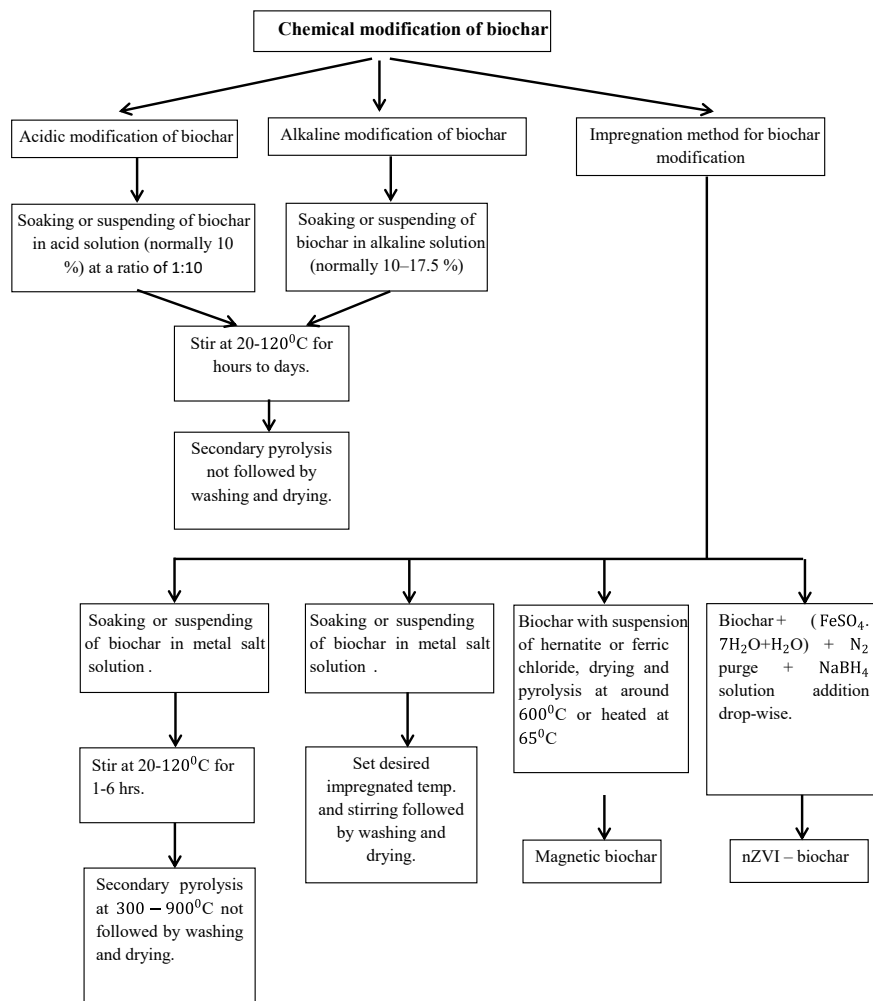
Fig. 1 Process chart of different modification routes of biochar

2.1 Acidic Modification

The primary objective of acidic modification is to remove impurities like metals and ash with the formation of the new acidic functional groups in the biochar. The removal of metallic impurities and ash improves the hydrophilic nature of biochar (Shen et al. 2008). In this modification, biochar is soaked or suspended in an acidic solution in a ratio of up to 1:10 (biochar:acid) at a temperature range of 25–120 °C followed by stirring and washing of biochar (Zhou et al. 2013; Jin et al. 2014; Zhang et al. 2015). The washed biochar is then dried followed by pyrolysis to obtain the desired modifications. The most familiar acidic agents are hydrochloric acid, sulfuric

acid, nitric acid, oxalic acid and citric acid (Rajapaksha et al. 2016). Acidic treatment of biochar increases the H/C ratio and O/C ratio in the biochar due to lower carbon content in the modified biochar. The increased O/C ratio leads to the higher oxygen content in the biochar which results in more acidic functional groups in the biochar. In addition, higher oxygen content decreases the hydrophobicity of the biochar.

Peng et al. (2016) modified the biochar developed from reed using 1 M HCl which effectively reduced ash content in biochar from 29.5 to 11.8%. In addition, acidic modification of reed biochar introduced new hydrophobic sites which significantly increased the adsorption of organic pollutant such as pentachlorophenol. In similar fashion, bamboo biochar treated using 2 M nitric acid developed new functional groups such as carboxylic, nitrogen, phenolic, lactonic and carbonylic groups on the surface of biochar (Li et al. 2014). The acidic treatments of biochar also alter the surface area of the biochar. In some studies, the surface area of biochar increased after acidic modification whereas in some cases it decreased. For example, Peng et al. (2016) modified the reed biochar with HCl and recorded an increase in the surface area from 55.75 to 88.35 m^2/g. On the other hand, Yakout (2015) reported a decrease in the surface area of rice straw derived biochar when treated with 2% sulphuric acid. Similarly, Taha et al. (2014) treated the biochar derived from paddy straw with 1 M phosphoric acid and reported that the surface area of biochar slightly decreased to 517.1 from 522.5 m^2/g. Therefore, it is clear that the change in the surface area usually depends on the concentration of acid, type of acid and type of raw material used for the modification. Similar to the strong acids, weak acids like citric and oxalic acids also develop new carboxylic functional group on the surface of biochar through esterification process however this treatment also decreases the surface area and pore size of the biochar (Lei et al. 2015). However, unlike other studies, biochar modified by oxalic acid (70%) and sulphuric acid (30%) increased the surface area of biochar significantly from 2.31 to 571 m^2/g. This deviation in results could be attributed due to the different corrosive strength of acids.

2.2 Alkaline Modification

Modification of biochar using alkaline reagents improves the physical and chemical characteristics of biochar. The primary objective of alkaline modification of biochar is to enhance its surface area and morphological properties. It also introduces the new oxygen-containing functional groups on biochar surface. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are some commonly used alkaline reagents for alkaline treatment of biochar. The modification process of alkaline modification is similar to acidic modification. In this modification, the biochar is soaked or suspended in different alkaline solutions. The solution is stirred for 6–24 h at 25–100 °C. After that, the biochar is washed using distilled water followed by drying in an oven. To get the desired characteristics, the dried biochar is further pyrolyzed in a nitrogen environment at 300–700 °C for 1–2 h. In comparison to acidic modifications, alkaline modification of biochar generally provides biochar

with enhanced specific surface area, higher H/C and N/C ratios and lower O/C ratio. A Low O/C ratio is an indication of decreased hydrophilic nature of biochar and increased surface aromaticity (Ma et al. 2014). A high N/C ratio leads to the presence of more nitrogen-containing functional groups on the surface of modified biochar. In addition, alkaline reagents have OH^- and NH_2^- ions that enhance the sorption of negatively charged as well as organic impurities from wastewater. Jin et al. (2014) modified the biochar derived from municipal solid waste using KOH and concluded that alkaline modification of biochar enhanced the surface area of biochar from 14.4 to 49.1 m^2/g. Thus, the improved surface area of biochar provides better adsorption capacity of As(V). However, in another study (Sun et al. 2015), the surface area of wheat biochar dropped from 4.4 to 0.69 m^2/g after alkaline modification using KOH. It can be established from the contrasting results of both studies that similar to acidic modification, the surface area of alkaline modified biochar is also a function of the type of raw material and method of modification. On the other hand, alkaline modification using NaOH has proved to improve the surface area of biochar significantly. Cazetta et al. (2011) compared the effect of both catalysts on the surface area of coconut-derived biochar and established that NaOH enhanced the surface area of biochar (2885 m^2/g) higher than KOH (1940 m^2/g). In addition, NaOH has less corrosive effect and is more economic to use as compared to KOH. The modified properties of biochar also depend on the ratio of base and biochar and different type of bases as well. The information about enhanced properties of biochar and mechanism involved due to acidic and alkaline modifications is provided in Table 1.

2.3 *Modification Using Oxidizing Agents*

Biochar modification using oxidizing agents induces formation of new oxygen-containing functional groups. A study on peanut hull-derived biochar prepared by hydrothermal carbonization revealed that the modification using hydrogen peroxide (H_2O_2) especially increases the carboxyl functional groups that results in increased lead (Pb) sorption capacity of biochar (Xue et al. 2012). Another research by Huff and Lee (2016) concluded that modification of pinewood biochar using hydrogen peroxide reduces the pH content from 7.16 to 5.66 along with the increase in oxygen-containing functional groups. They also reported that the modified biochar using an oxidizing agent (>10% of H_2O_2) consists of a lower methylene blue number as compared to the raw biochar. These studies imply that the sorption capacity of oxidizing agent modified biochar varies with the targeted pollutant. So, the implementation of hydrogen peroxide oxidization should be done by considering all properties of targeted pollutants. Potassium permanganate ($KmNO_4$) is also used as a modifying agent to increase the resultant oxygen-containing functional groups in biochar along with the increased specific surface area of biochar about 101–205 m^2/g. The increment in specific surface area of hickory wood-derived biochar by $KmNO_4$ modification ensures enhanced sorption capacity to Pb(II), Cu(II) and Cd(II) (Wang et al. 2015a).

Table 1 Improved properties of biochar due to acidic and alkaline modifications

Modification agent	Pollutant	Changed biochar properties	Mechanisms	Functionalities	References
H_2PO_4, KOH	N/A	Increase of water extractable organic carbon content	Hydrolysis of the ester groups produced during the pyrolysis	N/A	Lin et al. (2012)
H_2SO_4, Malic acids	Sulphamethazine	N/A	Ligand and proton-enhanced processes; increase in surface area by acid treatment	N/A	Vithanage et al. (2015b)
H_2SO_4, KOH	Tetracycline	Increase in surface area and pore volume; higher carbon and oxygen content; lower inorganic ash content	π-n electron donor acceptor (EDA) interaction between biochar surface and aromatic ring	Oxygen functional groups	Lin et al. (2012)
KOH	Cu^{2+},Cd^{2+}	Increase in adsorption capacity	Electrostatic attraction, ion exchange, surface complexation, and/or surface precipitation	Aromatic carbon	Regmi et al. (2012)
KOH	As^{3+}	Increase in adsorption capacity	–	N/A	Jin et al. (2014)
NaOH	Chloramphenicol	Increase of surface graphitic carbon and O-containing groups	EDA and formation of H bonds between N-containing group in CAP and adsorbent surface	Carbonyl and carboxyl groups	Fan et al. (2010)

2.4 Modification Using Metal Salts and Metal Oxides

The modification using metal salts or metal oxides alters the catalytic, magnetic and adsorption characteristics of biochar. The unmodified biochar is difficult to get recycled from the bulk after adsorption. The metal salts or metal oxides are the prominent biochar modifiers as they enable the easy recycling of biochar due to their magnetic characteristics. Iron salts or iron metal oxides modification enhances the magnetic properties of biochar, which can be used for the extraction of biochar after treatment. Biochar has lower anionic dye sorption capacity due to its negative surface charge. Furthermore, metal modification of biochar can increase the surface area of biochar enormously, which leads to higher adsorption capacity to anionic dyes/targeted pollutants. In addition, the metal salts or metal oxides modification enhances the catalytic characteristic of biochar. To increase the catalytic characteristic through the persulfate activation method, metal salts and metal oxides could be implemented individually to produce the metal-biochar composite (Wang and Wang 2018). Ferric hydroxide impregnated bagasse biochar (FeBBg), bamboo biochar (FeBBm) and tyre biochar (FeTy) were used for removal of phosphate and heavy metal i.e. Pb, Hg and Cu. Result of batch study adsorption revealed that maximum adsorption of phosphate was done by FeBBg (Freundlich model) and Pb by FeTy (Temkin model). This demonstrates that impregnation of ferric hydroxide imparted superior adsorption capacity to the biochar (Ramola et al. 2014).

The biochar modification using metal salts or metal oxides can be done by two different methods: (1) The metal salts or metal oxides are initially mixed with biomass, and then pyrolyzed to prepare biochar; (2) The biomass is first pyrolyzed to obtain biochar, then resultant biochar is impregnated in metal salts or metal oxides under prescribed conditions. These methods are equally popularized among researchers for biochar modification and iron (Fe), magnesium (Mg), aluminium (Al), manganese (Mn) are generally used as metal salts (Tan et al. 2016). Samsuri et al. (2013) implemented Fe(III) for rice husk-derived biochar modification for the adsorption of As(III) and As(V). Liang et al. (2017) used MnO_2 for the modification of swine manure-derived biochar for the adsorption of Pb(II) and Cd(II). Nano-composite Fe_3O_4 was used for modification of marine macroalgae-based biochar which results in magnetic characteristic increment (Jung et al. 2016). Liu et al. (2015) have investigated the effect of iron modified corn straw biochar and stated that it improves the phosphorus removal efficiency from aqueous solutions since the modified biochar surface was covered by small granules of Fe_3O_4.

2.5 Modification Using Carbon Nanotubes (CNTs)

Due to high surface area and nanostructure, carbon nanotubes (CNTs) are very efficient for the sorption of contaminant but their high cost and complex synthesis limits their use. There is a scope for using biochar microporous/mesoporous carrier of

carbon nanotubes to synthesize novel, reusable and efficient mediums for sorption of contaminants from water. Inyang et al. (2014) developed a hybrid multi-walled CNT-coated biochar by using the dip-coating procedure. The hickory chips and sugarcane bagasse biomass were placed into different concentrations of carbon nanotube solution and stirred for 1 h using a magnetic stirrer. The solution was further placed in a quartz tubular furnace for slow pyrolysis in N_2 environment at 600 °C. In another study, Zhang et al. (2009) also formulated the carbon nanotubes. The raw material i.e. bamboo was first treated with hydrochloric acid (HCl) before carbonization. After pyrolysis, bamboo biochar was ground using a ball mill and was then mixed into ferrocene and ethanol solution. The solution was then placed into a CVD reactor at 820 °C in a hydrogen and argon environment. A similar method was followed by Huang et al. (2012) for the development of CNT-coated char using ferric acid as a catalytic agent.

The CNT modified multi-walled biochar demonstrated a larger specific surface area and pore volume. The treated biochar showed better thermal stability in comparison to untreated biochar (Inyang et al. 2014). For instance, the specific surface area of biochar derived from bagasse increased from 9 to 120 m^2/g for 0.01% (w/w) loading of CNTs in the biochar. Further increase in CNTs loading (1% w/w) in the biochar increased the surface area of treated biochar up to 390 m^2/g. On the other hand, Huang et al. (2012) reported that the specific surface area and pore volume of carbon nanotubes loaded bamboo char was significantly lesser than untreated biochar. However, more acidic functional groups were observed on the surface of treated biochar. The increment in acidic functional groups resulted in better interaction with Pb^{2+} and the formation of a stable form which increased the sorption of Pb^{2+} on the surface of the composite. Inyang et al. (2014) studied the dye (methylene blue) sorption capabilities of untreated biochar derived from hickory and bagasse and compared them with their CNT-coated biochar. The study concluded that the sorption capacities of CNT-loaded biochar were about two folds in comparison to untreated biochar. This is due to the electrostatic attraction of methylene blue with active binding sites within carbon nanotubes in the biochar. In addition, the modified biochar itself provides active sites for methylene blue sorption after the filling of sorption sites of carbon nanotubes. Even though the sorption capacity of CNT-loaded biochar is much lower than several other hybrid carbon nanotubes materials, the development of CNT-coated biochar is easy and cost economic. Therefore, the scope of CNT-loaded biochar as sorbent for dyes and organic containments removal is promising and inexpensive.

2.6   Modification Using Clay Minerals

Biochar impregnated with clay minerals has better physico-chemical and functional properties (Ramola et al. 2020, 2021). The most common clay minerals are kaolinite, montmorillonite, calcite, dolomite and bentonite. Impregnation of clay minerals is a pre-carbonization process in which instead of biochar, the raw material is thoroughly

mixed with the suspension of clay minerals in the pre pyrolysis stage (Chen et al. 2017; Ismadji et al. 2016; Rawal et al. 2016; Yao et al. 2014). Rawal et al. (2016) mixed kaolinite and bentonite in bamboo with iron sulphate and reported high mineral phase impregnation and Al, Fe and S content in biochar. In similar fashion, Yao et al. (2014) developed montmorillonite and kaolinite impregnated biochar structure of three biomasses (bamboo, bagasse and hickory chips) and reported increased Al, Fe and Na content in the biochar. Chen et al. (2017) reported that treatment of bamboo powder with montmorillonite increased the surface area and pore volume of biochar. The change in surface area and pore volume of biochar may be attributed to the existence of layered montmorillonite. These montmorillonite layers are very similar to the clay structure morphology as evident by SEM images, although, the water content of clay minerals can be evaporated during the pyrolysis process resulting in a reduction in pore diameter and surface area of treated biochar (Chen et al. 2017; Rawal et al. 2016; Ismadji et al. 2016). Ramola et al. (2020) developed novel composite adsorbent for Pb removal from aqueous medium using minerals i.e. bentonite and calcite, and spent waste from cigarette factory. The chemical, structural and functional properties of composite changed as a function of both temperature and addition of bentonite or calcite. Both biochar-mineral composites act as excellent adsorbents for the removal of Pb in wide range of Pb concentration, pH, dose and contact time. Q_{max} value for both biochar-mineral composite was 500 mg/g which further proved their superior adsorbent quality. Chen et al. (2017) modified bamboo powder biochar with montmorillonite and reported that due to an increase in surface area, the capacity of sorption of NH_4^+ and PO_4^{3-} increased significantly as compared to unmodified biochar. Moreover, the treated biochar depicted more affinity for PO_4^{3-} as compared to NH_4^+. The more sorption affinity of treated biochar towards phosphate is due to the fact that it was adsorbed due to electrostatic interaction and ionic bonds between PO_4^{3-} and cations available in montmorillonite. However, the sorption of NH_4^+ is mainly governed by Van der wall forces. Rice husk is abundantly available as agricultural waste, and its conversion as biochar composite with calcite (BRH-C) for phosphate removal showed promising lab-scale results by Ramola et al. (2021). Maximum phosphate removal of 87.3% was achieved using rice husk and calcite at 4.2:1 (w/w) ratio, pyrolysis temperature of 700 °C and pyrolysis time of 2.3 h. Presence of SiO_2 and calcite in BRH-C acted synergistically to effectively remove phosphate, especially at low concentrations. Pyrolysis temperature was found to contribute significantly to phosphate removal as compared to other process parameters. Calcite played an important role to change the textural, functional and mineral properties of BRH-C that accounted for better removal of phosphate at low concentration.

2.7　Magnetic Modification of Biochar

Several studies establish biochar as a potential adsorbent for contaminants due to its multi-functional characteristics. The separation of powdered biochar from aqueous solution after treatment is difficult and limits its use. So, several researchers aimed

to produce biochar adsorbents with magnetic properties to facilitate efficient separation of biochar after water treatment (Chen et al. 2011; Mohan et al. 2014a; Wang et al. 2015b; Zhang and Gao 2013). The adsorption of anionic contaminants is relatively low since the biochar surfaces are mostly negatively charged (Beesley and Marmiroli 2011; Mukherjee et al. 2011). Preparation of biochar with magnetic modification can effectively enhance adsorption of anionic contaminants (Chen et al. 2011; Wang et al. 2015b). Chen et al. (2011) proposed a novel method of combining the processes of iron-oxidizing and biochar formation to reduce the additional cost of conventional loading of a magnetic medium to biochar. The magnetic biochar was produced by chemical co-precipitation of Fe3þ/Fe2þ on orange peel powder with successive pyrolysis at different temperatures (250, 400 and 700 °C). This process resulted in the production of iron oxide magnetite and biochar in a single step. The specific surface area of engineered magnetic biochar with chemical co-precipitation of Fe3þ/Fe2þ recorded lesser than non-magnetic biochar, however, the average pore size increased (Chen et al. 2011). The lower surface area can be explained by the fact that iron oxides have a lesser surface area and plentiful transitional pores (Chen et al. 2011). The hybrid adsorption properties of magnetic biochar ensure efficient sorption of organic pollutants and phosphate concurrently. The stable existence of magnetic characteristics of magnetic biochar makes it a potential adsorbent that can easily be separated after use. This helps in overcoming the limitation of using powdered biochar in the wastewater treatment process. Similarly, Zhang and Gao (2013) performed thermal pyrolysis at 600 °C to prepare magnetic biochar from $FeCl_3$ treated biomass. The final product of magnetic modification has colloidal or nano-sized g-Fe_2O_3 particles implanted in a porous matrix of biochar which acquires excellent ferromagnetic characteristics. The saturation magnetization of the resultant product was 69.2 emu/g which is very close to that of pure g-Fe_2O_3 (76.0 emu/g). The batch sorption experiments revealed that magnetic biochar exhibit high As3þ sorption capacity and the ferromagnetic characteristics help in easy separation/collection of exhausted biochar from the solution (Zhang and Gao 2013).

3   Advantages of Chemical Modifications

Chemical treatment of biochar enhances its physical, chemical and electrical properties as well as it is helpful in heavy metal removal from soil and waste water. The advantages of chemical treatments of biochar are depicted in Fig. 2. Some of them are discussed as follows.

3.1   Improvement in Physical Properties of Biochar

Acidic and alkaline treatments modify surface area and pore space of biochar that may improve its adsorption capacity by introducing new adsorption sites in the biochar. In
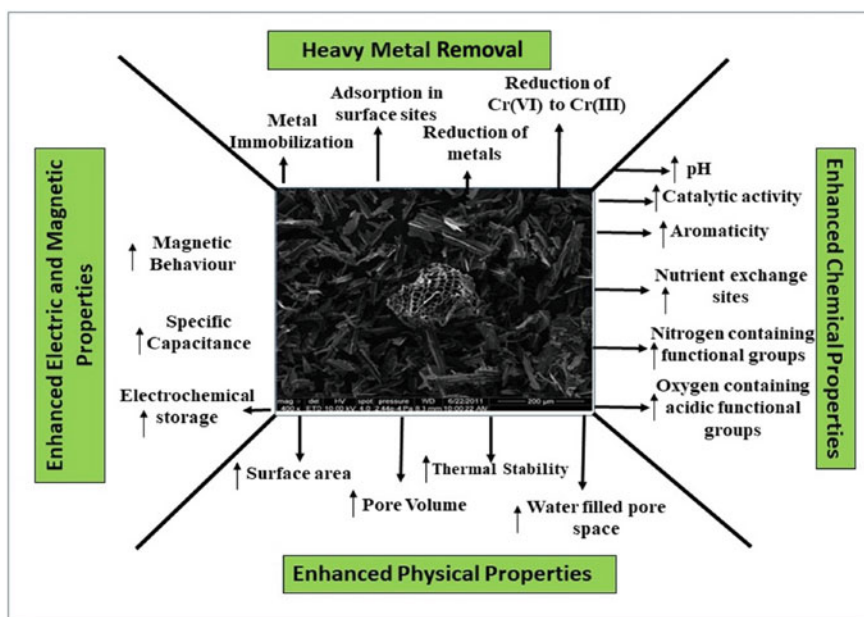
Fig. 2 Advantages of chemical treatment of biochar

similar fashion, loading of clay minerals and carbon nanotubes also increases the pore volume and specific surface area of biochar. Table 2 shows the enhancement in surface area and porosity by different chemical modification methods. Due to enhanced pore volume, the biochar shows higher adsorption affinity for pollutants as compared to unmodified biochar and activated carbon. Regmi et al. (2012) reported that after alkaline treatment of biochar using KOH, significant increase in the adsorption of Cu and Cd was achieved due to larger surface area and pore volume. Similarly, Jin et al. (2014) reported that biochar modified by KOH demonstrated better sorption capacity for As^{+5} due to enhanced surface area and pore volume. On the other hand, chemically engineered biochar demonstrates better thermal stability as compared to unmodified biochar. Inyang et al. (2014) reported that the thermal stability of biochar increased after modification with carbon nanotubes and graphene. Similarly, acidic treatment of lignocellulosic biochar enhances the thermal stability of biochar due to the presence of functional groups on the surface of biochar.

3.2   Enhancement in Chemical Properties of Biochar

The chemical properties of biochar such as aromaticity, pH and catalytic activity can be enhanced using the chemical modifications of biochar. In addition, several oxygen-containing functional groups and nitrogen-containing functional groups can

Table 2 Effect of different chemical treatments on physical and chemical properties of biochar

Treatment	Raw material	Modified/unmodified	Pyrolysis temperature °C	Ash %	C %	H %	O %	N %	Surface area m²g⁻¹	Pore volume cm³g⁻¹	References
H_2O_2 modification	Peanut hull	Unmodified	300	–	56.3	5.6	36.6	0.9	N_2:1.3 CO_2:96.9	–	Xue et al. (2012)
		Modified		–	48.3	5.8	43.8	0.8	N_2:1.4 CO_2:114.4	–	
KOH modification	Rice husk	Unmodified	450–500	42.2	42.1	2.2	0.5	12.1	34.4	0.028	Liu et al. (2012)
		Modified		3.5	76.4	3.3	0.9	16.9	117.8	0.073	
		Modified		0.9	71.3	3.6	23.4	0.8	66.0	0.051	
		Modified		–	–	–	–	1.0	351.0	0.130	
Clay biochar composites	Bamboo	Unmodified	600	–	80.9	2.4	14.9	0.1	375.5	–	Yao et al. (2014)
		Modified (montmorillnite)		–	83.3	2.3	12.4	0.2	408.1	–	
		Modified (kaolinite)		–	81.0	2.1	15.8	0.2	239.8	–	
Clay biochar composites	Bagasse	Unmodified	600	–	76.4	2.9	18.3	0.8	388.3	–	Yao et al. (2014)
		Modified (montmorillnite)		–	75.3	2.2	18.9	0.7	407.0	–	
		Modified (kaolinite)		–	70.2	2.4	24.4	0.7	328.6	–	
Clay biochar composites	Hickory chips	Unmodified	600	–	81.6	2.2	14.0	0.7	401.0	–	Yao et al. (2014)
		Modified (montmorillnite)		–	80.9	2.2	15.1	0.3	376.1	–	
		Modified (kaolinite)		–	78.1	2.1	18.1	0.3	224.5	–	

(continued)

Table 2 (continued)

Treatment	Raw material	Modified/unmodified	Pyrolysis temperature °C	Ash %	C %	H %	O %	N %	Surface area $m^2 g^{-1}$	Pore volume $cm^3 g^{-1}$	References
MnO_x-loaded biochar	Corn straw	Unmodified	600	5.0	85.3	1.7	5.2	0.8	61.0	0.036	Song et al. (2014)
		Modified (10% $KMnO_4$)		13.1	73.0	0.3	10.9	0.7	3.2	0.006	
		Modified (zero valent iron)	700	–	–	–	–	–	101.2	0.079	
Manganese oxide-modified biochar	Pine wood	Unmodified	600	4.0	85.7	2.1	11.2	0.3	209.6	0.003	Wang et al. (2015a)
		Modified (Mn oxide)		14.0	80.0	1.9	14.6	0.3	463.1	0.022	
		Modified (birnessite)		33.4	61.5	1.9	27.6	0.2	67.4	0.066	
Manganese oxide modification	Peeled pine wood	Unmodified	700	–	–	–	–	–	369	0.200	Wang et al. (2014)
		Modified		–	–	–	–	–	361.0	0.194	
Metal impregnated Activated carbon	Pulverized sub-bituminous coal	Unmodified	600 and 1000	–	81.6	–	17.9	–	190.0	0.079	Dastgheib et al. (2014)
		Modified		–	65.5	–	13.2	–	245.0	0.126	
		Modified		–	–	–	–	3.5 and 1.0	251.9 and 351.5	0.080 and 0.130	
Ca–Mg loaded biochar	Corncob	Unmodified	300, 450 and	4.0	35.5	6.3	–	0.7	ND	–	Fang et al. (2015)
		Modified	600	5.0	43.3	5.0	–	0.6	378.0	–	
$Zn(NO_3)_2$ loaded biochar	Pine cones	Unmodified	500	2.1	67.9	3.9	22.1	0.5	6.6	0.016	Van vinh et al. (2015)
		Modified		2.1	71.2	3.0	20.4	0.5	11.5	0.028	
Magnetic biochar	Orange peel	Unmodified	250	3.1	56.5	5.1	–	1.7	51.6	0.059	Chen et al. (2011)
		Modified (magnetite-Fe^{3+}/Fe^{2+})		42.4	35.1	3.6	–	1.1	41.2	0.052	

(continued)

Table 2 (continued)

Treatment	Raw material	Modified/unmodified	Pyrolysis temperature °C	Ash %	C %	H %	O %	N %	Surface area m²g⁻¹	Pore volume cm³g⁻¹	References
Magnetic biochar	Orange peel	Unmodified	400	6.9	65.7	3.5	–	1.80	28.1	0.041	Chen et al. (2011)
		Modified (magnetite-Fe^{3+}/Fe^{2+})		35.0	29.4	2.2	–	0.5	23.4	0.042	
Magnetic biochar	Orange peel	Unmodified	700	14.9	67.0	1.5	–	2.0	501.0	0.390	Chen et al. (2011)
		Modified (magnetite-Fe^{3+}/Fe^{2+})		95.7	0.4	0.2	–	0.2	19.4	0.033	
Magnetic biochar	Paper mill sludge	Unmodified	700	–	–	–	–	–	67.0	0.083	Devi and Saroha (2014)
		Modified (zero valent iron)		–	–	–	–	–	101.2	0.079	

be introduced in the biochar using chemical modification. Acidic treatment of biochar enhances the H/C ratio and O/C ratio in the biochar due to lower carbon content in the modified biochar. The modification in O/C, H/C and N/C ratios by different modifications is presented in Table 2. The increased O/C ratio leads to the higher oxygen content in the biochar which results in more acidic functional groups in the biochar. In addition, higher oxygen content decreases the hydrophobicity of the biochar.

The chemically engineered biochar generally has higher H/C and N/C ratios and a lower O/C ratio. A Low O/C ratio is a sign of a decreased hydrophilic behaviour of biochar and increased surface aromaticity (Ma et al. 2014). The higher N/C proportion results in the availability of more nitrogen-containing functional groups on the surface of treated biochar. In addition, alkaline activators have OH^- and NH_2^- ions which modify the sorption efficiency of negatively charged as well as organic contaminants from water. Also, chemical treatments of biochar induce additional nutrient exchange sites in the biochar. These active sites increase the catalytic activity of biochar. Also, these modifications are helpful for the application of biochar as a slow-release fertilizer.

3.3 Enhancement in Electric and Magnetic Properties of Biochar

It is difficult to separate powdered biochar from an aqueous matrix after treatment which makes it unappealing to the end-users. Therefore, induced magnetism by chemical treatments is important and provides a better separation of biochar from waste water. Along with the easy separation of impurities-loaded biochar from water, magnetic biochar also demonstrates better sorption capacity. The higher sorption capacity may be attributed to the higher electrostatic interaction of contamination with the iron oxide molecules and oxygen-containing functional groups. Moreover, the outstanding electrical conductivity of modified biochar makes it potential material for application in the fuel cell, supercapacitors and batteries (de Almeida et al. 2020; Qin et al. 2020; Li et al. 2020).

As discussed above, acidic modification of biochar enhances the oxygen-containing functional groups on the surface of biochar, which increases the capacitance of biochar due to occurrence of redox reactions in carbonyl-surface oxygen-containing functional groups (Qian et al. 2015). Jiang et al. (2013) reported that the capacitance of biochar derived from wood increased from 14 to 115 F/g with stability till 5000 cycles after modification with nitric acid. Moreover, the modified biochar showed a power output of 532 mW/m^2, if utilized as a microbial fuel cell (Chen et al. 2012). This power output is close to graphite and activated carbon.

4   Limitations of Chemical Modifications of Biochar

It is difficult to achieve high electrical conductivity and redox capacity together by chemical modification of biochar (Chacon et al. 2020). The chemical modification of biochar generally produces oxygen-containing functional groups which enhance the redox capacity of the biochar but reduce the electrical conductivity. On the other hand, thermal degradation of biomass enhances the electrical conductivity of the biochar by producing carbon sheets but removes the oxygen-containing functional groups from the biochar (Harvey et al. 2012). Therefore, according to the intended application, the modification protocol needs to be carefully selected for the desired properties of the biochar. From economic perspective as well, chemical modification adds cost to the production of biochar. The average price of untreated biochar is about $2480/ ton and addition of industrial grade chemicals further increases the cost of biochar (Campbell et al. 2018). There is a need to devise economically feasible routes for modification of biochar.

5   Conclusion

Chemical modification including treatment of biochar with different chemical entities can enhance the physico-chemical and functional properties of biochar. This includes pH, surface area, pore size and volume, aromaticity and introduction of characteristic functional groups and minerals onto the biochar. Similarly, magnetic modification of biochar resolves the problem of solid–liquid phase separation and increases the chances of biochar regeneration treatment of waste water. The chemical modification of biochar also increases the specific capacitance and electrochemical performance of biochar however the potential of biochar as a supercapacitor or as a fuel cell is still vague. Therefore, there is a scope for more studies in this direction to understand the effect of biochar structure on the electrochemical performance of biochar.

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Biological Treatment for Biochar Modification: Opportunities, Limitations, and Advantages

Deepshikha Azad, R. N. Pateriya, Rajat Arya, and Rajat Kumar Sharma

Abstract Biochar is a prominent adsorbent for environmental remediation. The physicochemical properties responsible for adsorption can be significantly enhanced by using physical, chemical, and biological treatments of biochar. The biological treatment methods are advantageous in terms of cost-effectiveness and reduced secondary pollutants. The present chapter summarizes the need, methodology, modification mechanism of biological modification of biochar, and its implementation for environmental remediation. The biologically modified biochar can be obtained by either ex situ (pyrolysis of anaerobically digested residue) or in situ (using extracellular enzymes) technologies. The process includes colonization and biofilm formation by microorganisms on biochar surface and attachment of microbes. Biologically modified biochar metabolizes organic/inorganic contaminants and helps in adsorption, biodegradation, and bio-adsorption simultaneously.

1 Introduction

Generally, the pristine biochar has less adsorption capacity for the removal of contaminants as compared to modified biochar. Different modification methods are developed to increase the adsorption capacity of biochar for its utilization in soil remediation, energy storage, and wastewater remediation. These practices for the production of engineered or modified biochar are termed as biochar engineering (Ok et al. 2015). So, engineered/modified biochar can also be defined as a derivative of biochar with improved specific surface area, porosity, cation exchange capacity, and surface functional groups through biological, physical, chemical, or combination of these methods. The improved physicochemical properties provide significantly better adsorption capacity of modified biochar as compared to pristine biochar (Rajapaksha et al. 2016; Yao et al. 2013a, b, c).

Biological modification using earthworms is emerging as a potential method of biochar modification for increment in surface area, better pore size distribution,

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surface functional groups, and adsorption capacity for heavy metal contamination in soil. The enzymes generated by gut epithelium of earthworm and other symbionts are catalase, b-Deglucuronidase, alkaline phosphatase, d-aminolevulinate dehydratase, and superoxide dismutase. The biochar particles bind with these enzymes through mucus. So, this process can be employed where earthworms can ingest the substrate and discharge the enzyme coated modified biochar. This biologically modified biochar consists of enormous exo-enzymes (molecular ligands). The ex situ modification can be performed by activation of waste/sludge obtained as cow dung, leaf litter, anaerobically digested biomass, etc. This chapter explains in detail the methodology, mechanism, applications, and need for biological modification of biochar through metabolic enzymes.

2 Biological Modification Techniques

The metabolic pathways possessed by microorganisms, viz. Aeromonas, Cellulosimicrobium, Chloroflexi, Shewanella, Streptomyces, etc. (Mohammadipanah and Dehhaghi 2017; Wink et al. 2017), enable the biochar to integrate with various organic compounds and result in usable metabolites (Dehhaghi et al. 2019a, b) and value-added products (Dehhaghi et al. 2018, 2020; Sajedi et al. 2018). Due to their microscopic size, they can penetrate into pores of biochar and develop a non-washable rigid structure of biofilm. The biological modification process includes colonization and biofilm formation by microorganisms on biochar surface. The general mechanism of pollutant removal by biologically modified biochar is illustrated in Fig. 1. Initially, microbes get attached to biochar surface through sticky extracellular polymers and the
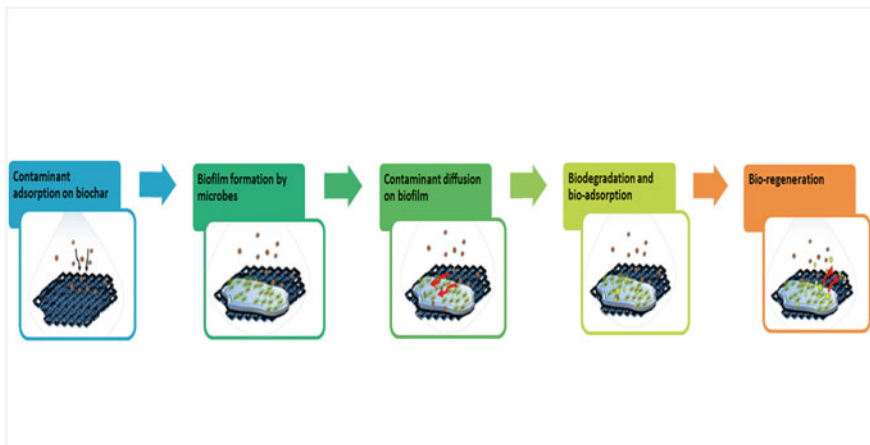
Fig. 1 Bio-adsorption, biodegradation, and adsorption on biologically modified biochar

contaminants get attached to it through molecular diffusion. These organic and inorganic pollutants get metabolized by microbes through various bio-electrochemical and biochemical reactions (Sharma et al. 2020). The biofilms perform degradation and removal of various inorganic, organic, and biological pollutant (Simpsosn 2008; Bouabidi et al. 2019; Sharma et al. 2020). A biologically modified biochar performs pollutant remediation in several steps, viz biofilm formation followed by biodegradation, desorption, and diffusion of contaminants at biochar–biofilm and air/soil/water interface (Wurzer et al. 2019).

Biological treatment enhances the desired physicochemical and functional properties of biochar. It enables the simultaneous adsorption of contaminants on biochar scaffold and their degradation by inoculated microorganisms. For example, several microorganisms (viz. Clostridium, Paenibacillus, Aeromonas, Cellulosimicrobium, Chloroflexi, Shewanella, etc.) possess bio-adsorbent characteristics for heavy metals (Hamedi et al. 2015; Mohammadipanah et al. 2015). The microbial colonization on biochar facilitates the adsorption of inorganic contaminants (heavy metals) with removal and degradation of organic contaminants (naphthenic acid) simultaneously (Frankel et al. 2016). It was observed that the biochar-active biofilm can efficiently perform adsorption and degradation (about 98% of carbamazepine) as compared to conventional sand-active biofilm (about 7% of carbamazepine) in a sewage treatment plant. The caffeine, ranitidine, and metoprolol adsorption characteristics were found similar for both conventional and biochar-based scaffolds (Dalahmeh et al. 2018).

2.1 Interaction of Biochar with Intestinal Enzymes of Earthworms

Earthworms can significantly change the physicochemical and biological properties of consumed substrates (Jones et al. 1994; Yuvaraj et al. 2019). The gut of earthworm/manure worm has various anaerobic (Clostridium, Paenibacillus, Aeromonas, Cellulosimicrobium, Chloroflexi, Shewanella, and Streptomyces) and aerobic (Photobacterium, Pseudomonas, and Bacillus) bacteria that releases many enzymes (Hong et al. 2011). The gut of *Perionyx millardi, Drawida willsi, Drawida calebi, Dichogaster bolaui,* and *Pontoscolex corethrurus* type of earthworms have sufficient quantity of phosphatase, lipase, urease, amylase, chitinase, protease, and cellulose enzymes (Parle 1963; Mishra and Dash 1980; Baskaran et al. 1986; Mishra 1993). The anterior portion of earthworms have higher enzyme secretion as compared to the posterior portion. It is due to that fact that fore-gut and stomach of earthworms have the enzyme secreting parts (Tillinghast and MacDonnell 1973). Mishra and Dash (1980) and Nakajima et al. (2003) have asserted that the cellulase, amylase, protease, and lipase are the most secreted enzymes from intestinal cells of earthworms. Urbasek and Pizl (1991) have stated that the mid-gut of *Lumbricus terrestris* earthworm releases 20 enzymes from three different sections, namely typhlosole, peripheral intestinal epithelium, and peripheral chloragocytes. More than

44% of enzymes (such as b-Deglucuronidase, superoxide dismutase, catalase, d-aminolevulinate dehydratase, and alkaline phosphatase) are produced in peripheral chloragogen. Also, the maximum proportion (about 70%) of glutamate dehydrogenase, isocitrate dehydrogenase, NADH, and NADPH diaphorase was also found in the mid-gut of earthworm. Similar to a tubular reactor, the gut also maintains the optimum temperature to avoid enzyme inactivation. During vermicomposting, the urease, dehydrogenase, acid, and alkali phosphatases catalytic activity increases initially and thereafter decreases as optimum concentration is reached. This phenomenon specifies earthworms as bioreactors for organic waste with microorganisms (Balachandar et al. 2020; Karmegam et al. 2019).

The interaction with earthworm enzymes can be a potential mode for biochar surface modification. An enormous quantity of organic waste can be ingested by earthworms and also an abundant amount of metal ions can get accumulated in chloragogen tissues of earthworms (Yuvaraj et al. 2020). The implementation of biochar with earthworms can significantly minimize the heavy metal concentration in soils (Shaaban et al. 2018; Sun et al. 2016). The abiotic components in biochar can enrich the soil with minerals and earthworms can induce the degradation process. The biochar particles bind with gut enzymes through mucus of earthworms (Urbasek and Pizl 1991). The mucus ejected from gastrointestinal epithelial cells consists of amino acids, mucopolysaccharides, and glycoproteins (Zhang et al. 2016a, b). The other enzyme originated from earthworm gut such as alkaline phosphatase, amylase, nitrate reductase, cellulose, and acid phosphatase can induce microbial growth. Therefore, the intestines of earthworms and symbionts can be seen as potential sources of extracellular enzymes for biochar activation.

The co-application of biochar with earthworms was found to contribute significantly to soil nutrient enrichment (Ameloot et al. 2013; Puga et al. 2015). During vermicomposting, the ingested biochar by earthworms interacts with intestinal enzymes and is discharged with humus-like substances (Domene 2016). Sanchez-Hernandez (2018) have experimented with *Aporrectodea caliginosa* and *Lumbricus terrestris* earthworms in biochar mixed soil and harvested b-glucosidase, alkaline phosphatase, and carboxylesterase enzyme coated biochar released by earthworms. In another experiment, Sanchez-Hernandez et al. (2019) mixed 2.5–5% (w/w) biochar with soil and interacted with *Lumbricus terrestris* earthworms, and obtained enzyme coated biochar on the top of soil surface. The carboxylesterases induce biological modification/activation of biochar and can effectively remediate organophosphorus-contaminated soils. It can be explained by binding of carboxylesterases with oxygen analogs of organophosphorus (Wheelock et al. 2008).

2.2 Pyrolysis of Anaerobically Digested (AD) Waste

Apart from microorganism incubation, the biologically modified biochar can also be produced from the residues obtained after anaerobic digestion (AD) of biomass. The biochar produced from AD residue possesses a higher specific surface area,

anion exchange capacity (AEC), cation exchange capacity (CEC), hydrophobicity, alkaline pH, and more negative surface charge as compared to conventional biochar (Yao et al. 2018). These variations in properties might be attributed to the alteration of redox potential and pH values of biomass during anaerobic digestion (Inyang et al. 2010). The enhanced AEC and CEC facilitate the utilization of biologically modified biochar for sequestration of both positive and negative ions from water. The higher cation adsorption capacity of AD biochar is due to the strong negative surface functional groups and negative zeta potential. The presence of strongly negative surface functional groups in modified biochar (due to negative zeta potential of AD waste) increases the cation adsorption capacity. The emerging industrial applications of modified biochar enhance the economic and environmental feasibility of biochar production from AD residue (Dehhaghi et al. 2019b; Tabatabaei et al. 2019). Another biological approach for biochar modification includes the utilization of mineral enriched biomass through bioaccumulation for the production of modified biochar (Yao et al. 2013b; Wang et al. 2017). This process results in value-added biochar nanocomposites and provides a safe disposal method for hyper-accumulating plants. Several studies on biochar production from bagasse stillage waste sugar beet residue, dairy waste, animal waste, and sewage sludge digested slurry were performed at different pyrolysis temperatures (300–1000 °C) under an inert atmosphere (Ma et al. 2018; Inyang et al. 2012; Yao et al. 2011, 2015, 2017a, b). Another study by Inyang et al. (2010) reported the comparative analysis of biochar produced from sugarcane bagasse and AD bagasse. These studies imply that the BET surface area of biochar produced from digested biomass was slightly higher than that produced from biomass pyrolysis. It facilitates the efficient utilization of modified biochar as a low-cost adsorbent for soil amendment, water holding capacity, and soil quality improvement that leads to sequestration of atmospheric carbon. It was concluded that the organic functional groups present in biochar and AD biochar were mainly hydroxyl, alkene, and aromatic groups. The major difference in organic groups was evident only as the presence of carbonyl groups in AD biochar (Inyang et al. 2010). Based on the physicochemical characterization, it is evident that AD biochar has higher adsorption and ion-exchange capacity relative to undigested biomass residues. Scanning electron microscopy (SEM) of AD biochar indicated the presence of several prismatic, hexagonal crystalline structures, and the pore diameter was found similar to the wood-based activated carbon (Ma et al. 2018; Gundogdu et al. 2013; Inyang et al. 2012). Studies indicate the significant effect of different AD biomass on the physicochemical properties of AD biochar. The AD biochar also possesses good heavy metal adsorption capacity from aqueous solutions. The results concluded that the animal waste AD biochar acquire a stronger affinity to Pb^{2+} (99%), Cu^{2+} (98%), and weaker affinity to Cd^{2+} (57%), Ni^{2+} (26%) as compared to sugar beet residue AD biochar (Inyang et al. 2012). Batch experiments of soil remediation indicated that the pH and coexisting anions in initial solution can significantly affect the phosphate adsorption capacity of AD biochar (Yao et al. 2011). The comparative analysis of biochar, anaerobically digested biochar (DBC), and commercially activated carbon (AC) asserted that DBC is the most efficient lead adsorbent in aqueous solutions. The lead adsorption capacity of DBC (653.9 mmol/kg) was twice of AC (395.3 mmol/kg)

and several times greater than that of BC (31.3 mmol/kg). Despite lower surface area of DBC, the lead adsorption capacity of DBC was observed higher than AC and BC. This phenomenon suggests the involvement of other mechanisms along with surface adsorption. Post-adsorption analysis using X-ray diffraction (XRD) and SEM identified lead minerals on the DBC surface as cerrussite—[$PbCO_3$] and hydrocerrussite—[$Pb_3(CO_3)_2(OH)_2$]. These mineral crystals were not observed on the BC or AC after Pb adsorption. It concluded that the lead adsorption capacity of DBC also depends partly on the precipitation mechanism. The precipitation of cerrussite and hydrocerrussite on DBC surface is due to the presence of specific organic functional groups (O=C=O) and high pH. Another study by Yao et al. (2011) proposed the predominance of adsorption over precipitation mechanism during the phosphate removal from aqueous solutions. High metal removal efficiency of biochar made from digested biomass suggests that it could be considered an efficient method of "biological activation" to produce biochar-based adsorbents.

3 Effect of Biological Modification

3.1 On Microbial Properties

Biochar application in soil induces the stabilization of organic matter and the exchange of electrons between microbial cells and organic matter (Fang et al. 2014). It can significantly affect the enzyme activities and community structure of microbes. These parameters can be examined using quantitative real-time polymerase chain reaction (q-PCR), ergosterol extraction, next-generation sequencing, phospholipid fatty acid quantitation (PLFA), gradient gel electrophoresis (DGGE), and fluorescence in situ hybridization (FISH) (Chen et al. 2013; Hale et al. 2014; Mackie et al. 2015; Rousk et al. 2009). Actinobacteria, Acidobacteria, Verrucomicrobia, and Gemmatimonadetes were observed to adopt high-throughput sequencing techniques in biochar-treated soils (Mackie et al. 2015; Nielsen et al. 2014). The different theories for the effect of biochar on microbial activity are explained by several researches. The first concept is that the high specific surface area with well-developed pore structure avails vacant space for microorganisms (Quilliam et al. 2013). Another research by Joseph et al. (2013) stated that the microorganisms extract the essential nutrients for their development from biochar. The biochar enhances the properties of substrate (such as pH, moisture, and aeration conditions) to alter its habitation (Quilliam et al. 2013). Another theory identified that biochar minimizes the toxicity to microorganisms by adsorbing the soil pollutants (Stefaniuk and Oleszczuk 2016).

3.2   On Biochar Properties

Biochar consists of various essential nutrients such as sodium, potassium, nitrogen, magnesium, and phosphorus for the enrichment of soil nutrients (Chathurika et al. 2016). With enriched soil nutrients, the rhizobacterial population increases which further leads to higher enzyme availability in soil. The enzyme adsorption depends on surface functional groups of biochar. The force (other than Coloumb force) between neutral protein molecules and polar disaccharides is linked to the neutral region of biochar surface. It leads to the biological activation of biochar through enzymes (Lammirato et al. 2011). Also, the biochar surface contains a significant amount of microalgae variants (Klebsormidium flaccidum and filamentous Cyanobacteria) that increase the activation process. Some extracellular enzymes (oxidoreductase enzyme) bind covalently with biochar surface and this biologically modified biochar can be efficiently implemented for heavy metal adsorption (Naghdi et al. 2018). The microbial activation is limited to bench-scale studies and biological activation of biochar through earthworms is been considered as a cost-effective method.

4   Mechanisms Involved in Biological Modification of Biochar

4.1   Biological Modification Through Intestinal Enzymes of Earthworms

The posterior part of earthworms has several enzyme-secreting glands and discharged digestive enzymes break the fed organic matter (Kaushik and Garg 2004). The earthworms can consume a diverse variety of substrates that can be divided into three classes (anecic, epigeic, and endogeic) according to their feeding habits (Domínguez and Edwards 1997; Huang et al. 2014). Epigeic earthworms (such as Eisenia fetida, Eudrilus eugeniae, and Perionyx excavatus) are most efficient in the degradation of complex organic substances and are recommended for biological modification of biochar (Khatua et al. 2018; Karmegam et al. 2021; Ananthavalli et al. 2019). Figure 2 depicts the process of biological modification of biochar by earthworms. The biological modification takes place in two stages. In the first stage (active stage), earthworms grind the consumed material in gut section, the gut-secreted enzymes crack the complex substances, and in the second stage (maturation stage), the earthworm releases biologically modified biochar with humus like substance (Gomez-Brandon et al. 2011; Gomez-Brandon and Domínguez 2014; Lores et al. 2006). During the active stage, the consumed organic material gets ground in gizzard, gut epithelium releases multiple enzymes, and induces biochemical reactions (Nozaki et al. 2009) for different enzymes, microbes, beneficial nutrients, and biologically modified biochar
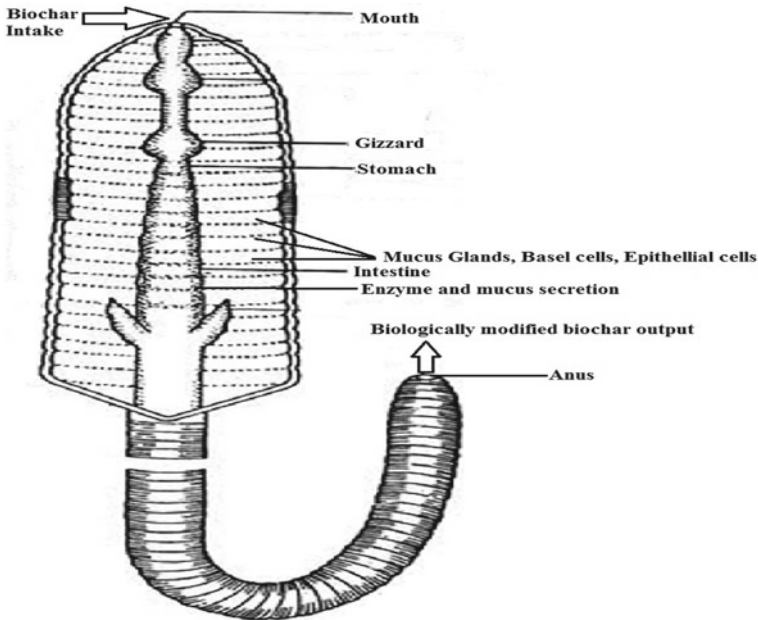
Fig. 2 Mechanism of biological modification of biochar by earthworms

(Balachandar et al. 2021; Domínguez et al. 2019). Therefore, the efficiency of vermi-composting increases by mixing organic waste with biochar (El-Naggar et al. 2019; Malinska et al. 2017). Along with the biological modification of biochar, the process also alters microbial properties by improving moisture availability, aeration level, toxicity adsorption, nutrient establishment, and pH neutralization (Ge et al. 2019; Zhu et al. 2017a, b; Quilliam et al. 2013; Ennis et al. 2012; Jeffery et al. 2011). The gut enzymes have various biomolecules which can be used as catalyst and affect soil pollutants (Burns et al. 2013; Gianfreda et al. 2016). The implementation of biochar increases the stability of enzymes and the biochar particles bind with extracellular enzymes due to highly affinitive surface functional groups. The ionic interactions and van der Waals forces are major contributors to binding (De Oliveira et al. 2000). It can be concluded from the above-mentioned studies that the co-implementation of biochar and earthworms is a feasible method for remediation of metal contamination. Various environmental researchers stated that the soil invertebrates (such as earthworms) efficiently produce biologically activated biochar with the use of gut enzymes. The experimental study of Zhu et al. (2017a, b) on cow manure-based vermi-modified biochar evidenced effective adsorption of Pb^{2+} and Cd^{2+} ions.

4.2 Biological Modification by Pyrolysis of Anaerobically Digested (AD) Biomass

The anaerobically digested waste can be efficiently converted to biochar by drying and pyrolysis. The studies concluded that the wood biomass components hemicellulose, cellulose, and lignin decompose at temperature ranges 200–325 °C, 240–375 °C, and 280–500 °C, respectively (Prins et al. 2006; Downie et al. 2009; Wani et al. 2021). The mechanism of biological modification by pyrolysis of AD biomass includes the degradation of different components (hemicellulose, cellulose, and lignin) present in the feedstock. The characteristics of resultant biologically modified biochar depend greatly on pyrolysis temperature, heating rate, heating time, raw material characteristics, inert gas flow rate, etc.

5 Applications of Biologically Modified Biochar

Biochar-based nanocomposites have been extensively utilized in heavy metal adsorption (for example, As(III), As(V), Pb(II), Cr (VI), Cd(II), Cu(II), and Hg(II)) from wastewater. The adsorption capacity of various inorganic contaminants vary with different nanomaterials, contaminant concentration, and biochar substrate (Li et al. 2016; Wang et al. 2017; Yao et al. 2013a, b; Zhang and Gao 2013; Zhang et al. 2013). Biologically modified biochar is generally used in advanced water remediation for biodegradation and adsorption of organic, inorganic, and biological contaminants which cannot be separated in primary and secondary water remediation (Çeçen and Aktas 2011) (Table 1).

With increased population and food demand, the use of chemicals in agricultural sector has been significantly increased in past decades. Therefore, there is a need to develop a safe and efficient soil remediation technique for contaminated soil. It is been evident from several studies that biochar with high specific surface area, oxygen containing surface functional groups, cation exchange capacity can be efficient inactivating, stabilizing, and adsorbing agent for even highly heavy metals concentrated soils (Beesley et al. 2011; Park et al. 2011; Uchimiya et al. 2010a, b, 2011a). The heavy metal stabilization capacity is higher for alkaline soil pH and higher intraparticle diffusion (Rees et al. 2014). The pristine biochar constitutes good adsorption capacity for heavy metals which significantly increases upon biochar modification. There are some lab scale observations on heavy metal adsorption using modified biochar but large-scale experimentation is still rare. Traditional technologies (precipitation, ion exchange, packed-bed filtration, electro-coagulation, membrane filtration) for heavy metal removal from wastewater were found to be effective in reducing pollutant concentrations. Though, these technologies involve high-cost and disposal problems. The bio-adsorbents are suggested as low cost alternative for wastewater treatment (Demirbas 2008; Sud et al. 2008).

Table 1 Biologically modified biochar for pollutant removal

S. No	Raw material	Characteristics of modified biochar	Pollutant	Remediation technique	Contaminant removal efficiency and mechanism	References
1	Anaerobically digested dairy waste residue	SSA—128 m^2/g Pore diameter—0.034 cm^3/g	Heavy metals (Pb^{2+}, Cu^{2+})	Mixing in digestion vessels	Removal efficiency 99% (Combined adsorption and precipitation)	Inyang et al. (2012)
2	Anaerobically digested sugar beet residue	SSA—555 m^2/g Pore diameter—0.147 cm^3/g	Heavy metals (Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+})	Mixing in digestion vessels	Removal efficiency $\geq$97% (Combined adsorption and precipitation)	Inyang et al. (2012)
3	Anaerobically digested bagasse	SSA—17.7 m^2/g Pore diameter—0.147 cm^3/g	Pb^{2+}	Batch experiments by mixing in plastic vials	Removal capacity 653.9 mmol/ kg (Combined adsorption and precipitation)	Inyang et al. (2011)
4	Anaerobically digested sugar beet tailings	SSA—449 m^2/g	PO_4^{3-}	Digestion vessels	Mono-nuclear and poly-nuclear adsorption	Yao et al. (2011)
5	Wheat straw	SSA—190 m^2/g Pore diameter—2 nm	As(III)	Batch filtration	Removal efficiency 90–95% (Combined biofilm biosorption and biochar adsorption)	Zhu et al. (2018)

(continued)

Table 1 (continued)

S. No	Raw material	Characteristics of modified biochar	Pollutant	Remediation technique	Contaminant removal efficiency and mechanism	References
6	Pine-spruce wood biochar	SSA—184 m²/g	Chemical oxygen demand (COD), ammonium nitrogen (NH4-N), total nitrogen (Tot-N), total phosphorus (Tot-P) and phosphate (PO4-P) from municipal wastewater	Column filters of biochar	COD 94–99% NH4-N 50% Tot-N 50–52% Tot-P 90–96% PO4-P 82–90% (Combined biosorption, biodegradation, and adsorption)	Perez-Mercado et al. (2018)
7	Aspen wood biochar	SSA—4 m²/g Pore volume (V_t)—0.01 cm³/g	Naphthenic acid removal in presence of As, Fe, Al	Effluent oil sand process wastewater	Naphthenic acid removal efficiency 34% (Combined biosorption, biodegradation and adsorption)	Frankel et al. (2016)
8	Softwood biochar	SSA—189 m²/g V_t—0.12 cm³/g	Naphthenic acid removal in presence of As, Fe, Al	Effluent oil sand process wastewater	Naphthenic acid removal efficiency 87% (Combined biosorption, biodegradation and adsorption)	Frankel et al. (2016)
9	Quercus wood biochar	SSA—210–250 m²/g V_t—0.12–0.13 cm³/g	Organic content from urban and synthetic wastewater	Snorkel bio-filters wastewater treated at two loading rates (170, 890 mg/l)	Organic content removal efficiency 92% (Bio-electrochemical interactions)	Prado et al. (2019)

Table 1 (continued)

S. No	Raw material	Characteristics of modified biochar	Pollutant	Remediation technique	Contaminant removal efficiency and mechanism	References
10	Pine wood biochar	SSA—15 m^2/g	Fe(III)	Batch filtration	Direct interspecies electron transfer (DIET)	Chen et al. (2014)
11	Anaerobically digested waste water sludge	SSA—110 m^2/g	Fluoroquinolone antibiotics	Mixed in sealed flasks	Maximum adsorption capacity 19.80 mg/g (Adsorption)	Yao et al. (2013c)
12	Anaerobically digested bagasse	NA	Sulfamethoxazole (SMX) and sulfapyridine (SPY)	Mixed in digestion vessels	Maximum adsorption capacity 54.38 mg/g (SMX) and 8.60 mg/g (SPY)	Yao et al. (2017a, b)

Heavy metal contamination in soil has been a serious environmental problem in recent time (Alloway 2013). Biochar is generally an alkaline substance which can increase soil pH and promote stabilization of heavy metal contamination. Biologically treated biochar have significantly higher specific surface area and microbial biofilm which provide high pollutant adsorption capacity (Ahmad et al. 2014). Apart from adsorption, application of biologically treated biochar is also beneficial for agricultural soil due to increased microbial growth, bio-adsorption, and degradation of heavy metal and organic pollutants. The biologically modified biochar helps in retaining the soil nutrients (Yao et al. 2011).

6 Advantages and Limitations of Biological Modification of Biochar

The biologically modified biochar is not only a potential substitute for activated carbon in environmental remediation but also avails an additional advantage of sustainable carbon sink (Yoder et al. 2011; Laer et al. 2015). The contaminant removal efficiency of activated carbon, biochar and biologically modified biochar differ significantly due to dependence on adsorption capacity, bio-adsorption capacity, specific surface area, and pore size distribution. These parameters assert the suitability of biologically modified biochar due to high bio-adsorption, biodegradation, and adsorption along with positive environmental impact. The biological treatment of biochar is cost-effective and eco-friendly process as compared to physical and chemical activation. The other activation methods require high initial investment and produce secondary pollutants (emissions, chemical wastes, etc.) during activation (Sanchez-Hernandez et al. 2019). Also, there is no need for biochar regeneration after phosphate removal from soil because the phosphate-laden biochar consists of valuable nutrients and can be utilized as a slow-release fertilizer and for carbon sequestration (Yao et al. 2011). Thus, the implementation of biologically modified biochar eliminates the drudgery and cost associated with regeneration process.

7 Conclusions

This chapter summaries the feasibility, efficiency, and cost-effectiveness of biologically modified biochar. Raw materials and production process significantly alter the physicochemical and functional properties of biochar. Biologically modified biochar facilitates the effective biodegradation and biosorption through various complex mechanisms. The safe, cost-effective production process of biological modification avails agricultural, environmental, and economic sustainability. The co-implementation of earthworms and biochar is a feasible method for microbial

growth, biochar modification, and soil nutrient enrichment. The biological modification of biochar through extracellular enzymes paved the path for efficient environmental remediation. There is a need for detailed study using statistical tools and mathematical modeling to accurately correlate the control parameters and properties of biologically modified biochar.

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New Trends in Pyrolysis Methods: Opportunities, Limitations, and Advantages

Hong Nam Nguyen and Duy Anh Khuong

Abstract The expanding demand for environmental treatment increasingly requires different types of engineered char with high performance. In this context, new trends in pyrolysis methods have emerged and contributed to the sustainable development of pyrolysis technologies, namely microwave-assisted pyrolysis, co-pyrolysis, pyrolysis under non-inert ambiances, hydrothermal carbonization (wet pyrolysis), and integrated pyrolysis techniques. The outstanding advantages of these technologies over conventional pyrolysis include: increase in biomass conversion efficiency of the process, use of nonconventional raw material, increase in adsorption capacity of biochar by enhanced activated oxygen species, porosity, and functional groups, and removal or immobility of contaminants. The biochar products can be widely applied in various environmental fields, such as carbon capture and sequestration, soil amendment, adsorption of contaminants in soil, water, and air, and energy production. Nevertheless, challenges remain for these new trends, such as the increase in cost for the installation and operation, the lack of knowledge of the mechanism involved during pyrolysis, the difficulty in scaling up, etc. Further studies are recommended to facilitate the application of these new trends, such as pilot tests or field experiments to evaluate the real effects of biochar products prior to large-scale applications or their long-term risk during use, or prediction of properties of biochar and their impacts on environmental applications using modeling or machine learning approaches.

Keywords Advantages · Biochar · Limitation · New trends · Opportunities · Pyrolysis

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1 Introduction

Although widely applied in biochar production, products from conventional pyrolysis are increasingly unable to meet demands in energy production and environmental applications. The expansion of the raw materials for biochar production, as well as the need to create biochar with new properties with high adsorption capacity and environmental safety, are increasingly focused (Mohammadi et al. 2020). In addition, optimizing performance with maximal energy saving represents a crucial factor for the sustainable development of pyrolysis technologies (Veiga et al. 2020). In this context, new trends in pyrolysis methods, namely co-pyrolysis (Veiga et al. 2020; Rodriguez et al. 2021), microwave-assisted pyrolysis (Motasemi and Afzal 2013; Fang et al. 2021), (Yu-Fong et al. 2015; Veiga et al. 2020), pyrolysis under non-inert ambiances (SASAKI et al. 2009; Shen et al. 2017; Mian et al. 2018), hydrothermal carbonization (wet pyrolysis) (Zhou et al. 2019; Olszewski et al. 2020), and integrated pyrolysis (Yek et al. 2019, 2020; Liu et al. 2020) have emerged with the potential of synthesizing engineered biochar with enhanced properties and better quality (Fig. 1). These new pyrolysis conditions affect both physical properties (e.g.,
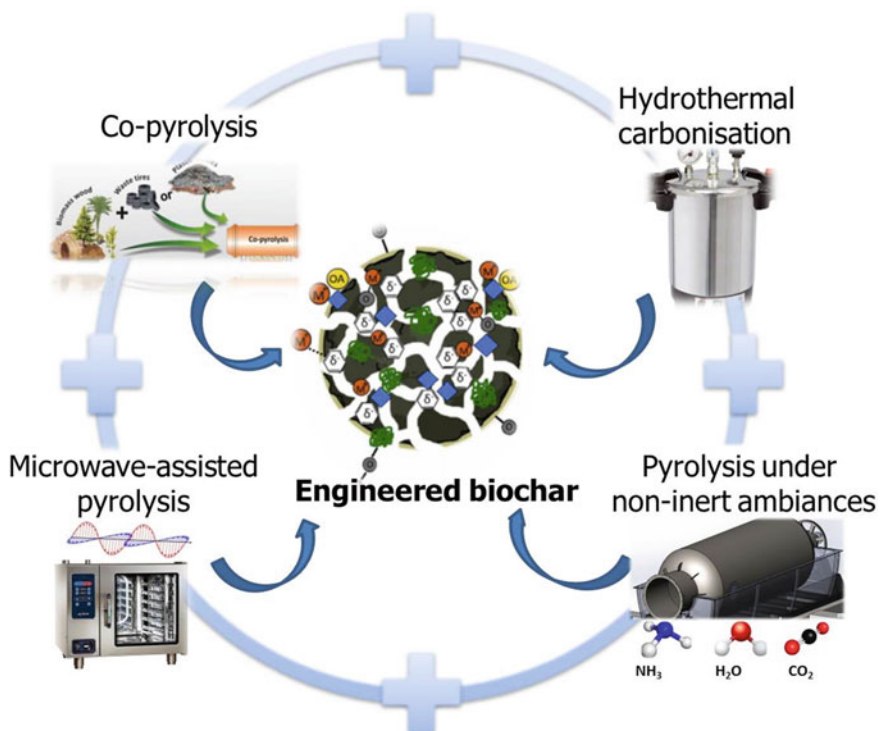
Fig. 1 New trends in pyrolysis of biomass

increase of specific surface area and porosity) and chemical properties (e.g., the introduction of functional groups and induce activated oxygen species on biochar surface) of the biochar, promoting the adsorption or degradation of different contaminants depending on the specific approach employed.

This chapter aims to summarize new trends in pyrolysis methods. Recent studies, advantages, and limitations/challenges related to each method are deeply discussed. Several research directions to facilitate the application of these new trends are also proposed.

2   Principle of New Pyrolysis Methods

2.1   *Co-pyrolysis*

Co-pyrolysis is a process that involves two or more feedstock as raw materials. For biochar applications, the biomass can be mixed with various types of other materials, from other biomass to municipal and industrial wastes (Johannes et al. 2013; Sewu et al. 2019; Rodriguez et al. 2021). The principle of co-pyrolysis is very similar to conventional pyrolysis. Prior to co-pyrolysis, the samples should be dried and well mixed to ensure an adequate homogeneity of the raw material. The ratio of raw material is an important parameter in co-pyrolysis that defines the quantity/quality of the biochar produced (Yao et al. 2021). The important key to the success of this technique is the contact of the different raw materials during co-pyrolysis (Fei et al. 2012; Johannes et al. 2013; Diao et al. 2021). Synergistic effects can be achieved through a series of radical interactions during the co-pyrolysis, namely initiation, formation of secondary radicals (depolymerization, formation of monomers, favorable and unfavorable hydrogen transfer reactions, intermolecular hydrogen transfer, isomerization via vinyl groups), and termination by disproportionation or recombination of radicals (Önal et al. 2014). Synergistic effects during co-pyrolysis can be complicatedly varied, depending on the type and contact of components, pyrolysis conditions (residence time, temperature, and heating rate), removal or equilibrium of volatiles formed, addition of catalysts, etc. (Fei et al. 2012; Johannes et al. 2013).

2.2   *Microwave-Assisted Pyrolysis*

Intrinsic drawbacks of conventional pyrolysis systems can be listed as heat loss to the environment, heat transfer resistance of materials, nonselective heating, a short lifetime of the system due to continuous heating, etc. (Salema and Ani 2011; Nan et al. 2015). Due to these limits, microwave-assisted pyrolysis (Fig. 2) is proposed as a novel method to effectively improve pyrolysis performance by enhancing chemical reactions with the help of heat transfer profiles through microwave irradiation
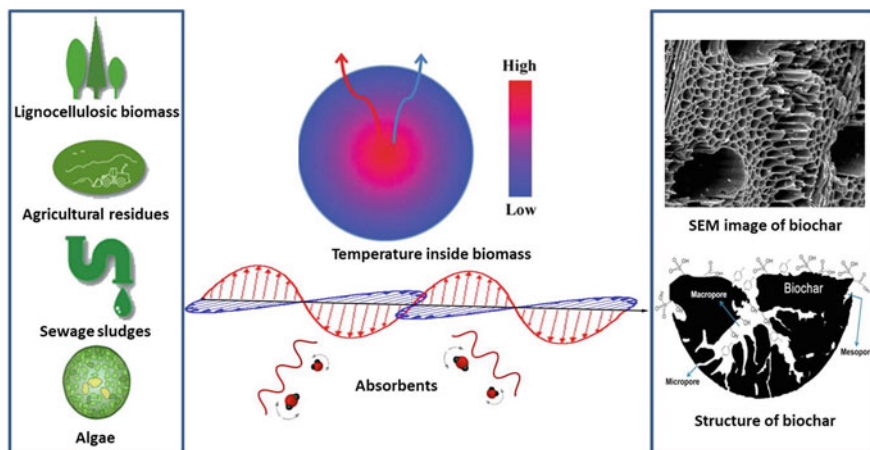
Fig. 2 Illustration of microwave-assisted pyrolysis of biomass

(Lidström et al. 2001; Fang et al. 2021). Microwaves fall in between the infrared and radio wave regions of the electromagnetic spectrum, i.e., wavelengths ranging from 0.01 to 1 m, corresponding to the range of frequency between 0.3 and 300 GHz (Motasemi and Afzal 2013; Calles-Arriaga et al. 2016). Most industrial microwave-assisted pyrolysis processes are conducted at the range of frequency between 0.915 and 2.45 GHz, which are assigned for heating applications (Mushtaq et al. 2014). Several reviews exist in the literature, highlighting the importance and the advantages of microwave-assisted pyrolysis (Lidström et al. 2001; Luque et al. 2012; Motasemi and Afzal 2013; Huang et al. 2016; Zaker et al. 2019).

The heating mechanism of microwave heating is mainly attributed to the interaction of dipoles or ions in the electric field, known as the dielectric response (Guerra et al. 2006; Taqi et al. 2020). The heating medium or reactants absorb electromagnetic energy from microwaves volumetrically to achieve self-heating in a uniform and rapid way. This contributes to a rapid moisture release from the raw material, improving its specific surface area and pore structure (Zbair et al. 2018; Taqi et al. 2020). A vital property of microwave heating is the formation of hot spots, as a result of the heterogeneity of the microwave field or dielectric characteristics of the material, generating a much higher inner than outer temperature (Vadivambal and Jayas 2010; Wang et al. 2016; Zhang et al. 2018). The temperature of the hotspots can significantly increase the pore creation inside the biomass.

Commonly, quartz reactors are employed inside a microwave chamber where biomass is placed. The microwave-assisted pyrolysis system is usually purged with N_2, He, or CO_2 to ensure a limited-oxygen environment (Zubairu et al. 2012; Lam et al. 2017). As biomass is often a poor absorbing material, microwave absorbers (also called dielectrics) are often homogeneously blended with the raw material before pyrolysis, to ensure a stable heat transfer and a high enough pyrolysis temperature inside the reactor (Ethaib et al. 2020). The selection of a suitable microwave

absorber is the key to the improvement of biochar characteristics. Similar to conventional pyrolysis, operational parameters can greatly affect the biochar yield and characteristics during microwave-assisted pyrolysis, such as microwave power—which has a direct link with pyrolysis temperature, or residence time (Mushtaq et al. 2014; Huang et al. 2016). Other than that, the types of absorbers and/or catalysts mixed with the raw material also determine the properties of the char produced (Fang et al. 2021).

2.3 Pyrolysis Under Non-inert Ambiances

Unlike conventional pyrolysis which often uses inert gases (especially N_2) to form an oxygen-limited environment, the use of non-inert atmospheres such as steam, CO_2, or NH_3 during pyrolysis has emerged as a promising trend for pyrolysis (Lee et al. 2017a; Chen et al. 2018; Grottola et al. 2019). As opposed to post-pyrolysis activation using reacting agents at high temperatures (usually superior to 700 °C), steam, CO_2, or NH_3 are introduced from the beginning of the pyrolysis process at low temperatures to create a non-inert atmosphere. Flow rates and concentrations of these gases are well controlled to obtain desired pyrolysis conditions suitable for each type of raw material. An example of a Macro-TGA system for investigating pyrolysis under different atmospheres is presented in Fig. 3. The reactor, containing a ceramic tube (1), is placed in an electrical furnace with three independent heating zones (T_i) to maintain a uniform temperature. The pyrolysis atmosphere is generated by a mixture of N_2 and a pyrolysis agent (CO_2, NH_3, or H_2O) in selected proportions. Gas flows can be precisely controlled by mass flow meters (M_i). The gas mixture at atmospheric pressure moves across a 2-m-long coiled tube (3) located in the upper part of the reactor before reaching the sample. Then the sample holding (4) containing the sample is lifted from the bottom to the desired position.

Compared to conventional pyrolysis, pyrolysis under non-inert ambiances offers some special characteristics. Steam can efficiently penetrate the biomass during pyrolysis, enhancing desorption, distillation, and efficient removal of the pores (Pütün et al. 2006; SASAKI et al. 2009). Meanwhile, the CO_2 atmosphere hinders polymerization reaction and secondary char formation by reacting or cracking tar compounds that may lead to its formation (Choi et al. 2020; Lee et al. 2020). In addition, CO_2 has an affinity to react with hydrogenated and oxygenated groups, resulting in a carbon-rich char (Shen et al. 2017). Regarding NH_3-assisted pyrolysis, a significant activation of N-containing surface functional groups on biochar occurs as NH_3 breaks down to some radicles of NH_2, NH, and H^+ and they chemically react with the biochar surface oxides groups (Mian et al. 2018).
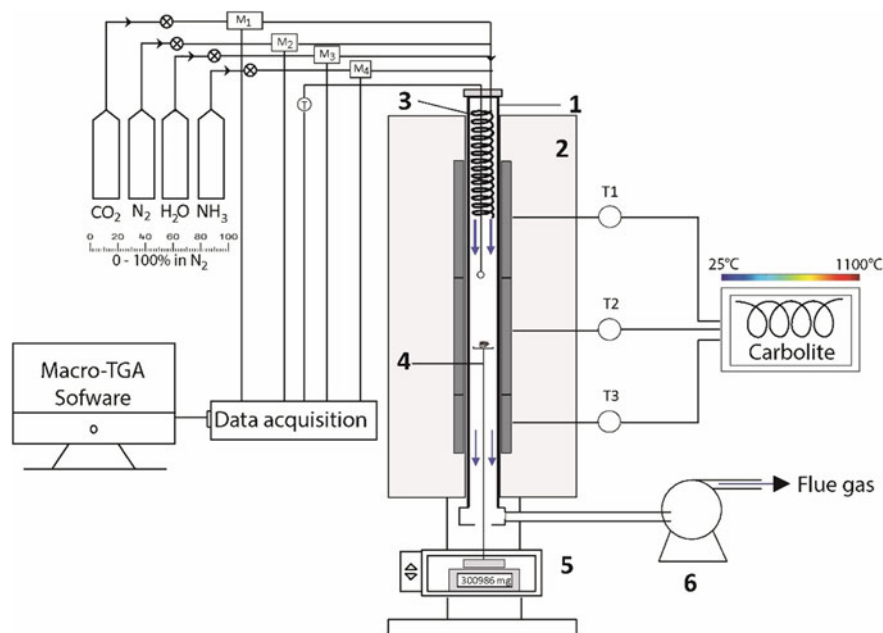
Fig. 3 A Macro-TGA system for pyrolysis under non-inert ambiances. The desired atmosphere is generated by different gases (CO_2, H_2O, NH_3, or a mixture of each with N_2) and regulated by flow meters (M_i). (1) Ceramic tube, (2) Electrical furnace, (3) 2-m coiled preheater, (4) Sample holder, (5) Weighing scale, (6) Extractor, (T_i) Regulation thermocouples

2.4 Hydrothermal Carbonization (Wet Pyrolysis)

During the hydrothermal carbonization (or wet pyrolysis) process, the raw material is heated in subcritical water (between 100 and 374 °C) or supercritical water (above 374 °C) at autogenic pressures in a high-pressure reactor (Ischia and Fiori 2021). Many similar reaction mechanisms occur during both dry pyrolysis and wet pyrolysis. Macro-molecules degrade to form liquid and gaseous products, while solid–solid interactions led to a rearrangement of the original structure (Libra et al. 2011). However, the difference in the pyrolysis atmosphere plays a defining role in the characteristics of the resulted biochar. The degradation of biomass during wet pyrolysis is initiated by hydrolysis, which exhibits lower activation energy than most of the pyrolytic decomposition reactions. Therefore, the principle biomass components are less stable under wet pyrolysis, leading to lower decomposition temperatures. Hemicelluloses decompose between 180 and 200 °C, most of the lignin between 180 and 220 °C, and cellulose above approximately 220 °C (Hydrothermal degradation of polymers derived from plants 1994). For comparison, in dry pyrolysis of biomass, hemicellulose generally decomposes at temperatures between 220 and 315 °C, cellulose between 315 and 400 °C, and lignin between 160 and 900 °C (Yang et al. 2007). This method actively introduces hydroxyl and carboxyl functional groups onto the

surface of biochar, improving the biochar contaminant adsorption. Moreover, with such low process temperature and high-pressure conditions, most of the organics in the input raw material remain, and/or are transformed into solids, and only a little gas is produced (<5%) (Libra et al. 2011). Therefore, hydrothermal carbonization is highly suitable for the production of biochar.

2.5 *Integrated Pyrolysis Techniques*

Several recent attempts seek to combine the above-mentioned techniques, namely microwave-assisted hydrothermal (co-)pyrolysis and microwave steam/CO_2 (co-) pyrolysis. During microwave-assisted hydrothermal carbonization, the raw material is subjected to microwave heating to obtain moderate temperatures (180–250 °C) in a tight-closed space for a short reaction time (dozens of minutes to a few hours). The decomposition of biomass then occurred under high pressures (2–10 MPa, usually autogenously). Meanwhile, in microwave steam/CO_2 (co-) pyrolysis, microwave heating is initially conducted to transform biomass into a precursor, after which pyrolysis was performed under a CO_2 or steam atmosphere (Yek et al. 2019, 2020). Lots of complex reactions take place during these processes, such as dehydration, decarboxylation, hydrolysis, polymerization, poly-condensation, and aromatization. With these techniques, water inside biomass has good absorption properties of microwave energy due to its high dielectric constant (δ') and loss tangent ($\tan \delta$), which help in increasing the heating rate and reduce the energy consumption for the process (Tsubaki et al. 2012, 2016; Antonetti et al. 2015).

3 Advantages of New Pyrolysis Methods

3.1 *Co-pyrolysis*

The co-pyrolysis technique could significantly improve the biochar yield and its quality without any improvements in the system process (Yao et al. 2021). Some minor modifications may be needed, but only for the feed preparation system. The interaction or synergy between agricultural and industrial materials in co-pyrolysis can improve certain properties of biochar, such as reduction of electrical conductivity, increase in water-holding capacity, neutralizing power, stability, and enabling the release or concentration of macro and micronutrients (Rodriguez et al. 2021).

Another important advantage of co-pyrolysis lies in the synthesis of novel biochar composites. Sewu et al. (2019) produced a biochar composite from the co-pyrolysis of bentonite and kelp seaweed (Sewu et al. 2019). The product had a higher carbon sequestration potential and adsorption capacity of dye than the kelp biochar. In another study, biochar/layered double hydroxides composite was synthesized using

co-pyrolysis after pre-loading MgAl-layered double hydroxides on the surface of rice husk powder through precipitation (Lee et al. 2019). Results showed a significant enhancement of phosphate adsorption due to the effective adsorption of anionic contaminants by the biochar through ion exchange with negatively charged groups located between hydroxide layers. Co-pyrolysis of cigarette industry-based waste with bentonite and calcite (5:1 w/w) at 700 °C helped in enhanced Pb removal in comparison to the control biochar with no mineral additives (Ramola et al. 2020). Similarly, rice husk and calcite (4.2:1 w/w) co-pyrolyzed together imparted synergistic effects for superior adsorption capacity for phosphate removal at lower concentration in comparison to control rice husk biochar and calcite separately (Ramola et al. 2021).

Table 1 presents some recent studies on co-pyrolysis of biomass, the effect of co-pyrolysis on the resulted char, and its applications.

3.2 Microwave-Assisted Pyrolysis

High heating rates obtained during the process are a major advantage of microwave-assisted pyrolysis, as this can help produce a type of biochar with a higher surface area and pore volume than those obtained with conventional pyrolysis (Luque et al. 2012; Zhang et al. 2017b; Zaker et al. 2019). Furthermore, it is indicated that biochar obtained from this technique achieves a high uniformity and cleanness (Yagmur 2012; Huang et al. 2016). This method also comfortably accepts the addition of cheap absorbers or catalysts, or the blending of materials together during pyrolysis without any modification of the system to create biochar products with better adsorption capacity (Chen et al. 2008; Fang et al. 2021). Some up-to-date microwave-assisted pyrolysis studies are presented in Table 2.

3.3 Pyrolysis Under Non-inert Ambiances

This technique is relatively energy-efficient and eco-friendly compared with other approaches aiming at improving the adsorption capacity of the biochar (e.g., pyrolysis at high temperatures, catalyst pyrolysis). Steam has the effect of removing tar and other trapped products of incomplete combustion during pyrolysis on the surface of biochar, creating a clean final product (SASAKI et al. 2009; Kurian et al. 2015). Meanwhile, CO_2-assisted pyrolysis helps simultaneously improve the quality of pyrolysis gas and biochar produced (Lee et al. 2017b). In a recent study, the CO_2-assisted pyrolysis of teabags increased the gas yield, particularly hydrogen, and prevented the formation of pollutants (e.g., phenolic compounds, benzene derivatives, and polycyclic aromatic hydrocarbons) (Lee et al. 2021). The biochar product also had a high calorific value (HHV = 26.8 MJ kg^{-1}) comparable to that of coal. Regarding NH_3-assisted pyrolysis, it can be considered a novel way to synthesize

Table 1 Some recent studies in co-pyrolysis of biomass

Raw material	Pyrolysis conditions	Effect on biochar properties	Application	References
Dried municipal sludge and tea waste	– Temperature: 300 °C in 2 h – Raw material ratio: 1:1	– Enhanced active adsorption sites – Formation of some new aromatic groups	Cadmium removal from aqueous solution	Fan et al. (2018)
Agricultural wastes (poultry litter, swine manure) and industrial wastes (construction wood, tire, PVC plastic)	– Temperature: 300–700 °C – Raw material ratio: 1:1	– Low H:C (0.06) and O:C (0.30) molar ratios – Reduction of electrical conductivity, Increase in water-holding capacity, neutralizing power, and stability	Carbon sequestration in soil, soil quality improvement	Rodriguez et al. (2021)
Rape straw and phosphate rock	– Temperature: 500 °C in 2 h – Heating rate: 10 °Cmin^{-1} – Raw material ratio: 5:1 to 2:1	– Increase in carbon retention (up to 27.5%) – Decrease in aromaticity and graphitization – Positive effect on Pb removal capacity with a low additive amount of phosphate rock (ratio 5:1)	Improvement of carbon sequestration and enhancement of Pb removal	Gao et al. (2019)
Seaweed-rice husk-pine sawdust	– Temperature: 500 °C in 1 h – Raw material ratio: 7:3	– Enhancement of thermal stability, aromaticity, pH balance, ash content, and yield	Soil ameliorant, contaminant remediation	De Bhowmick et al. (2018)
Bituminous coal and wheat straw Wu et al. (2019)	– Temperature: 950 °C in 0.5 h – Raw material ratio: 3:1 – Heating rate: 10 °C min^{-1}	– Increase in specific surface area – Inhibitory of the ordering and uniformity of microscale structure	Enhancement of kinetics during biomass gasification	Wu et al. (2019)

Table 2 Recent studies on microwave-assisted pyrolysis of biomass

Raw material	Pyrolysis conditions	Effect on biochar properties	Application	References
Empty fruit bunch	– Power: 2.6 kW – Frequency of 2.45 GHz – Temperature: 253 °C – Duration: 90 min	– High HHV (26.4 MJ kg^{-1}) – Higher O/C and (N + O)/C ratios – Stable burning characteristics	Solid fuel in power generation to substitute coal	Azni et al. (2019)
Switchgrass	– Power: 700 W – Frequency: 2.45 GHz – Temperature: 300 °C – Catalyst: K$_3$PO$_4$, clinoptilolite, bentonite, and their mixtures (catalyst-to-biomass ratio 10–30%)	– Increase in specific surface area and plant nutrient contents – High sorption affinity and high cation exchange capacity	Improvement of water-holding capacity and fertility of sandy soil	Mohamed et al. (2016)
Sugarcane bagasse	– Power: 600 W – Duration: 30 min – Catalyst: Ferric oxide	– Increase of porous structures and pore size – Increase of specific surface area – Ferromagnetic properties observed	Adsorbent for the removal of Cd^{2+} from aqueous solutions	Noraini et al. (2016)
Soapstock	– Power: 1000 W – Frequency: 2.45 GHz – Temperature: 550 °C – Bentonite: soapstock ratio: 1:1:2	– Decrease in carbon content, increase in ash content and porosity – Increase in removal efficiency of Cd^{2+} compared to biochar without catalyst (77.9% vs. 50.5%)	Adsorbent for the removal of Cd^{2+} from aqueous solutions	Dai et al. (2017)
Horse manure	– Power: 1000 W – Frequency: 2.45 GHz – Catalyst: coconut shell-based activated carbon	– High heating value (35.5 MJ kg^{-1}) – High surface area and pore volume	Adsorbent or soil improvement additives	Mong et al. (2020)

N-doped biochar. Promotion of stable N-containing groups and a significant decrease of O-containing groups in the biochar could be obtained with this technique (Chen et al. 2020). The functional char with more active sites and surface functional groups obtained by NH_3 ambiance pyrolysis could also significantly enhance its adsorption capacity (Shen et al. 2017; Mian et al. 2018). Table 3 summarized some recent studies on pyrolysis under non-inert ambiances and its effects on the biochar product.

3.4 Hydrothermal Carbonization

The advantage of hydrothermal carbonization lies in the capability of converting the "wet" raw material into carbonaceous solids at a relatively high yield in the absence of an energy-intensive drying process, hence lowering the requirement of excess auxiliary drying equipment (Zhou et al. 2019; Olszewski et al. 2020). This solution helps handle a wide range of unconventional sources of biomass, such as sewage sludge, municipal solid waste (bio-fraction), livestock and aquaculture residues, as well as the very new types of biomass of interest such as algae. To some extent, hydrothermal carbonization helps minimize the harmful effects to the environment from these types of biomass, because some of them are continuously generated in large quantities and require expensive management or treatment stages. Moreover, hydrothermal carbonization can be followed by an activation process to produce functional biochar. The latter is superior to ordinary biochar in some features such as adsorption abilities versus flue gases or heavy metals (Tu et al. 2021). Table 4 presents some examples of wet pyrolysis and the corresponding results on the char product.

3.5 Integrated Pyrolysis Techniques

The combination of several pyrolysis techniques in a correct way can optimize the strengths and limit the weaknesses of each method. Therefore, integrated pyrolysis techniques provide various advantages, such as high conversion efficiency, low processing temperatures, and the capability to process wet and aqueous raw materials (Liu et al. 2020; Luo et al. 2020; Zhang et al. 2021a). As an example, in our study, biochar prepared from cashew nut shell, bagasse, macadamia nut shell under conventional pyrolysis process at different temperatures and residence times in an N_2 environment were compared to microwave-hydrochar generated in a 1200-W microwave hydrothermal system (temperature: 200 °C in 15 min, with a biomass-to-water ratio of 1:10). Results highlighted a significant increase in the porosity, expressed by the higher position of the N_2 adsorption–desorption isotherms in Fig. 4.

Table 3 Recent studies on pyrolysis under non-inert ambiances

Raw material	Pyrolysis conditions	Effect on biochar properties	Application	References
Poplar, giant reed	– Temperature: 600° – Steam mass flow rate: 0.25 g s^{-1}	– High surface area (347.5 m^2 g^{-1}) – Lower metals mobility	Immobility of retained potentially toxic elements	Grottola et al. (2019)
Populus nigra	– Temperature: 480–700 °C; – Steam flow rate: 0.25 g s^{-1}	– Biochar with narrow microporosity and average pore sizes from 0.55 and 0.6 nm	CO_2 adsorption and separation	Gargiulo et al. (2018)
Bamboo	– Temperature: 500 °C in 45 min; – Steam flow rate: 5 ml.min^{-1}	– Low surface area (2.12 m^2 g^{-1}) with mesoporous structure – Enhancement of active sites	Adsorption of Cu^{2+} and tetracycline	Wang et al. (2020)
Red pepper stalk	– Temperature: 600 °C – CO_2 concentration: 50% (in N$_2$) and 100% – Total flow rate: 500 ml min^{-1}	– Increase in surface area compared to biochar produced with N$_2$ (109 m^2 g^{-1} vs. 32.46 m^2 g^{-1}) – Lower pH and electrical conductivity – Higher ash content, degree of carbonization, hydrophility, and polarity	Waste management, energy recovery, and biochar production	Lee et al. (2017b)
Bamboo waste	– Temperature: 600 °C – NH$_3$ concentration: 40% in Ar – Total flow rate: 200 ml min^{-1}	– Increase of N$_2$ content (4.85 wt%) and N-containing groups; – Increase of specific surface area (369.59 m^2 g^{-1}) – Excellent electrochemical property (120 F g^{-1})	Production of N-doped biochar	Chen et al. (2018)

Table 3 (continued)

Raw material	Pyrolysis conditions	Effect on biochar properties	Application	References
FeCl$_3$-laden agar biomass	– Temperature: 600 and 800 °C in 1 h – NH$_3$ concentration: 28% in N$_2$ – Total flow rate: 500 ml min^{-1}	– High Cr (VI) adsorption capacity (up to 142.86 mg g^{-1}) – Increase of magnetic properties and activated N-functional groups	Removal of Cr (VI)	Mian et al. (2018)

Table 4 Recent studies on hydrothermal carbonization

Raw material	Pyrolysis conditions	Effect on biochar properties	Application	References
Bamboo	– Temperature: 220–260 °C in 1 h – Biomass: solution ratio: 1:10 (0.1 M HCl, H_2SO_4, and HNO_3) – Heating rate: 3 °C min^{-1}	– Low specific surface (3–16 m^2 g^{-1}), small pore size (1–10 nm) – HCl and HNO_3 can form a single micron carbon sphere – H_2SO_4 can form irregularly shaped hydrochar particles groups	Production of functional hydrochar microspheres	Zhang et al. (2021b)
Olive pulp	– Temperature: 190–250 °C between 2 and 15 h – Biomass: deionized water ratio: 1:3.15 – Heating rate 5 °C min^{-1}	– Increase the residence time to 15 h increased the hydrochar yield by 8%; – Higher temperatures and longer residence times increased HHV from 24 to 30 MJkg^{-1}, and decreased electrical resistivity from 800 to 200 mΩm	Production of pellets at low compression pressure without a binder for use as metallurgical reducing agents	Surup et al. (2020)
Defective coffee beans	–Temperature: 150–250 °C for 40 min – Biomass: deionized water ratio: 1:10	– Decrease in ash content, N content, H/C, and O/C molar ratios with increasing temperature	Production of functional and energy-dense solid biofuels	Santos Santana et al. (2020)
Tobacco stalk	– Temperature: 220 °C in 6 h – Biomass: catalyst: deionized water ratio: 2:1:30	– High surface area (1498 m^2 g^{-1}) and volume (0.712 cm^3 g^{-1}) – Nitrogen functions on the surface significantly increased	Enhancement of CO_2 capture performance	Huang et al. (2021)
Wood and parchment of *Coffea arabica*, *Eucalyptus sp.* wood, and giant bamboo	– Temperature: 180–240 °C in 3 h – Biomass: deionized water ratio: 1:8	– HHV, fixed carbon content, and energy density increased with increasing reaction severity – High HHV (24.6–29.2 MJ kg^{-1}) at temperatures ≥ 220 °C	Energy and value-added products generation	Mendoza Martinez et al. (2021)
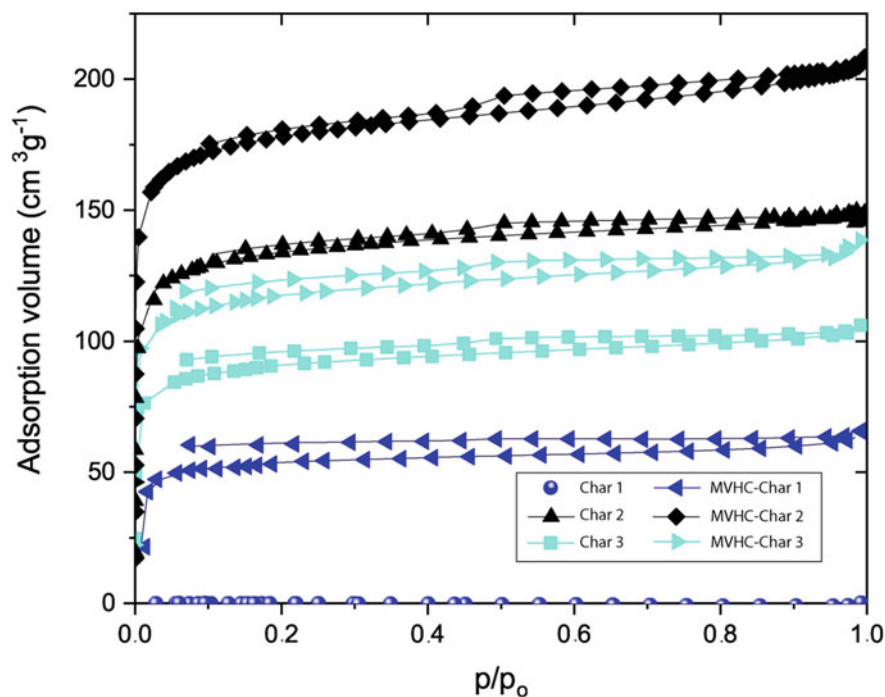
Fig. 4 The N_2 adsorption–desorption isotherms of different "normal" biochars (Char) and microwave-hydrothermal chars (MVHC-Char). Char 1: Cashew nut shell, Char 2: Macadamia nut shell, Char 3: Bagasse

4 Limitations of New Pyrolysis Methods

4.1 Co-pyrolysis

The primary disadvantage of co-pyrolysis lies in the instability of the product quality. Given that this technique deals with many types of biomass, the mechanism involved in co-pyrolysis generally goes through a series of complex reactions that is hard to control, especially on large scales (Abnisa and Wan Daud 2014). Moreover, it varies from one raw material to the other, and is highly dependent on the mixing ratio and the pyrolysis conditions. Knowledge of the synergistic effects during pyrolysis, therefore, remains poor.

4.2   Microwave-Assisted Pyrolysis

The energy conversion efficiency of microwave-assisted pyrolysis is relatively low. The energy conversion of the input electric energy to heat by microwave heating is typically in the range of 20–60% (Yao et al. 2014; Sun et al. 2016; Rosa et al. 2017). Moreover, the energy loss in the transformer and the magnetron during microwave-assisted pyrolysis of biomass is approximately 26%, and the power loss caused by the heat loss is approximately 29% (Xiqiang et al. 2014; Zhang et al. 2017a). The interference between electromagnetic irradiation and thermocouple sensors also limits the accurate measurement of the temperature in a microwave reactor (Yin 2012). In addition, the penetration depth in materials of microwave-assisted pyrolysis is quite limited, inhibiting the size of the reactor (Sajjadi et al. 2014; Sun et al. 2016).

4.3   Pyrolysis Under Non-inert Ambiances

The biggest limitation of substituting N_2 with other atmospheres for pyrolysis lies in the cost of the substitutes. The higher cost of pure NH_3 and compressed CO_2 may hinder the development of this technique. For the case of steam, it needs another piece of equipment to generate superheated steam, or supercritical steam before injecting it into the pyrolysis system. This requires cheaper gas/chemical sources with comparable efficiency. In addition, the optimum concentration of reactive agents in pyrolysis depends on many factors. The quality of the biochar produced is not necessarily proportional to the increase in the concentration of these gases or chemicals (Chen et al. 2018; Yang et al. 2018), asking for intensive research for each individual process and material.

4.4   Hydrothermal Carbonization

Hydrothermal carbonization (wet pyrolysis) is an energy-intensive process, from heating up the water in a high-moisture content raw material, powering the process to drying the char product after the process, so the energy balance should be well established if the generated char is used for energy purposes. A longer treatment time and further treatments that are often required for wet biomass waste also present disadvantages of this technique (Ischia and Fiori 2021). Moreover, some previous studies report lower stability of the biochar produced from wet pyrolysis, in comparison with the char produced from dry pyrolysis (Liu et al. 2021). Thus, possible toxic effects or risks of the biochar produced from wet pyrolysis in long-term applications, such as in soil amendment, have to be carefully evaluated. This knowledge is still

lacking in the literature. The high-pressure requirement for raw material decomposition is also a big limitation to the upscale of this technology. Further improvements in hydrothermal carbonization need to be explored to use simplified devices.

4.5 Integrated Pyrolysis Techniques

The complexity of integrated pyrolysis techniques represents the biggest limitation for their applications on larger scales. The characteristics of the product are influenced by a set of various factors with mutual effects, where the degradation mechanism of the raw material depends on the nature of each raw material in each specific condition. The sensibility of these methods versus pyrolysis factors is relatively high, causing high difficulty in process control. To date, no pilot studies have been published, and information on the economic efficiency and stability of these methods is very sketchy and requires more research in the future.

5 Conclusion and Future Prospects

Various pyrolysis strategies of biomass have emerged as new trends in biochar production to enhance sustainability. These trends include co-pyrolysis, microwave-assisted pyrolysis, pyrolysis under non-inert ambiances, hydrothermal carbonization (wet pyrolysis), and integrated pyrolysis techniques. Each process has its own advantages—such as treatment of a wide range of unconventional raw materials, synthesis of novel biochar composites, or enhanced biomass conversion efficiency, but also limitations—such as instability of the product quality, high investment costs, or difficulty in up-scaling. The effects of these novel methods on the biochar characteristics can be categorized into four groups: (a) improvement of specific surface and pore structure, (b) increase of certain functional groups, (c) promotion of the activated oxygen species, and (d) immobility of heavy metals in biochar. Opportunities for the application of these techniques are numerous, from adsorption of contaminants, soil amendment, reduction of risks of using contaminated biomass-derived biochar, and energy production.

Further investigations should be implemented to facilitate the application of engineered biochar. Information on the relationship between the raw materials, catalysts, and pyrolysis conditions on the characteristics of the resulted biochar is still very limited and incomplete, requiring more systematic studies. As new characteristics of biochar are developed, pilot tests or field experiments are also recommended to evaluate the real effects of biochar prior to large-scale applications or their long-term risk during use, especially for biochar derived from different types of sludge or other contaminated biomass. Novel statistical analysis methods such as modeling or machine learning would be a good idea to predict the properties of biochar and their impacts during environmental applications.

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Characterization of Engineered Biochar: Proximate Analyses, Ultimate Analyses, Physicochemical Analyses, Surface Analyses, and Molecular Analyses

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Abstract   In recent times, biochar production, its modification, and utilization have gained much attention. The uniqueness of biochar properties allows its ease in modification to meet up with the application requirements. Low production cost, abundance of raw material, and its applications have contributed to enhancing the research work of biochar. Various biochar production pathways (raw material, process conditions) and their utilization require standardization to maintain quality. In this chapter, the characterization of engineered biochar is explained in detail, which provides robust insight into the analyses, procedures, and expected results for a typical biochar. Specifically, proximate, ultimate, physicochemical, surface, and molecular analyses are described.

Keywords Biochar · Pyrolysis · Thermal conversion

1   Introduction

The area of biochar production, utilization, and engineering is attracting attention due to its applicability in many different fields, low-cost production, environmental-friendly impact, and its use as a tool that can help solve global problems related to climate change, environmental pollution, and soil degradation (Mayer et al. 2014). Different applications, for example, solid fuel productions, pollutants removal, carbon sequestration, soil amelioration (Oliveira et al. 2017), odors mitigation from

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livestock production (Chen et al. 2021a; Lee et al. 2021), biological processes of organic waste treatment (methane fermentation and composting) (Malinowski et al. 2019), supercapacitor and high yield sorbent material production (Bartoli et al. 2020), geoengineering (Wani et al. 2021) require biochar with completely different properties.

Different analyses have been either developed or adopted from other fields to analyze and compare biochar. In this chapter, standard methods and results to be expected are described. The methods are ordered from the most used like proximate analysis to more sophisticated molecular analyses. Analyses and biochar properties described in this work are presented in Fig. 1. The presented classification is simplified, because some methods/properties may belong to more than one group of analyses. The analyses are divided into five subsections, namely: proximate, ultimate, physicochemical, surface, and molecular analyses. The chapter ends with the main conclusions and future prospects of biochar analyses.
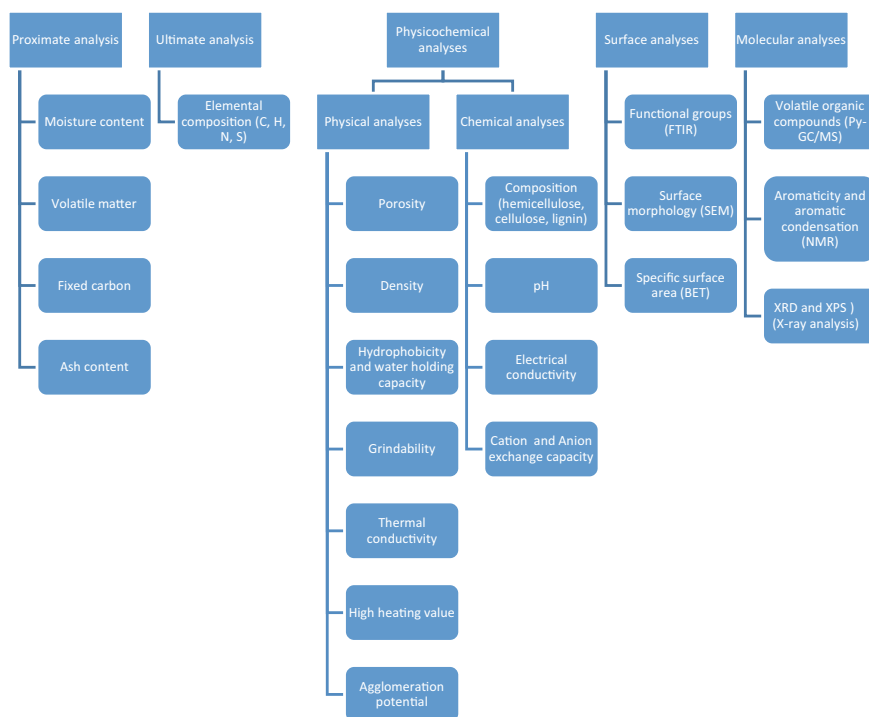
Fig. 1 Analyses classification covered in present chapter

2 Proximate Analysis

The proximate analysis has been used for over 180 years (Suárez-Ruiz and Ward 2008). It is one of the most basic, and widespread analyses used mainly for solid fuels comparison. The data from the analysis provides information about moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash (AC) in fuel. These properties are related to the amount of water, materials that burn in either gaseous and solid state, and the mass of inorganic residues contained in the fuel, respectively (Nunes et al. 2018). There are many standards for proximate analysis such as ISO (International Organization for Standardization), ASTM (American Society for Testing and Materials), and a lot of variations for materials, e.g., ASTM D3172-13 for coals, or ISO 18122 and ISO 18123 for biofuels. Though proximate analysis is a relatively simple analysis, some methods were developed to perform it quicker, for example, by using thermogravimetric equipment (Torquato et al. 2017). As biochar is made from biomass and its properties resemble coal properties, using the aforementioned standards or methods appears fitting.

Regardless of the standard used, the proximate analysis is about the heating of analyzed material in specific conditions (temperatures, times, and atmospheres). Different standards varied mainly by slight differences in temperature, time, and device used. First, a raw sample is dried at 105 °C until the mass losses resulting from water evaporation stops. During drying some volatile organic compounds may also be released. Then the difference in mass before and after drying moisture content is calculated. The dry sample is then pyrolyzed at 950 °C for 7 min. The difference in mass before and after pyrolysis is the mass of volatile matter. Then, the sample is burned at 600–700 °C, and the residue that result is ash. After that, the fixed carbon is calculated by subtraction from 100%, the sum of the percentage share of moisture content, volatile matter, and ash content.

The results of the proximate analysis can be given in four ways. The air-dry sample is related to mass after surface water is removed. Additionally, the dry basis presents the result that is related to the mass of the sample after all possible removal of moisture (by drying at 105 °C). A dry ash-free (daf) basis presents results that are related to the mass of the sample after all moisture and ash have been removed (Torquato et al. 2017).

The properties of proximate analysis differ significantly between biochar, and the main reason for this is the variation in pyrolysis conditions and raw materials. The temperature typically varies from 200 to 800 °C, from several minutes up to hours. Biochar can be made from any organic materials like wood, or non-wood raw material, e.g., agricultural waste (plants, manures), sewage sludge, algae, etc. (Jafri et al. 2018). In general, higher temperatures and longer residence times promote an increase in fixed carbon and ash content in biochar. It follows from the fact that during pyrolysis all moisture content is removed and most volatiles are released. The more severe the process conditions, the more volatiles are released. Moreover, some volatiles can be converted into fixed-carbon if they stay too long in the reactor due to secondary reactions (Safdari et al. 2018). As a result, depending on the used

raw material, ash content differs from 1 to 20%, wherein it is higher for non-wood biochar than wood-based biochar. The content of volatile matter in biochar differs from 6 to 88%, whereas fixed carbon differs from 11 to 86% (Jafri et al. 2018).

Based on the proximate analysis results, the fuel ratio (FR) can be calculated. FR is the ratio of fixed carbon to volatile matter. The FR for different coals is $\geq$10 for anthracite, 6–10 for semi-anthracite, 3–6 for semi-bituminous, and <3 for bituminous (Thrush 1968). In comparison wood and wood-based biochar made at 220, 350, and 550 °C in 30 min, have an FR value of 0.13, 0.16, 1.23, and 5.6, respectively (Wang and Howard 2018). Kim et al. (2019) have established a correlation between FR and the emission of NO_x for coal. Their work showed the possibility of predicting NO_x emission during biochar/coal combustion (Kim et al. 2019).

The additional useful biochar properties are total solids (dry mass) and the volatile solids (VS) content (loss of ignition or organic matter content). Both TS and VS are not a part of the proximate analysis but their determination is done by a similar method. The TS can be determined by subtraction from 100% of the moisture content. The VS is determined after dry sample incineration at 550 °C, where the difference between initial mass and residues is a mass of VS. The % share of VS is always related to the dry mass of the sample (Kelly Orhorhoro et al. 2017). These parameters are important for biochar used as an additive for biological processes like methane fermentation/ composting (Kelly Orhorhoro et al. 2017; Stegenta-Dąbrowska et al. 2020).

3 Ultimate Analysis

The ultimate analysis (elemental analysis) is the term given for the determination of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) content in the sample. The C, H, N, S, and O elements are the main constituents of solid biofuel (Caillat and Vakkilainen 2013). Besides the different analyzers, there are equally varied approaches to determining the elemental composition, but the basic principles remain the same. The sample is combusted at 1000 °C by using pure oxygen. As a result, the elements C, H, N, and S are converted into carbon dioxide, water, oxides of nitrogen, and sulfur dioxide, respectively (Ramola et al. 2014). Next, combustion products are carried by using helium gas heated at around 600 °C in a copper tube. The copper removes all residual oxygen and converts any nitrogen oxides into nitrogen gas. Then, combustion gases are carried further through the absorbent traps in order to remove unwanted gases, e.g., hydrogen chloride. Finally, the clean carbon dioxide, water, nitrogen, and sulfur dioxide can be quantified by using gas chromatography, or by separate infrared and thermal conductivity cells (Thompson 2008).

From an energetic point of view, biochar with high carbon content is desired. C, H, and S are elements that contribute to increasing the heating value. Nevertheless, during pyrolysis, most of the H will go to the volatile matter, and S will be the source of unwanted SO_x emissions. Also, N contained in the fuel is the main source of NO_x emission (Caillat and Vakkilainen 2013). The concentration of elements in

biochar varies significantly depending on substrate and pyrolysis regime. In previous work, 10 substrates were pyrolyzed from 300 up to 500 °C and residence times of 20–60 min (with intervals of 20 °C and 20 min) (Świechowski et al. 2020). The results showed that for some materials, the pyrolysis process results in increasing the carbon content with an increase in temperature. Materials that followed this trend were fabrics, and wood, where C content increased from 44 and 47% up to 71 and 67%, respectively, for biochar made at 500 °C. Other materials like kitchen waste or paper were characterized by an initial increase in the carbon content at lower temperatures in comparison with the raw material, but with increasing temperature, the C content decreased. Moreover, for materials like plastic, rubber, or refuse solid fuel, the C content decreased compared to raw material at all temperatures (Świechowski et al. 2020, 2021). Regardless of processed material, the devolatilization results in hydrogen and oxygen removal. The mass of removed H and O depends mainly on the temperature and it increases with an increase in temperature. As result, biochar has lower H and O content in comparison with raw materials used for their production (Ramola et al. 2014; Świechowski et al. 2020, 2021). Since each of the elements is removed at a different rate depending on process conditions, the final elemental composition is the result of the weight loss of the individual components and ash residues (Zhang et al. 2018).

Besides, the elemental composition is used to perform graphical solid fuel classification. It is done by plotting a modified Van Krevelen diagram that shows the degree of coalification and energy densification (Pudasainee et al. 2020). The diagram has two axes, on the y-axis is the atomic H to C ratio, whereas on the x-axis is the atomic O to C ratio (Pudasainee et al. 2020). The atomic ratios can be calculated by using the following equations; H/C = (H/1)/(C/12), O/C = (O/16)/(C/12), where the numbers stand for the atomic masses of elements (Świechowski et al. 2019). Commonly, the diagram is ordered into 5 groups; anthracite, coal, lignite, peat, and biomass. The value of the H/C ratio varied from 0.1 for anthracite to 2 for biomass, and the value of the O/C ratio varied from 0.1 to 1 for anthracite and biomass, respectively. Generally, the lower the O/C and H/C ratios, the greater the energy and the higher coalification (Pudasainee et al. 2020). By plotting the biochar elemental composition on the modified Van Krevelen diagram, biochar classification and end uses determination are possible. Depending on the raw material and pyrolysis conditions, biochar H/C ratio values vary from 0.4 to 1.2, and the O/C ratio varies from 0.2 to 0.4 (Santín et al. 2017). Additionally, the knowledge of the elemental composition of biochar allows the indirect calculation of the higher heating value of biochar. For example, a modification of Dulong's formula can be used (Hosokai et al. 2016).

$$HHV = 33.8C + 1.223\left(H - \left(\frac{O}{8}\right)\right) + 9.4S \qquad (1)$$

where

HHV—high heating value of fuel, MJ kg^{-1},

C—elemental carbon content in dry fuel, %

H—elemental hydrogen content in dry fuel, %

O—elemental oxygen content in dry fuel, % and

S—elemental sulfur content in dry fuel, %.

Besides the ultimate analysis, other elements are also determined for biochar. When used for energy purposes (e.g., co-fired in boiler), the knowledge about oxides is useful for the calculation of slagging and fouling indicators. There are many different indicators and most of them are based on SiO_2, CaO, K_2O, P_2O_5, Fe_2O_3, Al_2O_3, MgO, Na_2O, and SO_3 composition (Lachman et al. 2021). When biochar is used as an additive for biological processes or a soil amendment, other elements need to be determined. These include macronutrients (P and S) and micronutrients (Ca, K, Mg, Na, Fe, Mn, Zn) (Morales et al. 2015). These macro- and microelements are determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) according to ISO 11885:2009 standard. Morales et al. (2015) analyzed micro and macro elements in 102 different biochar. The amount of P, S, Ca, K, Mg, Na, Fe, and Zn varied significantly depending on pyrolyzed substrate and process conditions. An increase in temperature slightly increased the P content for manure and kitchen waste-derived biochar, while a slight decrease was observed for wood biochar. For other materials the changes were imperceptible. For most of the tested biochar, the increasing temperature had no significant effect on Ca and S content. In general, the value of Ca slightly increased or remained unchanged. The highest increase in Ca was observed for biochar made of paper and chicken manure. An increase in process temperature led to an increase in the amount of K, Mg, and Mn in the biochar. For some materials, the increase was insignificant, while for materials such as manure, corn, and kitchen waste the increase was significant. Regardless of the raw materials, pyrolysis resulted in a slight increase in Fe content, especially for materials like cattle manure waste, food waste, and paper waste (Morales et al. 2015).

4 Physicochemical Analyses

4.1 Physical Analyses

4.1.1 Porosity

In pyrolysis when temperature increases beyond 500 °C, the degree of porosity differs in different raw materials. It was investigated that biochar produced at 350 °C resulted in an average porosity ≤10 μm (Weber and Quicker 2018; Batista et al. 2018).

Porosity is described as the percent of the biochar particle volume not filled by solid (Brewer et al. 2014). This would include all pore volumes that open directly to the exterior of the biochar particle, yet are smaller than the Dry*Flo*® particle standard size of 75–8000 μm (Wade et al. 2015). According to Plötze and Niemz (2011) porosity of biochar can be calculated as follows:

$$n = 1 - \rho/\rho s \times 100 \qquad (2)$$

where

    n—porosity in percent,

    ρ—oven-dry bulk density, and

    ρs—specific solid density.

Some parameters have been associated with porosity, like pore accessibility and mercury porosimetry. Pore accessibility is when pores within given particles would not all have access to the exterior (Brewer et al. 2014). Mercury porosimetry can be used to determine the pore size distribution and porosity of biochar. It is used by applying pressure to a sample immersed in mercury. The applied external pressure for mercury penetrates the biochar pores, because of the high contact angle of mercury. The specific amount of pressure required to intrude into the pores is inversely proportional to sample pores size. The larger the pore, the smaller the pressure needed to penetrate the pores (Anderson 2021). This can be determined, for example, using Auto Pore IV mercury porosimeter (Micromeritics, Norcross, GA) (Brewer et al. 2014).

4.1.2 Density

The density simply refers to a measure of mass per unit volume. The density of wood biochar is a very vital parameter especially after it undergoes the pyrolysis process. Just like how hardwood is different from softwood, different types of wood raw material would vary across biochar density with pyrolysis temperature (Plötze and Niemz 2011; Brewer et al. 2014; Weber and Quicker 2018). Some parameters have been associated with density. These include envelope density, skeletal density, and true density/true particle density. The envelope density is the ratio of the sample mass of biochar particles to the sum of the volume of wood biochar sample in each piece and the voids within each piece. This means that within close-fitting imaginary envelopes surrounding each piece and it takes the solid structure, all pores, and surface irregularities into consideration (Webb 2001). Envelope density typically is determined by (ASTMD3766), using, for example, Geopyc 1360 Envelope Density Analyzer (Micromeritics, Norcross, GA). The ratio of wood biochar particle mass can also be measured by the BSI standard (Webb 2001; Brewer et al. 2014). The bulk density of wood biochar refers to the total mass of solid material divided by the volume occupied, which include the space between the biochar particle (Webb 2001). As gases devolatilize from the wood biomass structure during pyrolysis, a porous char remains behind. Higher porosity means lighter char per unit volume (Plötze and Niemz 2011). Bulk density can be measured by (ASTMD5004). The skeletal density involves two facets namely: (a) the mass of the discrete pieces of solid material; and (b) the sum of the volume of solid material in the pieces and closed pores within the pieces. Understanding the skeletal density requires the ratio between these above-mentioned two facets, and it can be determined by ASTMD3766 (Webb

2001; Brewer et al. 2014). The true density/true particle density of biochar particle is the mass of a wood material after it has undergone the pyrolysis process, divided by its volume without including open and closed pores (Webb 2001).

4.1.3 Micropore Volume

Micropore, mesopore, and macropore volume, respectively, are categorized by pore sizes <2 µm, <50 µm, and >50 µm, all of which occur in biochar (Paar). Micropore volume is influenced by the pyrolysis temperature. The type of raw material also influences the total pore volume. Biochar formed at 400, 600, and 800 °C with a micropore volume range (5–30 µm) of biochar produced from woody biomass are larger than those formed by another raw material (Kameyama et al. 2019). Micropore volume can be measured by using an Autosorb-3b gas sorption analyzer (Quantachrome Instruments, Boynton Beach, FL) (Brewer et al. 2014).

4.1.4 Hydrophobicity and Water-Holding Capacity

The decrease in functional groups alters the affinity of biochar toward the water and an increase in porosity changes the amount of water that can be adsorbed (Brewer et al. 2014). Depending on the pyrolysis temperature, samples produced at 400 °C would appear to have higher hydrophobic properties than that biochar samples formed at a temperature range of 600–800 °C. This simply reflects that low pyrolysis temperature might increase the hydrophobicity of biochar, resulting in limiting the water retention capacity (Kameyama et al. 2019; Masís-Meléndez et al. 2020). Hydrophobicity and water-holding capacity of biochar can be measured by using the mercury intrusion porosimetry (MIP) method, plant-available water capacity (AWC), and water-retention curve (WRC). According to some workers (Kinney et al. 2012), the surface hydrophobicity of biochar samples can be determined by using the molarity of an ethanol drop (MED) test.

4.1.5 Grindability

Grindability refers to the ability of a (wood) biomass material to be made smaller by grinding. Typically, grindability explains the characteristic of coal particularly the ease by which it pulverizes. It can also be considered as mechanical properties of given biochar that could limit its overall applicability (Weber and Quicker 2018). However, the pyrolysis or torrefaction usually reduces the energy required for grinding biomass material and the process temperature is the most important parameter that influences grindability, as the grindability index of the processed biomass increases with the temperature (Repellin et al. 2010; Basu 2018). The standard method of biochar grindability analysis is Hardgrove Grindability Index (HGI). It was investigated by numerous studies that the lower HGI measure depicts that the

biomass material is poorly grindable and the higher measure value indicates that the material is grindable (Weber and Quicker 2018).

The HGI measuring method involves the use of a miniature ball mill type of pulverizer that comprises ground coal of standard mass size (50 g) within a specific time and known force. The resultant product, when subject to a sieve of standard mesh size (75 µm), would be compared with the amount of the material sieve size of the desirable/specified reference standard (Basu 2018). The grindability index of biomass samples is influenced by the pyrolysis temperature and it also depends on the biomass type. For example, poplar wood investigated by Basu (2018) showed that process temperatures of 210 and 270 °C resulted in 8 and 47 HGI, respectively.

4.1.6 Thermal Conductivity

The thermal properties and yields of biochar depend on raw material, pyrolysis temperature, and the direction of heat flow (Yang et al. 2017; Weber and Quicker 2018). Moreover, the higher density of biomass material typically leads to a higher conductivity value and porous structure results in decreased thermal conductivity of biochar compared to the raw material (Weber and Quicker 2018). The direction of the heat flow impacts the value of thermal conductivity (Weber and Quicker 2018) as the highest value is obtained when the heat flow is parallel to the biomass sample direction at a range of 1.5–2.7 times in comparison to the perpendicular direction. Thermal conductivity and heat flow in the context of biochar can be measured by using NETZSCH HFM 446 Heat Flow Meter following ASTM C518 (Jeon et al. 2021).

4.1.7 The High Heating Value (HHV)

The HHV of biochar produced from raw material is one of the important parameters in the consideration of energy analyses, which can be defined as the energy released per unit mass (Yang et al. 2017). The HHV of biomass material depends and varies with pyrolysis temperature and raw material. (Yang et al. 2017) analyzed biochar produced from eight different biomass types that undergo pyrolysis process in two selected temperature values (350 and 500 °C). HHVs of pyrolyzed biochar produced from Miscanthus and bamboo sawdust at 500 °C were higher than samples formed at 350 °C, while the opposite result was obtained in the case of rice straw and bamboo leaves biochar. However, most of these examined raw materials had similar HHVs values (ranging from 18.44 to 20.10 MJ kg^{-1}) except pecan shells and rice straw which appeared lower at 15.85 and 16.95 MJ kg^{-1}, respectively. HHV can be measured using bomb calorimeter ASTM 200. Briefly, this would involve a given amount of sample (1 g) placed into the bomb chamber that is linked to the ignition wire by a specific thread. This would follow by the vessel being filled with oxygen at a pressure of up to 30 bar. After the ignition, the core temperature of the crucible

can increase to 1,000 °C during the combustion of organic material. Finally, the heat value can be determined (Basu 2018).

4.1.8 Agglomeration Potential

Agglomeration of pyrolyzed biochar is typically a way to increase the strength and density of biochar, to make it easier to transport for economical benefit, preservation, and suitable handling (Weber and Quicker 2018). The agglomeration potential in the context of biochar can be performed in two common ways such as press agglomeration, which can be achieved by applying pressure and tumble agglomeration method, which can be done by the tumbling process. Weber and Quicker 2018 stated that agglomeration potential is slightly influenced by process temperature, in the sense that at <200 °C, it is higher while seems to be stable at temperature >200 °C. Basu 2018 showed the impact of raw materials such as straw, sunflower husk, wood chips, sawdust, and rice husk on agglomeration potential values (5, 4, 1, 1, and 0) respectively.

4.2 Chemical Analyses

4.2.1 Composition (Hemicellulose, Cellulose, and Lignin)

Wood and agricultural waste-derived biochar are made up of hemicellulose, cellulose, and lignin constituents. As a result, the concentration of these constituents does impact the pyrolysis process and the physical properties of biochar. For example, biochar produced from animal litter has lower carbon content, specific surface area, and higher cation exchange capacity than biochar produced from wood. The reason for this is the difference in lignin and cellulose content (Tomczyk et al. 2020). During pyrolysis, hemicellulose and cellulose are mainly responsible for volatile matter production, whereas lignin is responsible for solid products (Narzari et al. 2015). Hemicellulose is a complex mixture of polysaccharides, and most of them almost completely decompose at 200–380 °C (Werner et al. 2014). Cellulose is more temperature resistant and its degradation takes place at 300–350 °C. Lignin is the most thermal resistant and decomposes at 300–500 °C (Carrier et al. 2011). There are two main ways to determine the composition of these constituents. According to wood industry methodology, tested material is pre-treated at the beginning to remove extractives. Then lignin, holocellulose, and α-cellulose extraction are done. According to food industry methodology, tested materials are pre-treated for neutral detergent fiber (NDF) determination. Then, acid detergent fiber (ADF), and acid detergent lignin (ADL) are determined. Both methods with procedures are described in the work of (Carrier et al. 2011).

4.2.2   pH Analysis and Electrical Conductivity (EC)

The pH value of biochar is an important property for agricultural applications such as soil amendment (Weber and Quicker 2018). Biochar pH value and electrical conductivity (EC) are measured with a glass electrode connected to a digital pH meter. Biochar is a dry material, and pH and EC can be obtained from a sample mixed with deionized water or KCl. Samples are generally stirred thoroughly and allowed to stand for a different time before measurement (Fig. 2). Different biochar-to-water or biochar -to - KCl ratios, are (i) biochar-to-water/KCl ratio of 1:10 (Al-Wabel et al. 2013), (ii) biochar-to-water/KCl ratio of 1:20 solution, after 12 h rest and stirring of suspension (Rodriguez et al. 2021), (iii) 1 g of sample with 60 ml distilled water, the solution was then shaken for 1 h in a shaker and allowed to cool to room temperature (Bian et al. 2018).

Zhao et al. (2021) showed that, under different pyrolysis temperatures, the electrical conductivity varied in the biochar. EC of biochar increased with the increment of temperature. For example, EC of biochar at 400, 600, 800, and 1000 °C was 0.001, 0.03, 0.8, and 6.3 S m^{-1}, respectively. Additionally, the EC increased drastically when the temperature exceeded 800 °C (Zhao et al. 2021). The electrical conductivity of biochar positively depends on the degree of carbonization.

Interestingly a new phenomenon has been termed, i.e., "elastic behavior of electrical conductivity of biochar" meaning EC increased with compressive loading and dropped to the pre-compression level when the loading is released (Gabhi et al. 2017). In general, biochar generated from various organic waste is characterized by lower electrical conductivity compared with other carbon materials (Shao et al. 2019). Higher pyrolysis temperature increases the pH of most biochar. Ahmad et al. (2012)
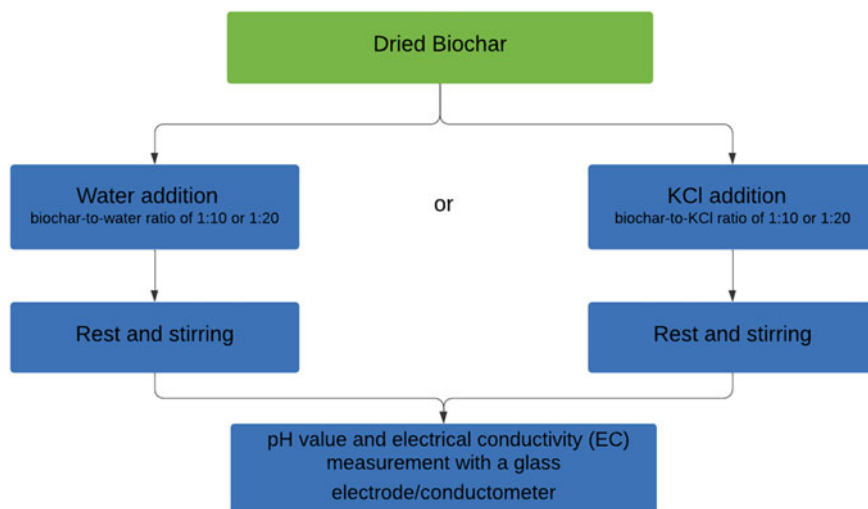
Fig. 2 Scheme of pH analysis and electrical conductivity (EC) measurement in biochar

discovered that pH value is a direct result of an increasing degree of carbonization. Increasing pyrolysis temperature generally increases the pH of biochar by producing more alkaline components, ash contents, and exchangeable and soluble cations (Li and Chen 2018).

4.2.3   Cation Exchange Capacity and Anion Exchange Capacity

The cation-exchanging ability or lack thereof of biochar is evident by the magnitude of its cation exchange capacity (CEC) (Das et al. 2010). The CEC is defined as the number of exchangeable cations (e.g., K^+, Na^+, NH^{4+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, and Zn^{2+}), often expressed as centimoles (cmol) or millimoles (mmol) of total or specific cations per kilogram (kg) of soil. <50 mmol kg^{-1} of CEC in the soil is regarded as serious deficiency, >50 and ≤ 250 mmol kg^{-1} is a moderate CEC range, and >250 mmol kg^{-1} is exceptionally high CEC Lee et al. (2013).

CEC measurement is performed in modified protocol from AOAC method 973.09 (Rippy and Nelson 2007). The procedure for CEC analysis is given elsewhere (Huff et al. 2018).

(Rizwan et al. 2016) reported that the higher cation exchange capacity of the biochar means higher adsorption of metals. However, the cation exchange capacity decreased with pyrolysis temperatures >350 °C.

CEC content in biochar gives important information for biochar usefulness as a possible adsorbent of different pollutants. The exchange of protons and ionized cations with dissolved salts on the biochar surface is the main principle of the CEC mechanism. Biochar adsorption capacity to remove heavy metals depends upon the pollutant size and surface functional group of the biochar (Rizwan et al. 2016). For example, (Trakal et al. 2016) investigated the removal of Cd and Pb using biochar prepared from different raw materials such as wheat straw, grape stalk, grape husk, plum stone, and nutshell. The results showed higher Pb and Cd removal efficiency for the raw material containing iron oxides. The presence of iron in the raw material enhanced the cation exchange capacity of the biochar (Ambaye et al. 2021).

It is known that biochar which has an increased CEC generally possesses a greater nutrient retention capacity. These biochars with greater CEC generally possess a significant amount of hydrophilic oxygen-containing groups, such as phenolic and carboxylic groups, which impart the greater cation exchangeability (Das et al. 2010). The mechanisms responsible for the change of CEC in biochar are well established. However, the evidence presented by Cheng et al. (2008) indicates that biochar AEC pathways are not fully understood. Furthermore, biochar with high AEC has the potential to be used in water treatment for the removal of anionic contaminants; hence high AEC is a potentially useful property that may contribute to biochar value. Biochar AEC is limited under neutral and alkaline conditions (Lawrinenko and Laird 2015).

AEC is measured by Cl^- for Br^- compulsive exchange of 1 g biochar samples in water for which Br^- is assayed by ion chromatography using a Dionex® 1100 ion chromatograph equipped with an ASRS 300 4 mm conductivity detector. The

mobile phase is 8 mM Na_2CO_3/1 mM $NaHCO_3$ and the method is run isocratically at 0.7 mL min^{-1} using an IonPac® AG14A 5 μm 3 × 30 mm guard column and an IonPac® AS14A 5 μm 3 × 150 mm analytical column (Lawrinenko et al. 2017). Lawrinenko et al. (2017) reported that pyrolysis temperature and the distribution of metal oxyhydroxides in biochar prepared by slow pyrolysis of biomass pre-treated with Al or Fe trichlorides strongly influenced biochar AEC. Biochar produced at 700 °C exhibits greater AEC than biochar prepared at 500 °C.

5 Surface Analyses

5.1 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is a quick and cost-effective method to examine the surface of materials. The laboratory-based FTIR and Raman spectroscopy imaging effectively provides a deeper understanding of the chemical reactions occurring during biochar production, and the distribution of chemical phases on micron and millimeter scales (Chia et al. 2012). Multiple linear regression functions could explain the infrared absorption behavior as analyzed by FTIR spectra for specific regions of functional groups with coefficients of determination mostly from 60 to 90% (Janu et al. 2021). FTIR analyses can be performed using infrared spectroscopy for example the Thermo Scientific Nicolet iZ10 FT-IR spectrometer—the module of Thermo Scientific Nicolet iN10 MX microscope equipped with a Smart iTX accessory with a diamond plate (Wiercik et al. 2020) or DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy; instrument: Bruker Tensor 37 with microtiter plate module Bruker HTS-XT) (Rodriguez et al. 2021). Each spectrum is usually an average of 32 or 64 scans in the 400–4000 cm^{-1} wave-number range at the 4 cm^{-1} spectral resolution (Janu et al. 2021).

Pyrolysis temperature impact the functional groups of biochar. Some workers (Sahoo et al. 2021) reported a decrease in the polar functional groups with an increase in pyrolysis temperature. Hydrophobic chars with very few functional groups were obtained at a higher pyrolysis temperature of 600 °C, due to more dehydration and deoxygenation reactions. They were characterized by a well-assembled layer of carbon. This agreed with the findings of another group of workers (Ahmad et al. 2014). This method could help to get a quick overview of the usability of different biochar for the immobilization of specific environmental contaminants or long-term carbon sequestration (Janu et al. 2021).

5.2 *Scanning Electron Microscope (SEM)*

A scanning electron microscope (SEM) is used to characterize the biochar morphology. SEM images give detailed descriptions regarding the microporous/mesoporous distributions and pore arrangement present in the biochar. The surface morphology before and after the adsorption process can be predicted using SEM (Yaashikaa et al. 2020). For SEM analyses, the samples are placed on supports with copper surfaces, followed by the application of a thin layer of gold (Veiga et al. 2021). The microscope used has a resolution of 3 nm and a zoom range of 10 × 60,000 (Munar-Florez et al. 2021). SEM pictures of biochar demonstrate changes in the surface morphology of the biochar particles due to pyrolysis. Additionally, the increasing temperature may bring about a huge improvement in the pore properties of biochar (Yaashikaa et al. 2020). However, intensified degree of carbonation of biochar at 700 °C leads to the destruction of the porous structure of biochar (Maljaee et al. 2021).

5.3 *Specific Surface Area (BET)*

In the process of pyrolysis, the pore structure is formed as there is the precipitation of volatile matter from the biomass. The process of carbonization makes a certain specific surface area and pore volume in biochar (Kong et al. 2021). The surface area of biochar can be examined using BET analysis. The study of the specific surface area is important because this property of biochar is mainly responsible for pollutant removal from soil and aqueous environment.

The higher temperatures of pyrolysis result in mass loss increase while providing biochar with a higher specific surface area (Howell et al. 2021). In general, the high carbonization temperature (450, 550, 650 °C) allows an enlarged specific surface area of produced biochar (Kong et al. 2021). On other hand, some workers (Ramola et al. 2020) found that the surface area of the biochar-mineral composite increases up to pyrolysis temperature of 500 °C, and then above 700 °C starts to decrease. It shows that optimum temperature is required for a high surface area of biochar. The reason for this can be the recondensation of volatilized organic compounds from the biochar-mineral composite on its surface that resulted in blocked pores and decreased surface area.

6 Molecular Analyses

Besides the positive effects of biochar, some negative effects "the dark side of the biochar" have also been reported (Bernardo et al. 2010; Gell et al. 2011; Rogovska et al. 2012; Quilliam et al. 2012; Loppinet-Serani et al. 2013; Oleszczuk et al. 2013;

Kloss et al. 2014; Buss and Mašek 2014; Białowiec et al. 2018). Contaminants within biochar may pose an environmental risk. Several studies have determined the total and bioavailable concentrations of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in biochar prepared from various raw materials under various torrefaction and pyrolysis conditions (Spokas et al. 2011). It has been also confirmed that PAHs in biochar is suspected to have been responsible for acute toxicity to various organisms (Rogovska et al. 2012; Oleszczuk et al. 2013).

Biochar has the potential to introduce toxic chemicals into the soil that could damage soil functions. Three groups of potentially toxic substances, namely: metals and metalloids (such as, As, Cu, Pb, Ni, Zn, etc.); PAHs; dioxins, and other compounds, are the most likely agents to be present in biochar. Although environmental impacts attributable to metals, metalloids, PAHs, and dioxins associated with biochar are likely to be minimal (Hale et al. 2012; Freddo et al. 2012), special care is required to ensure the raw material, particularly biowastes, are not overly burdened with high concentrations of metals, metalloids, or chlorinated compounds (that may serve as dioxin precursors). Spokas et al. (2011), studied 77 different biochars produced from various raw materials in temperatures ranging from 200 to 800 °C. The analyses showed that biochar contained 140 different chemical compounds and 77 of these chemicals were common for each biochar.

Biochar prepared at lower pyrolytic temperatures ($\leq$350 °C) produced VOCs consisting of short carbon chain aldehydes, furans, and ketones. Biochar prepared at elevated temperature (>350 °C) typically were dominated by aromatic compounds and longer carbon chain hydrocarbons. Similar conclusions came from (Wang et al. 2017) as the minimum concentration of PAH was observed in slow pyrolysis and longer retention (inside reactor) time. All the identified compounds in biochar prepared from RDF are organized into five groups (Białowiec et al. 2019). These are: (i) alkyl derivatives of benzene or phenols (32 compounds), (ii) alkyl derivatives of two-ring aromatic hydrocarbon (16 compounds), (iii) derivatives of heterocyclic amines (7 compounds), (iv) compounds that are generally considered as lower risk (e.g., present naturally in food) (22 compounds), (v) compounds that belong to other groups or with unknown structures (7 compounds).

The content of heavy metals including As, Cd, Cr, Co, Cu, Zn, Pb, Mo, and Ni can be easily analyzed with the application of ICP-AES or MP-AES after microwave-assisted aqua regia digestion. Organic pollutants content in biochar may be determined with the application of the following methods and protocols:

(i)   Qualitative and quantitative analyses of PAH is determined using the approach described in (Hilber et al. 2012; Wang et al. 2017; Geiss et al. 2018). The sample of biochar is extracted with a nonpolar solvent (hexane or dichloromethane), and if necessary concentrated on MIP-SPE cartridges. Samples may be analyzed in liquid injection techniques on GC–MS. Quantification is based on available standards covering Acenaphthylene, Anthracene, Benz[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[ghi]perylene Benzo[a]pyrene, Chrysene,

Dibenz[a,h]anthracene,   FluoreneIndeno[1,2,3-cd]pyrene,   Phenanthrene,
Pyrene.
(ii)   Dioxins/Furans (PCDD/Fs) are analyzed according to US EPA 8290 (2007).
(iii)   The NMR analyses of biochar are performed according to (Mao et al. 2013;
        Hmid et al. 2014) to characterize wide varieties of leachable compounds.
(iv)   PAH and PCA (polychlorinated aromatic) are also analyzed using the LC–
        MS approach. Biochar sample is extracted with nonpolar solvent (hexane
        or dichloromethane), and if necessary concentrated on MIP-SPE or equiv-
        alent cartridges. A sample is submitted to LC–MS with MRM (multiple
        reaction monitoring) mode. Quantification is based on standards. Equipment
        parameters may be set according to (Bucheli et al. 2015).
(v)   Measurements of VOCs may be done according to (Białowiec et al. 2018)
        headspace (HS) solid-phase microextraction (SPME) methodology for gas
        extraction and gas chromatography coupled with mass spectrometry (GC–
        MS) for analyses.

The application of the presented protocols allows for the determination of
potentially harmful effects of biochar on the environment and humans. Moreover,
humans can be exposed to biochar-associated (toxic) heavy metals, PAHs, and VOCs
either directly through inhalation of particles or indirectly through the ingestion of
fruits/vegetables grown in biochar-amended soil. Such exposure can pose a signifi-
cant threat to human health due to the toxic, mutagenic, and carcinogenic effects of
VOCs and PAHs. People involved in the handling, storage, and application of VOC-
rich biochar could be exposed to VOCs that can pose a threat to health. Therefore, it
is important to monitor these threats.

7   Limitations of Characterization of Engineered Biochar

The term "biochar" as a research topic, started to grow in 2009 when only 41 docu-
ments on this topic were available on the Web of Science. Since then, the research
about biochar has grown exponentially reaching well over 5000 publications in
2021. In the early years of biochar research, awareness and understanding of the
properties of biochar were low and it resulted in applying methods originally estab-
lished for soils, fertilizers, and composts instead of developing analytical methods for
biochar. As a result, biochar characterization methods vary and are not standardized
(Igalavithana et al. 2017).

Some workers (Bachmann et al. 2016) considered the challenges associated with
biochar analyses standardization. In their study, 3 biochar were prepared and homog-
enized, and subsequently sent to 22 independent laboratories in 12 countries for
the determination of their properties. Roughly, 38 physical and chemical parame-
ters were analyzed by each laboratory. The laboratories applied their discretion to
choose the preferred method(s) to adopt for biochar characterization since their objec-
tive involved comparing the estimated reliability of the obtained analyzed results.

These workers demonstrated a good or at least acceptable degree of intralaboratory repeatability, despite the variations in interlaboratory results (Bachmann et al. 2016).

8 Conclusions and Future Prospects

Biochar properties can be measured by a wide range of analyses from basic physical to advance molecular analysis and each analysis can be conducted in several ways. Each type of analysis has a different purpose and meaning. However, due to the wide variability of biochar and their numerous application, specific analyses should be considered regarding the final application. Some recommendations about biochar analyses performance have been put forward (Nartey and Zhao 2014; Bachmann et al. 2016; Igalavithana et al. 2017). However, considering the vast biochar types, their applications, and various laboratory equipment available for researchers, the development of an international standard for use in the near future by the majority seems unlikely. It is more probable that the current existing/sophisticated analytical methods will continue to undergo modifications, which would enable the adoption/creation of enhanced/novel descriptions of biochar properties to emerge.

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Engineered Biochar: Applications

Engineered Biochar as Adsorbent for Removal of Heavy Metals from Soil Medium

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Abstract Almost all of the world's fertile land is being used to its full capacity. Researchers and policymakers are paying close attention to the restoration and utilization of contaminated land for sustainable agricultural production. Different physical, chemical and biological treatment methods are used for remediation of pollutants. Chemical treatments take less time to remediate contaminated soil by adding organic and inorganic components. Biochar is a pyrolyzed material with a higher surface area, CEC, carbon and nutrient contents. It also helps in increasing the soil carbon-sequestration potential. Due to enhanced surface area, functional groups, mineral content and CEC, it increases the metal adsorption and reduces the labile fractions of heavy metal in soil solution. The impact of biochar in heavy metal dynamics in terms of soil health and plant yield potential is discussed in this chapter.

Keywords Biochar · Heavy metal adsorption · Plant nutrient · Phytoremedition process · Soil health

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1 Introduction

Agriculture has faced numerous challenges in the twenty-first century. It needs to produce more food and fibre to feed a growing population with shrinking natural resources. The world's population has exploded in the recent century, reaching 8.6 billion in 2030 and 9.8 billion in 2050, with Africa playing a large role (Foresight 2011). The vast bulk of the world's population (60%) lives in Asia (4.4 billion people), followed by Africa (1.2 billion people), Europe (738 million people), Latin America and the Caribbean (634 million people) and the rest of the world (5%) (Table 1). China (1.4 billion) and India (1.3 billion) are the world's two largest countries, accounting for 19% and 18% of the global population, respectively (UNDESA 2015).

Food security is a relevant and important issue for many countries, with a particular focus on developing countries. There is growing concern about the world's future food consumption and supply. The global food system is under an unparalleled convergence of forces, which is expected to worsen by 2050 (Foresight 2011). Increased food production will necessitate more inputs, such as land, water or energy, or a combination of these. By 2050, demand for cereals for food and animal feed is expected to reach 3 billion tonnes, up from almost 2.1 billion tonnes currently. According to the forecasts, feeding a world population of 9.1 billion people in 2050 will necessitate a 70% increase in overall food production between 2005/07 and 2050. In poorer countries, production would have to nearly quadruple. This would result in considerable increase in the production of a number of important commodities. Annual cereal production, for example, would need to increase by about one billion tonnes, and meat production by more than 200 million tonnes, to a total of 470 million tonnes in 2050, with 72% of that in developing nations, up from 58% today. To sufficiently feed the world's population, it would be necessary to produce the types of foods that are currently unavailable in order to provide nutrition security (UNEP 2014).

India (24.3%) and China (16.7%) account for a major portion of world food demand (Dotaniya et al. 2022a). Because of rising incomes, emerging countries will seek more animal origin foods in the future. The rate of increase in global cereal

Table 1 Population of the world by region (UNDESA 2015)

Major region	Population (million)			
	2015	2030	2050	2100
World	7349	8501	9725	11,213
Africa	1186	1679	2478	4387
Asia	4393	4923	5267	4889
Europe	738	734	707	646
Latin America and the Caribbean	634	721	784	721
Northern America	358	396	433	500
Oceania	39	47	57	71

Table 2 The top 20 countries that influence global CE food demand (Emiko and Will 2017)

Country	Change (million tonne)	Share (%)	Cumulative (%)
India	1715.9	24.3	24.3
China	1176.6	16.7	41.0
Nigeria	357.6	5.1	46.1
Indonesia	301.0	4.3	50.4
United States	241.0	3.4	53.8
Pakistan	217.9	3.1	56.9
Brazil	178.5	2.5	59.4
Bangladesh	140.1	2.0	61.4
Egypt	139.8	2.0	63.4
Mexico	133.8	1.9	65.3
Philippines	128.8	1.8	67.1
Ethiopia	105.1	1.5	68.6
Turkey	91.8	1.3	69.9
Vietnam	91.2	1.3	71.2
Tanzania	81.1	1.2	72.4
Russia	76.0	1.1	73.4
Sudan	74.5	1.1	74.5
Iran	73.5	1.0	75.5
Uganda	73.4	1.0	76.6
Thailand	67.7	1.0	77.5

demand will slow until 2050. Cereals account for the majority of global food demand (49%) and will continue to do so until 2050. Global cereal demand grew at a constant rate of 1.3% per year from 1969 to 2007 and is expected to dip further to 1.2% in 2030 and 0.9% in 2050, despite a large increase in world cereal demand from 940 million tonnes in 2005/2007 to 3 billion metric tonnes by 2050. Developing countries will account for nearly all of the increase in cereal consumption. The top 20 nations account for about 77.5 of global CE food demand (Table 2).

2 Soil Fertility Status of Indian Soils

Increased soil erosion, declined soil fertility and reduced biodiversity at the local level, depletion and pollution of groundwater and eutrophication of surface waters at the regional level, and changes in atmospheric composition and climate at the global level are all known negative effects of agricultural intensification. Ramamurthy and Bajaj (1969) produced the first systematic soil fertility map of Indian soils in 1967. Around 4% of samples were rich in available P at the time. According to a soil fertility

map released in 2002 (Motsara 2002), roughly 20% of soil samples have high levels of accessible P. Muralidharudu et al. (2011) used GIS to create district-level soil fertility maps in India, which revealed that 57% of districts had low available nitrogen, 36% had medium and 7% had high. In terms of available P, around 51% of districts had low soils, 40% had medium soils and 9% had high soils. The soils of roughly 9% of districts had low available K status, 42% had medium available K status and 49% had high available K status. Farmers' indiscriminate use of phosphatic fertilizers has resulted in excessive P levels in some soils. Because Indian soils have a low-to-medium organic matter level, the nitrogen deficit is likely to persist. The three estimations of soil fertility for K show that the percentage of samples that test high has risen over time (Ramamurthy and Bajaj 1969; Ghosh and Hasan 1980; Motsara 2002).

Different soils have their own set of difficulties that prevent them from obtaining long-term high production. Acidity in hill and laterite soils; nutrient leaching in sandy soils; nutrient fixation in red, laterite and clayey soils; obstructed drainage in swell-shrink soils; N volatilization losses from calcareous soils; Zn deficiency in low organic matter, sandy, high pH, high-water table soils; and B deficiency in highly calcareous leached acid soils. Zn deficiency was found in 49% of the soil samples tested, followed by S (41%), Fe (12%), Cu (3%), Mn (4%) and B (4%) (32% in some selected areas such as Bihar). In the case of P (15–20%), N (30–50%), S (8–12%), Zn (2–5%), Fe (1–2%) and Cu (1–2%), the current state of nutrient usage efficiency is fairly low (1–2%). In India's intensive cropping systems, fertilizer partial factor productivity is dropping.

Soil organic matter is essential for maintaining soil fertility. Organic matter status of soil in Alfisols of Ranchi deteriorated over time in the soybean-wheat system due to a lack of balanced fertilizer input. In the soybean-wheat system at Jabalpur, balanced fertilization with NPK and NPK + FYM increased the organic matter status in Vertisols. During the last three and a half decades, the partial factor productivity of fertilizers has decreased, from 15 kg food grains/kg NPK fertilizer in 1970 to 5 kg food grains/kg NPK fertilizer in 2005. In the rush to increase production, little thought was given to long-term soil quality and high productivity. As a result, main crop annual compound growth rates have decreased from 3.36% in 1981–85 to 0.11% in 2001–05. Deterioration in soil quality causes a drop in partial factor productivity and compound growth rates of key crops in intensive cropping systems as well as low nutrient use efficiency. Continuous cropping reduces organic C levels by 50–70%, bringing them closer to the climatic and precipitation-driven equilibrium values. The following are the primary causes of soil quality degradation: a large nutrient gap between demand and supply; high nutrient turnover in the soil–plant system combined with low and imbalanced fertilizer use; emerging deficiencies of secondary and micronutrients in soils; soil acidity; nutrient leaching in sandy soils; nutrient fixation in red, laterite and clayey soils; and obstructed drainage in Swedish soils.

3   Heavy metal

Metals are necessary for the survival of all living species on the planet. These are required for the plant, animal and human life cycles to be completed. Deficiency of these metals in a living body can cause a variety of symptoms or limit an organism's capacity to develop and operate (Minhas et al. 2021; Dotaniya et al. 2022b). Some metals are required for life, but if their concentration in the body exceeds their required concentration, they become poisonous (Dotaniya et al. 2014a). These metals are divided into groups depending on their toxicity, origin and concentration in the living body, among other factors. Several metals have been found harmful to human health, and their introduction into the human body via food chain pollution requires scientific supervision. Heavy metals have a geogenic origin and are distributed by anthropogenic activities such as industrial waste, geochemical structure, agriculture and mining (Table 3). These metals form compounds with other ambient elements, making them more harmful to living things (Singh et al. 2020). The toxicity of a metal is determined by the metal's type, chemical form, climatic variables and other factors. Heavy metals including As, Cd, Cu, Pb, Ni and Zn are prevalent contaminants that originate from both natural and anthropogenic sources (Dotaniya et al. 2018a).

3.1   Adverse effects of heavy metals on Plant

According to Arnon and Stout's (1939) essentiality criterion, a plant's heavy development necessitates 17 essential plant nutrients. Micronutrients such as zinc, copper,

Table 3   Sources of hazardous metals (CPCB 2009)

Metal	Industry
Chromium (Cr)	Leather tanning, mining, industrial coolants, chromium salts production
Lead (Pb)	Lead-acid batteries, paints, e-waste, smelting operations, coal-based thermal power plants, ceramics, bangle industry
Mercury (Hg)	Chlor-alkali plants, thermal power plants, fluorescent lamps, hospital waste (damaged thermometers, barometers, sphygmomanometers), electrical appliances
Arsenic (As)	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning
Copper (Cu)	Mining, electroplating, smelting operations, vanadium (Va) spent catalyst, sulphuric acid plant
Nickel (Ni)	Smelting operations, thermal power plants, battery industry
Cadmium (Cd)	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations and fuel combustion
Zinc (Zn)	Smelting, electroplating

Table 4 Adverse effects of heavy metals on plants (modified from Saha et al. 2017)

Pollutant	Its impact on plant
As	Red brown necrotic spots on old leaves, yellow browning of roots, growth reduction
Cd	Brown margin on leaves, chlorosis, necrosis, curved leaves, brown stunted roots, reddish veins and petioles, reduction in growth, purple colouration
Cr	Affect seed emergence, stunted plant growth and decrease dry matter production
Pb	Dark green leaves, stunted foliage, increased number of shoots
Ni	Chlorosis, necrosis, stunting, inhibition of root growth, decrease in leaf area
Hg	Severe stunting of seedlings and roots, chlorosis, browning of leaf tips, reduction in growth
Cu	Chlorosis, yellow colouration, purple colouration of the lower side of the midrib, less branched roots, inhibition of root growth
Se	Interveinal chlorosis, black spots, bleaching and yellowing of young leaves, pink spots on root

manganese, iron and nickel are regarded as important plant nutrients, yet larger concentrations of these metals are phytotoxic. Other heavy metals/toxic metals that are known to cause harm to humans and animals include Cd, Cr, Hg and Pb. These metals do not appear to play a defined role in plant physiology, and at high concentrations, they cause plant toxicity symptoms and reduce plant biomass (Dotaniya et al. 2018b, 2019a) (Table 4). Few plants in nature have the ability to modulate heavy metal uptake patterns from the soil–water system, as well as tolerance to a specific metal or combination of metals (Dotaniya et al. 2020b). However, these metals have a specific tolerance level, beyond which plants exhibit the same toxicity as common plants. Heavy metal toxicity resulted in the production of reactive oxygen, and the plant's enzyme cofactors are replaced (Sytar et al. 2013). Heavy metal toxicity, according to Saha et al. (2017), has a negative impact on transcription and antioxidative processes, cellular redox imbalance, ionic trafficking, DNA synthesis and damage, and amino acid synthesis. According to Haider et al. (2021), cadmium toxicity changed the uptake pattern of Ca, Mg, P and K from soil and cause water scarcity in plants, resulting in low growth and production. According to Panday and Sharma (2002), heavy metals (Co^{2+}, Ni^{2+}, Cd^{2+}) reduce chlorophyll content, Fe activities and associated enzymes (catalase, peroxidase), as well as chlorophyll heme biosynthesis in cabbage. Ni toxicity was more than Cd and Co toxicity in this experiment (Pandey and Sharma 2002).

3.2 Adverse effects of heavy metals on human

Toxic metals are found to have a negative impact on the cell membrane as well as mitochondria, endoplasmic reticulum, nuclei and numerous enzymes associated with metabolism, detoxification and damage repair in biological systems (Table 5)

Table 5 Effects of heavy metals on human

Pollutant	Its impact on human
As	Bronchitis, dermatitis
Cd	Kidney damage, bronchitis, gastrointestinal disorder, bone marrow cancer
Cr	Hemolysis and ultimately, kidney and liver failure
Pb	Liver, kidney, gastrointestinal damage, mental retardation in children
Ni	Nausea, vomiting, diarrhoea, headache, cough, shortness of breath
Hg	Damage to nervous system, protoplasm poisoning
Cu	Harmful effect on brain, liver and lungs
Se	Nausea, vomiting, nail discoloration, brittleness, hair loss
Mn	Inhalation or contact causes damage to central nervous system
Zn	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane

(Wang and Shi 2001; Dotaniya et al. 2014b, 2017). DNA damage and conformational changes caused by metal ions have been reported to affect cell cycle regulation, cancer or apoptosis when metal ions interact with cells (Kasprzak 2002; Beyersmann and Hartwig 2008). The production of reactive oxygen species (ROS) and oxidative stress have been implicated in the toxicity and carcinogenicity of metals like As (Tchounwou et al. 2004a, Yedjou and Tchounwou 2004b), Cd (Tchounwou et al. 2001), Cr (Patlolla et al. 2009; Dotaniya et al. 2019b) and Pb (Tchounwou et al. 2004b), among others (Sutton and Tchounwou 2007). Due to their extreme toxicity, these five elements are considered priority metals with substantial public health consequences. Toxins in the system have been proven to damage several organs at low levels. In addition, the United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) classify these metals as "known" or "probable" human carcinogens based on epidemiological and experimental studies that demonstrate a link between exposure and cancer incidence in humans and animals.

4 Heavy metal pathway in human being

Heavy metal concentrations in soil and their absorption by plants are increased when low-quality inputs are used, impacting the crop's yield and level of heavy metal in soil. Heavy metal concentrations have a negative influence on soil biota and other features (Muchuweti et al. 2006). Health risks are associated with elevated levels of heavy metals in soil and plant components, which can harm humans (Meena et al. 2020a). Toxic heavy metals can enter the human body from the soil through plants (Solanki et al. 2020). This means that identifying the numerous methods by which heavy metals are transported from soil to plants is vital. There are a variety of factors that influence how heavy metals accumulate in agricultural plants (Dotaniya
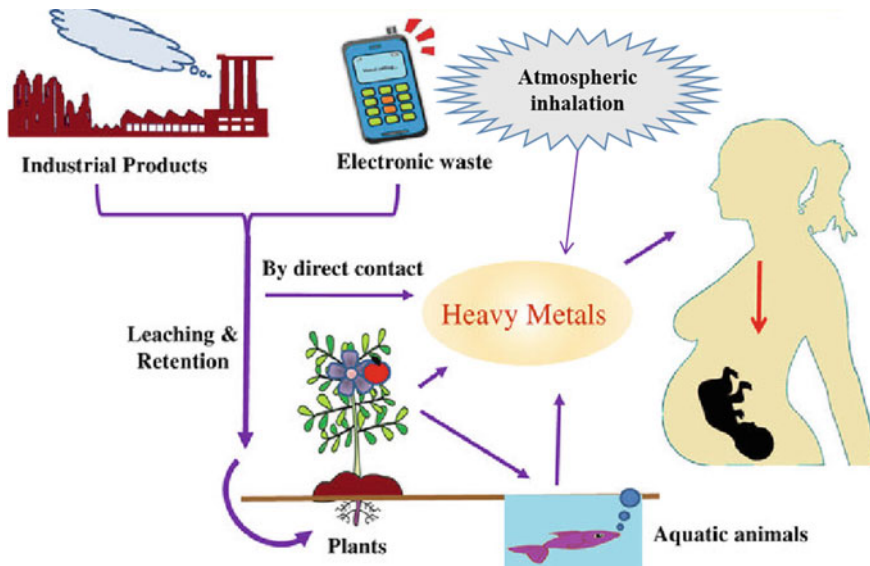
Fig. 1 Heavy metal pathway in human

et al. 2020b). Some plants are better at absorbing metal particles than others. For the transfer coefficient, the bio-concentration factor and accumulation factor are utilized (Rattan et al. 2005; Dotaniya et al. 2020c). It is more likely that heavy metal contamination will arise in peri-urban areas with sewage or polluted water (O' Connor et al. 2018a, b). Heavily contaminated vegetables provide a greater threat to human health than other crops (Dotaniya et al. 2020a; Meena et al. 2020b). Toxic metal ingestion inhibits the operation of other metal ions as well as the immune system, resulting in stunted growth, poor mental development as well as other human impairments (Fig. 1) (Iyengar and Nair 2000; Türkdogan et al. 2003).

5 Role of Biochar in Agriculture

Farmers in developing countries burn more than 10 billion tonnes of crop waste in their fields each year. This contributes to the release of 16.6 billion tonnes of CO_2, 11.2 billion tonnes of CO_{2e}, 1.1 billion tonnes of smog precursors and 65.7 million tonnes of $PM_{2.5}$ into the atmosphere. Crop waste burning produces enough CO_2 and CO_{2e} emissions to equal the annual emissions of 714 coal-fired power plants. Instead of burning the waste, converting it into biochar removes three tonnes of CO_2 from the atmosphere for every tonne produced; when added to fields as a soil amendment carbon is permanently sequestered. The use of biochar in soil remediation provides a number of environmental benefits that are consistent with GSR (Shen et al. 2019). For example, (1) biochar can be made from agricultural, household or industrial waste;

(2) co-products of biochar pyrolysis, such as syngas and bio-oil, can be used as green energy sources; (3) biochar can help increase soil fertility by adding nutrients or improving soil structure or pH and (4) biochar production converging.

Climate change is threatening global food security. Farmers who use biochar as a soil amendment will benefit in terms of higher yields, healthier soil, lower acidity, better water retention, stronger plants, richer soil life, less contamination, higher fertility and better seed germination (Novotny et al. 2015). Because of its high moisture adsorption capacity, it is extremely useful in reducing mildew in damp areas. Biochar adsorption properties make it an ideal solution for soil pollution remediation (Tripathi et al. 2016). The long-term benefits of producing biochar include a significant reduction in greenhouse gases, which contribute to global warming (Sullivan and Ball 2012). It is widely acknowledged as a powerful solution for reducing global warming.

5.1 Properties of biochar

5.1.1 Larger surface area

Biochar is a porous carbonaceous material that can hold massive amounts of water. The porous structure of biochar also serves as an excellent habitat for soil microbes. Larger surface areas are helpful for regulating the nutrient concentration in soil solution (Cao et al. 2018; Sakhiya et al. 2020). The pore size of biochar varies greatly, with nanopores (0.9 nm), micropores (2 nm) and macropores (>50 nm). When pyrolysed at 800 °C, biochar made from malt wasted rootlets had a surface area of 340 m^2/g and a porosity of 0.21 cm^3/g (Manariotis et al. 2015). Manure and biosolid biochar have a substantially lesser surface area (5.4–94.2 m^2/g) than plant biochar (112–642 m^2/g) such as wheat, oak wood, maize stover and pine needles (Li et al. 2017).

5.1.2 pH value

Plants prefer soil with a pH of 6.5–7, but most soils in the developing world are acidic to very acidic (4–5.5). Even if nutrients are present in the soil, most plants cannot absorb them in acidic soils. The addition of biochar to such soils raises the pH by up to a whole point. More nutrients become available to crops as the pH rises.

5.1.3 Cation exchange capacity

Composting of biochar with calcium, iron, magnesium, phosphorous, potassium and sulphur may enhance the nutrient efficiency. Biochar provides long-lasting, slow-release nutrition effect on crop. Biochar in a heavy metal-contaminated field can make cadmium, lead or mercury chemically bound to it (adsorbed), where plants will no longer take them up and water will no longer wash them away. The cation exchange capacity (CEC) of biochar is an important property for improving soil nutrient retention and reducing fertilizer runoff. However, CEC estimations for biochar in the literature are highly diverse, ranging from 5 to 50 cmol (+)/kg and even reaching as high as 69–204 cmol (+)/kg (Munera-Echeverri et al. 2018).

5.1.4 Carbon substrates in soil

Plants cannot consume their elements in their natural state. They cannot just suck up nitrogen, no matter how much they need it; they need microbes to digest it first and release it out as nitrates or nitrites. Because of its high carbon content (60–90%) (McGlashan et al. 2012), the incorporation of biochar into soils is regarded as a significant and long-term approach to sinking atmospheric CO_2 in terrestrial ecosystems. Aside from the benefits of reduced emissions and GHG sequestration, biochar has a number of positive effects on soil quality (Lehmann and Joseph 2015). Adding biochar to soils boosts crop production by improving soil physico-chemical and biological properties such as water retention, pH and microbial activity (Ahmad et al. 2014). Furthermore, because of the lower fertilizer requirements, biochar can help to reduce agricultural emissions from fertilizer use (McGlashan et al. 2012).

6 Remediation methods of heavy metal from ecosystems

On the basis of practicality and resources, several types of remediation technologies are being used to remove heavy metals from the environment (Solanki et al. 2020). Metal concentration, shape and kind, as well as moisture in the soil, have a key role in the removal of heavy metals from ecosystems (Meena et al. 2020b). A brief description is given in Table 6.

6.1 Role of biochar in heavy metal remediation

Biochar comes under chemical remediation strategy for heavy metals removal. It is an environment-friendly method of removing heavy metals from the soil. In addition

Table 6 Heavy metal remediation methods

Method	Mode of action	Descriptions
Physical	Physical removal, filtration, scrapping	Heavy metal polluted soil is removed from the field, metal-contaminated waste is pre-filtered before being dumped, contaminated locations are segregated and pollutants are contained, preventing off-site dispersion and on-site bio-exposure to the contaminants
Chemical	Addition of organic and inorganic substances, chemical precipitation, adsorption, ion exchange, membrane filtration, coagulation-flocculation and floatation process	Metals are immobilized, and other than binding agents, stabilization, precipitation reagents/stabilizing chemicals are added into the contaminated soil to create physio-chemical interactions between the stabilizing reagents and heavy metals, reducing their mobility
Biological	Microbial bioremediation—use of microorganisms to break out pollutants by feeding them. Bioaugmentation is a technique that involves biostimulation.	Use of microorganisms to reduce the heavy metal concentration in soil
	Mycoremediation—breaks down of pollutants such as pesticide, hydrocarbon and heavy metals with the help of fungus' digestive enzymes	Use of the different fungal population to reduce heavy metal toxicity in soil–water systems
	Phytoremediation techniques—plant-based methods are used to bind, remove and clean up contaminants such as pesticides, petroleum hydrocarbons, metals and chlorinated solvents	*Phytodegradation* is breakdown of organic pollutants by internal and external metabolic processes triggered by the plant. *In Phytovolatilization,* plants absorb water-soluble pollutants and release them into the atmosphere as they transpire water. *Rhizofiltration* is similar to phytoextraction in concept, but it focuses on the treatment of contaminated groundwater rather than damaged soils. *Rhizodegradation* (also known as improved rhizosphere biodegradation, phytostimulation and plant-assisted bioremediation) is the process of soil-dwelling bacteria breaking down organic pollutants in the soil, which is aided by the presence of the rhizosphere. *Phytostabilization* is the use of plants (*Festuca rubra* L, *Agrostis tenuis*) to immobilize pollutants in soil and water.

to metal removal, it also adds nutrient-rich compounds to the soil that enhances crop output (Meena et al. 2021).

Recent biochar research basically explains two methods of adsorption by biochar: first, direct adsorption, and second, improving the physico-chemical properties of soil such as pH, CEC, mineral and organic matter (OM) content (He et al. 2019a, b; Wang et al. 2021). Physical sorption, ion exchange, electrostatic interaction, precipitation and complexation are some of the mechanisms involved in controlling the removal of heavy metals from polluted soils via direct adsorption by biochar (Dotaniya et al. 2016; Inyang et al. 2016). The surface of biochar possesses various functional groups, including hydroxyl, carbonyl and carboxyl (Tan et al. 2015), and their abundance is the most important factor for regulating the sorption-based heavy metal stabilization (Guo et al. 2020). Organic matter in the soil can assist reduction of trace metal availability in the soil solution, which can harm agricultural plant nutrition and growth (Zhang et al. 2017).

Researchers have suggested utilizing biochar as a binder to immobilize heavy metals from soil systems. It is used as a soil conditioner because it is high in organic carbon. Plants that have a higher capacity for water absorption have a better ability to transfer nutrients around. There is also an increase in cation exchange capacity as well as the ability to absorb heavy metals, resulting in a less contaminated soil solution. Biochar functions as a climate change mediator and enhances soil carbon sequestration, according to Hayyat et al. (2016).

For soil microbial populations, biochar application increases the amount of soil organic carbon and food sources that are available to them. By altering microbial community composition (Igalavithana et al. 2017), increasing variety (Cheng et al. 2018), and therefore stimulating particular microbial activities, soil biochemical cycles can be improved, increasing nutrient absorption and crop yield (Hayat et al. 2010). *Rhizobacteria* (bacteria belonging to the groups; *Azospirillum, Enterobacter, Klebsiella* and *Pseudomonas*) can be directly influenced by biochar-induced alterations in plant development (Tu et al. 2020). It has been observed that biochar reduces the accessible heavy metal concentration by 55.5% (Ahmad et al. 2014), while another study found that it reduces acid-soluble $Pb^{2,3+}$ and Cu^{2+} by 18.8–77.0 and 19.7–100.0%, respectively.

Pyrolysis temperature of biochar and the chemical composition of the biomass have an impact on the adsorption capacity of biochar (Uchimiya et al. 2011; Xu et al. 2014). Biochar is commonly added to heavy metal-contaminated soil to raise its pH (Seneviratne et al. 2017; Soudek et al. 2017). This is largely due to variations in raw material that results in varying amounts of alkaline ash. Biochar made from mineral-rich raw materials that are pyrolyzed at high temperatures have a high ash content that results in soil alkalization (Cao and Harris 2010; Lehmann et al. 2011). In general, adding charcoal and raising the soil pH reduce the competition for sorption sites between H^+ and metal cations (Mn^+), lowering the mobility and availability of heavy metals in the soil (Gomez-Eyles et al. 2013).

The efficiency of bioavailability is affected by the biochar's source material, pyrolysis temperature, metal form and concentration and soil characteristics. Biochar incorporation creates various carbon–metal complexes in soil and aquatic systems,

lowering metal bioavailability. The coordination of metal electrons to C=C (-electron) bonds in peat moss biochar decreases the mobility and bioavailability of copper, cadmium and lead (Park et al. 2016). Heavy metal bioavailability is reduced due to the presence of biochar functional groups and their affinity for heavy metals. Table 7 lists some of the biochar and their effects on availability of heavy metals in soil.

Table 7 Type of biochar and their effect on bioavailability of heavy metals in soil

Raw materials	Production temperature(°C)	Metal (s)	Effect/reaction	References
Rice straw	–	Cd, Cu, Pb	Lower down the bioavailability of Cu, Pb, Cd	Jianga et al. (2012)
Wheat straw	485	Cd, Pb	Reduced concentration of metal in dry soil conditions	Sui et al. (2018)
Cotton stacks	450	Cd	Enhance the adsorption and co-precipitation of Cd	Zhou et al. (2008)
Eucalyptus	550	As, Cd, Cu, Pb, Zn	Potential reduction of the Cd, Pb, Zn and Cd; enhance CEC and water retaining capacity	Namgay et al. (2010)
Sewage sludge	500	Cu, Ni, Zn, Cd, Pb	Reduction in bioavailability of metals	Méndez et al. (2013)
Pigeon pea straw		Cu	Reduce Cu toxicity	Coumar et al. (2016a,b)
Wood	450	As	Immobilization of As	Hartley et al. (2009)
Oakwood	400	Pb	Bioavailability reduced more than 75% whereas bio-accessibility reduced by 12.5%	Ahmad et al. (2012)
Chicken manure	550	Cr	Promote conversion rate of hexavalent Cr to trivalent Cr	Choppala et al. (2012)
Bamboo wood	750	Cd, Pb	Less plant uptake of Cd and Pb	Xu et al. (2016)
Coconut husk, sewage sludge	500	Cu	Reduce bioavailability of Cu	Li et al. (2019); Gonzaga et al. (2020)

Cheng et al. (2018) demonstrated that an increase in soil microbial richness and diversity, caused by a rise in pH from using biochar, results in favourable physico-chemical changes of the soil as well as an increase in the supply of accessible nutrients. Some of the positive and negative effects of biochar on soil properties are listed in Table 8.

Limitations of biochar applications:

1. High CEC may help in adsorption of heavy metal in biochar and release it during the high crop growth stages by release of root exudates.
2. The present experiments of use of biochar for heavy metals are limited to lab scale. It is critical to make biochar for practical field use. Future research should focus on improving the biochar pyrolysis process to fully exploit its potential for treating metal-contaminated environment.
3. Biochar aged in soil inhibits the growth of earthworms and/or fungi.
4. Use of biochar at high rates (15 t/ha) induces increased weed growth and immobilized plant nutrients.
5. Higher application of biochar may also disturb the soil organic matter decomposition rate by mediating the soil microbial population and diversity.

7 Conclusions and future prospects

A rise in industrial pollution has caused negative impact on soil health and food crop productivity. One of the biggest challenges is heavy metal toxicity, as these are very harmful for the health of environment. Biochar improves soil fertility for sustained crop production and it is an option worth considering to maintain the health of soil. Biochar has a high carbon-sequestration capacity and is climate robust. Larger surface area and CEC improve adsorption capacity, resulting in increased heavy metal immobilization. It also improves soil fertility and nutrient mineralization over time by regulating the variety and count of soil microbes. The stable C pool increased and CO_2 emissions from the soil are reduced under biochar application. More study should be done to know the effects of biochar immobilized heavy metals on the rhizospheric characteristics over time.

Table 8 Biochar effect on soil properties

Process	Positive changes	Negative changes
Abiotic: physico-chemical changes of the soil	• Reduction of heavy metal mobility, bioavailability and solubility to levels below the hazardous regulatory threshold • Increased soil pH, CEC and ECE • Increased soil organic matter, quantity of easily accessible C substrates, soil TOC and N status • Stabilization of soil aggregates • Increased soil WHC and decreased leaching of nutrients and heavy metals	• Some heavy metals are more mobile in biochar (indicating that albeit biochar application reduces heavy metal mobility, some biochar may also increase it) • Decreased availability of nutrients under conditions of increased biochar dose • Reduced soil N availability when biochar dose is increased
Biotic: microbiological and biological changes of the soil	• Improved microbial community composition and structure • Increased bacterial richness and diversity • Increased microbial respiration, microbial C utilization efficiency and microbial biomass C, N and P • Increased enzymatic activity	• Reduced relative concentrations of some bacteria (including the dominant species) at high biochar rates, with the prospect that biochar application would alter the indigenous microbial community • Increased earthworm mortality at high biochar rate • Reduced Arthropod reproductive stimulation at high biochar rate
Effects on plants, food chain and the environment	• Reduced abiotic stress that enhances soil fertility, seed germination, root characteristics, plant development and biomass output • Increased chlorophyll, protein and carbohydrates • Lower heavy metal root absorption and migration to above ground plant parts (i.e. shoots, leaves) and reduced heavy metal concentrations (phytotoxicity) in edible plant parts (i.e. fruits and grains) • Reduced heavy metal contamination in the food chain • Reduced leaching and danger of heavy metal migration to aquatic, biotic and abiotic environments	• No improvement in plant growth with increasing biochar application • Decreased heavy metal absorption in wet and flooded soil conditions than in dry and draught soil situations

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Engineered Biochar as Adsorbent for Removal of Emerging Contaminants from Aqueous and Soil Medium

Agnieszka Medyńska-Juraszek and Irmina Ćwieląg-Piasecka

Abstract Emerging contaminants (ECs) consist of pharmaceuticals, personal care products, pesticides, organic solvents and dyes, and other nitrogen and phosphorus contaminants that cause adverse effects on environment and human health. Many of these compounds are presently not tested for municipal water systems. This chapter focuses on the application of pristine and modified biochar as adsorbents for emerging contaminants from water and soil. The first part of the chapter describes ECs problem in general, presenting different types of emerging contaminants and challenges related to their removal from soil and water. Further, the biochar applications for removal of ECs are presented, based on the detailed review of literature providing characterization of the adsorbents and the different approaches that can be followed to enhance biochar sorption capacity for ECs. A description of the main challenges in designing the biochar properties for its multifunctional application as adsorbent is also discussed.

Keywords Biochar · Contaminants · Pharmaceuticals · Endocrine disruptors · Pesticides · Agricultural runoffs

1 Introduction

Emerging contaminants (ECs) have recently been recognized as new and significant environmental pollutants representing a wide group of chemicals, such as pharmaceuticals, personal care products (PPCPs), endocrine-disrupting compounds (EDCs), and industrial effluents (Lei et al. 2015). Due to their rapidly increasing use in industry, transport, agriculture, and urbanization, these chemicals are entering the environment at elevated levels (Gavrilescu et al. 2015). The presence of ECs in natural water systems and soils is a major concern worldwide as these substances, even in very low concentrations, may have negative effects on human health, causing environmental risks to animals and plants. EC originates from various anthropogenic

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sources and are distributed throughout the environmental matrices (Sehonova et al. 2018). The most significant source of hazardous substances are wastewaters and effluents produced during anthropogenic activities. ECs, when released into the environment, undergo biodegradation processes, causing contaminant transformation induced by the presence of specific constituents in matrix-like organic matter and microorganisms. One of the major problems is that ECs found in industrial and municipal wastewater treatment plants cannot be easily remediated through conventional treatment technologies (Fan et al. 2018). Among all treatment methods that have been developed, adsorption is the one most pertinent and promising one for removing organic and inorganic micropollutants (Sophia and Lima 2018).

Many different materials have been investigated as ECs adsorbents, however, the most attention has been paid to carbon-based materials like activated carbons, carbon nanotubes, peat, or graphene. Recently, efforts have been made to propose an alternative carbon source for generating ECs sorbent at lower costs. Carbon production from several wastes such as agricultural crop and forestry residues, biodegradable fraction of municipal wastes or animal manure seems to be a win–win solution solving two major environmental problems—of waste management and wastewater treatment. Biochar is a highly stable material, having strong adsorption capabilities and natural origin. In terms of microscopic structure biochar possess porous characteristics, large surface area, and aromaticity, that can be designed by adjusting raw material type and temperature of pyrolysis. In particular, while higher proportions of aliphatic carbons and functional groups are typical of biochar pyrolyzed at low temperatures, biochar obtained at higher temperatures contains mainly polyaromatic carbons and has a higher microporosity, which enhances hydrophobic organic compounds adsorption (Chen et al. 2008). Many emerging organic micropollutants are more polar than "conventional" contaminants (e.g., polycyclic aromatic hydrocarbons) and may have numerous acidic and/or basic functional groups (Kim et al. 2016) that are able to interact with bonding sites on biochar surface.

However, the mechanisms of ECs adsorption on biochar can be related to various processes depending on multiple factors including, (1) structural properties of the adsorbate, (2) physiochemical properties of the sorbent surface such as specific surface area, pore size distribution, surface functionality, or ash content, and (3) the conditions at which the sorption is carried out such as pH and the nature of the matrix (Azhar et al. 2016; Peiris et al. 2017). In general, pristine biochar has lower adsorption capacity than activated carbon (Kearns et al. 2019). Therefore, in the recent years, a number of studies in the scientific literature have dealt with production of the engineered or modified biochar having desirable properties. Majority of these studies are focused on biochar modifications, enabling effective immobilization of pesticides. The extensive and inefficient use over the last decades resulted in serious soil and water contamination (Liu et al. 2018). Modulation of biochar properties, in order to obtain higher retention of particular chemicals, is very often based on optimization of process engineering to improve its adsorption capacity and hence to increase the economic benefits of its implementation. The simplest modifications concern the pyrolysis route variables. One of them is temperature as either high or low has both positive and negative effects on sorption of chemicals, one by larger

surface area and the other by a large number of functional groups (Gaffar et al. 2021). Nevertheless, in the recent years, biochar studies are mainly focused on designing a sorbent with precisely defined properties, selective to the particular chemical class of compounds. In order to obtain biochar with superior, carefully modulated, and application-oriented properties, different modification methods of biochar are tested. They refer to the pre-treating biomass using chemical reagent (so called—activators) before or after the pyrolysis process (Tan et al. 2016) or activation with the use of physical and chemical methods—to achieve the desired purpose (Liu et al. 2018). The multifunctionality of biochar can also be enhanced by its coating with nanoparticles (e.g., chitosan, graphene, graphene oxide, carbon nanotubes, ZnS nanocrystals, layered double hydroxides, nanoscale zero-valent iron, graphitic C_3N_4) (Tan et al. 2016). Such approach combines the advantages of biochar matrix and functional nanoparticles, improving and modifying surface functional groups, surface area, porosity, and thermal stability of biochar, which contribute to better performance of contaminants removal (Leng et al. 2021).

As removal of emerging contaminants from aqueous and soil medium is a relatively new application of biochar, in this chapter, we will summarize the state of the art about its use in environmental decontamination.

2 Pharmaceuticals

The definition of a PPCP broadly includes any product that has healthcare or medical purpose for humans or animals. These products are usually subdivided into categories on the basis of their nature and use. Pharmaceuticals is a large group of chemical substances, however, based on their use and occurrence in environment, these antibiotics and anti-inflammatory drugs are most frequently detected as water and soil contaminants.

2.1 Antibiotics

Biochar has been extensively investigated as an effective sorbent of several groups of antibiotics (tetracycline, sulfonamides, fluoroquinolones, macrolides) and many different mechanisms of antibiotics adsorption have been described depending on biochar and contaminant properties. In general, biochar is considered a good sorbent for hydrophobic organic contaminants because of its relatively high hydrophobicity and aromaticity (Lian et al. 2014). Unlike activated carbon (AC), biochar is generally not fully carbonized. As a result, both carbonized and non-carbonized domains regulate its sorptive behavior (Chen et al. 2008). Sorption of antibiotics on biochar can occur through a variety of mechanisms, including π–π electron–donor–acceptor interaction, nucleophilic addition, electrostatic attraction, pore filling, partitioning

into noncarbonized fraction, and formation of charge-assisted hydrogen bonding (CAHB) with surface oxygen groups (Ahmed et al. 2017).

Biochar capacity for antibiotics can be modified by the specific interactions between micropollutant and biochar surface groups. Presence of surface functional groups on biochar (e.g., phenyl, amino, alcohol, and ketone) and moieties, acting either as H donors (amino, amide carbonyl, and hydroxyl groups) or H acceptors (carbonyl and dimethylamino groups), deliberately modifies the surface of biochar, enhancing the sorption interaction (Jing et al. 2014). Ahmed et al. (2017) described that hydroxyl groups on aromatic rings are stronger adsorbents for sulfonamides, in comparison to the low-temperature biochar, containing more carboxyl groups acting as π acceptors. The sorption magnitude depends mainly on the physicochemical properties of the micropollutants (Li et al. 2019), type of solid matrices, surface area, porosity, pore diameter, and environmental conditions (Pavlović et al. 2014). Preliminary research presented very divergent results of biochar capacity for antibiotics adsorption, however, in most cases, pristine biochar had significantly lower adsorption rates compared to even simply modified biochar, e.g., by steam activation.

Steam activation and acid modifications are commonly used to introduce oxygen-containing functional groups (e.g., carboxylic, carbonyl, ether, and phenolic hydroxyl groups) onto biochar surfaces, increasing its hydrophilic nature. Opposite effects—an increase in biochar hydrophobicity and aromaticity can be obtained during heat treatments at high temperature >600 °C. In terms of designing a biochar with high sorption capacity for pharmaceuticals, preparation of materials with aromatic structure and low content of volatile chemical is desired. This function can be obtained either by high-temperature pyrolysis or heat activation of biochar obtained during low-temperature processes. Biochar deashing by material acid-washing can also be an efficient method of increasing biochar sorption capacity (Srinivasan and Sarmah 2015, Luo et al. 2018) for pharmaceuticals. Shimabuku et al. (2016) comparing low and high ash biochar derived from wood wastes observed that high ash biochar contains a surface rich in oxygen due to metal oxides, which weaken the sorption capacity for sulphmetoxazole. In contrast, certain studies have reported an opposite behavior, where the sorption capacity of low-temperature biochar was higher, though this mechanism and the effect of pyrolysis temperature on antibiotics sorption efficiency is still uncertain and needs further investigation. Competition between components for sorption sites is one of the major concerns when biochar is applied to natural mediums.

Different matrix components present in natural waters and soil, e.g., humic acid or metal cations can compete with the antibiotics for biochar sorption sites, resulting in lower sorption efficiency. Antibiotic adsorption to soils depends on the chemical species and soil properties including pH, clay minerals, and organic matter content, but also on the concentration and type of divalent cations present in the soil solution (Kim et al. 2011, Wang et al. 2018). Organic matter can strongly interact with the polar fraction of BC through H-bonding and with hydrophobic fraction through $\pi - \pi$ EDA interactions (Lian et al. 2015). In general, humic acids are able to mitigate antibiotics sorption on biochar, mainly due to sorption competition (Xie et al. 2014). Sun et al. (2016) described that biochar sorption capacity for sulfamethoxazole can be

greatly enhanced by interaction with low molecular weight organic acids (LMWOAs) present in rhizosphere. Metal ions including K^+, Cu^{2+}, Cd^{2+}, or Pb^{2+} coexisting in soil solution tends to have the opposite effect, enhancing antibiotic sorption on biochar, due to formation of very stable complexes (Jia et al. 2013; Han et al. 2013). Similarly in the presence of clay minerals, e.g., kaolinite in soil and water sediments, antibiotics sorption capacity of biochar may increase what was described by Bair et al. (2016). When antibiotic is entering soil it is primarily degraded by abiotic rather than biotic processes, that is why most of the groups like suflonamides are not readily biodegradable, but leachable (Rajapaksha et al. 2014b). It means that they can be easily transferred from soil to groundwater or taken up by edible plants, due to its low molecular weight (Rajapaksha et al. 2014a). Biochar application to soil can directly or indirectly modify these conditions, mitigating the problem of antibiotics transfer in the food chain by decreasing antibiotics bioavailability and leachability (Vithanage et al. 2014). Large surface area and aromatic surface properties developed during high-temperature pyrolysis as well as low ash content, tends to enable biochar to effectively adsorb most of the antibiotic groups present in water and soils.

Indirectly biochar can modify soil properties like pH, cation exchange capacity, or organic matter content, enhancing or reducing the sorption capacity of soil. In general, ionizable molecules sorption process is pH depended. Solution pH affects both the ionization of the pharmaceuticals and the surface charge of the biochar which, in turn, influences the different mechanisms of pharmaceutical adsorption onto biochar (Ndoun et al. 2021, Chen et al. 2018). Kahle and Stamm (2007) described that antibiotic sorption on organic sorbents decreased with the increase of pH. The highest sorption efficiency is usually observed in very narrow pH, e.g., 5.5–7.0 or 4.0–4.25 depending on the testing speciation of the ionizable antibiotic (Teixidó et al. 2011; Ahmed et al. 2017). Similar findings were observed by Ndoun et al. (2021) describing pH-depended adsorption capacity for sulfapyridine on two different biochars derived from cotton gin waste and guayule bagasse. The removal of sulfapyridine was approximately 70% at pH 10–11 but was significantly reduced (40%) at pH 7. Biochar surface becomes negatively charged at lower pH, and the adsorption capacity is improved due to cation-π bonding and electrostatic attractive force (Jia et al. 2013, Qin at al. 2020). At pH > 6.0 negative charge-assisted hydrogen bond (CAHB) dominates the adsorption as the antibiotics and biochar both have negative surface charge (Masrura et al. 2020). As most pharmaceuticals charge is pH depended, adjusting pH and dose of biochar used to achieve the highest sorption capacity is very challenging in a natural system that has contaminants present in mixture.

2.2 Anti-inflammatory Pharmaceuticals

Non-steroidal anti-inflammatory drugs (NSAIDs) are an extensive range of medication used to treat and alleviate pain as well as inflammation (Mlunguza et al. 2019). NSAIDs are regarded as emerging pollutants in water bodies and they are among

the most detectable organic pollutants in the aquatic systems. Long-term exposure of NSAIDs has created an urgent need of finding a proper solution to minimize the risk of NSAIDs transfer in the food chain. As this group of pharmaceuticals is represented in the environment by wide groups of chemicals (paracetamol, ibuprofen, ketoprofen, diclofenac, aspirin) the removal of these substances from water and soil by application of sorbents is challenging. The adsorption efficiency of NSAIDs depends on their biodegradability and other physicochemical properties such as the likelihood of immobilization by organic or mineral constituents, water solubility and their tendency to volatilize (Quintana et al. 2005). However, various sorbents showed different efficiency of the process depending mainly on their sorption capacity and surface properties. The knowledge about biochar utility for NSAIDs removal from wastewaters is still insufficient. Hence, very limited data suggest that biochar adsorption capacity for inflammatory drugs and their metabolites can be more compared with often studied activated carbons (Yi et al. 2016; Luo et al. 2020).

Modified biochar application for NSAID removal from wastewaters is reported in relatively high number of publications, nonetheless, studies of pristine biochar are rare. Composite formation, coating, chemical or steam activation are commonly studied methods that are employed for increasing biochar sorption capacity for anti-inflammatory pharmaceuticals. These modifications increase carbon content (Mondal et al. 2016), number of oxygen functional groups on biochar surface or abilities of the material to adsorb negatively or positively charged ions (de Souza dos Santos et al. 2020). In terms of inflammatory drugs mechanism of adsorption on biochar is similar to the one of antibiotics. Nevertheless, substance molecular size and partitioning, hydrophobicity, and porosity of the sorbent are crucial when considering biochar as NSAIDs sorbents. Jung et al. (2015) studied competitive sorption of diclofenac (DCF), naproxen (NPX), and ibuprofen (IBP) on loblolly pine chip biochar and observed difference in adsorption capacity for these three pharmaceuticals, depending mostly on molecule size. Smaller molecules are able to occupy smaller biochar pores making process of adsorption more efficient. In addition, chemical properties of some inflammatory drugs, e.g., salicylic acid and the formation of carboxylate anions increase the likelihood of H-bonding with phenolic hydroxyls on biochar surface. Mechanisms of NSAIDs adsorption on pine wood biochar was studied by Essandoh et al. (2015) showing higher efficiency of the process at low pH. Increase of pH causes increased electrostatic repulsion of adsorbate carboxylate anions, decreasing the adsorption capacity. Biochar adsorption strength is also dependent on surface negative charge density. Nonetheless, this property for both biochar and NSAIDs molecule is a complex function of pH, because surface carboxylic acids, phenols, and aliphatic hydroxyls ionize at different pH ranges and their concentrations also differ, that makes it very difficult to predict occurrence of optimum adsorption. Tran et al. (2020) observed that morphological characteristics (especially pore size distribution) of the biochar should be also considered when designing a proper sorbent for pharmaceuticals. In the study, two different kinds of biochar (spherical and non-spherical) exhibited similar physicochemical properties, but their adsorption affinities and behaviors toward paracetamol molecules in solution were remarkably dissimilar due to differences in porosity.

Chakraborty et al. (2018) studied pristine and steam-activated *Aegle marmelos* (wood apple) fruit shell biochar that showed promising efficiency for ibuprofen removal, pointing out that biochar surface modification and development of highly porous biochar during high-temperature pyrolysis or steam activation increase the sorption efficiency up to 95%. Similar findings were described by Show et al. (2020) where tamarind seeds biochar showed high efficiency for ibuprofen removal from an aqueous solution. Recently, a lot of attention has been paid to caffeine (1,3,7-trimethylxanthine) that is used in cold and flu medicines and as a stimulant in beverages. Álvarez-Torrellas et al. (2016) reported that natural organic matter has high capacity for caffeine (CF) removal, while Keerthanan et al. (2020) confirmed that biochar was successful in CF removal from wastewaters. Knowledge about biochar efficiency for NSAIDs adsorption from soil is still very limited and there is an urgent need to develop scientific projects dedicated to soil—biochar—NSAIDs interactions.

2.3 Antidepressants

Antidepressant pharmaceuticals are typical anthropogenic pollutants. The knowledge about antidepressant medicine sorption on biochar is limited, however, some data can be found on biochar sorption capacity for nitrazepam, diazepam, and fluoxetine from aqueous solution. Fernandes et al. (2019) evaluated the use of twelve biochars derived from different forest and agri-food wastes for removal of fluoxetine. Raw material type had a great influence on sorption capacity and significant difference between pine biochar (36% of efficiency) versus eucalyptus residue (100% of efficiency) was found. This dissimilarity in behavior of biochar can be related to different physical (particle fractionation and pore size distribution, specific surface area) and chemical, e.g., abundance of surface functional groups and biochar alkalinity, properties. Typical to other pharmaceuticals, removal of antidepressant by biochar is pH-dependent and the maximum efficiency can be obtained at pH between 4 and 6. Differences observed between sorption efficiency at different pH values can be related to electrostatic interactions between chemical compounds and biochar. According to various studies, biochar at pH ranging between 5.0 and 9.5 becomes positively charged, contributing to electrostatic repulsion. The other factor that should be considered as antidepressant sorption mechanism on biochar is the role of its surface functional groups, which become deprotonated when pH increases and therefore negatively charged, thus favoring adsorption of ECs (de Souza dos Santos et al. 2020). Nazal et al. (2021) studied the efficiency of macroalgae biochar for nitrazepam removal from wastewaters presenting high efficiency of the process (up to 98%). Similar results were obtained by Escudero-Curiel et al. (2021) describing high efficiency of commercially available biochar on antidepressant sorption and enhanced sorption capacity in the presence of Fe^{3+} cations in the solution.

3   Personal Care Products Components

Recently a lot of attention has been paid to personal care and household products containing endocrine-disrupting chemicals (EDCs). EDCs can mimic the biological activity of natural hormones, occupy hormone receptors, or interfere in the transport and metabolic processes of natural hormones (Danzo 1998; Diamanti-Kandarakis et al. 2009). The main source of EDCs in the environment is municipal sewage sludge and manure. As a result of this material usage in soil fertilization and irrigation of agricultural lands from surface water reservoirs, EDCs enter soil and can be easily leached to groundwaters (Sun et al. 2011). EDCs are relatively hydrophobic organic compounds that's why conventional biological wastewater treatment processes have shown satisfying results for contaminant removal (Ahmed et al. 2018a). Adsorption of EDCs on carbonaceous materials has been studied using mainly activated carbon, while biochar studies are limited.

3.1   Synthetic and Natural Hormones

A lot of studies have been done recently to study on potential sorption of estrogens and estradiols (natural and synthetic) on biochar. Sorption mechanisms are similar to other described ECs. Biochar can act as either an electron acceptor or donor depending on the extent of functionalization and graphitization of its surface (Peiris et al. 2017). Generally, EDA interactions take place in between the phenolic moiety of estrogen and the electron-accepting moieties attached to biochar (Liu et al. 2019b). H-bonding occurs between the phenolic and hydroxyl groups of the estrogens and oxygen surface functional groups on biochar (Ahmed et al. 2018b). Another mechanism that has been reported is the electrostatic force of attraction that occurs between the phenolate ion of the estrogen and the positively charged surface of biochar (Liu et al. 2019a). Estrogen adsorption capacity is pH dependent. Over a wide range of pH (pH 3–12), the hydroxyl groups attached to the arene rings on the biochar surface can function as electron donors, whereas the electron-deficient carbon atom of the carbonyl groups can function as electron acceptors (Peiris 2020). Sun et al. (2011) reported higher adsorption capacities for synthetic estrogen ethinyl estradiol due to an increase in oxygen surface functional groups on the hydrochar produced from poultry litter and swine solids. Alizadeh et al. (2018) demonstrated that biochar could act as an efficient adsorbent in removing two manure-borne estrogens from sandy soil. As Guo et al. (2019) reported, biochar addition significantly improved the adsorption rates and capacities for 17-ethinyl estradiol and perfluorooctane sulfonate removal in sediments. Zhou et al. (2020) tested graphene-like magnetic sawdust biochar showing that it is a promising adsorbent of 17-estradiol (E2) from wastewaters. Sorptive uptake of estrogens from natural water systems is influenced by the different matrix components such as natural organic matter (NOM). Organic matter carries negative charge and a lot of carboxyl and phenolic moieties exhibiting

competitive effect and significantly reducing removal of estrogens (Dong et al. 2018). Regkouzas and Diamadopoulos (2019), reported that sewage sludge biochar can be effectively used to remove organic micropollutants from water or treated wastewater in realistic initial concentrations, with removal rates ranging between 35 and 99%. Bisphenol A (BPA) is one of the EDCs that widely occurs in the environment mainly due to plastic disposal and abiotic degradation. BPA has affinities to human estrogen being called "environmental estrogen" (Takeshita et al. 2001). Little is known about sorptive behavior of pristine biochar in BPA removal mechanism. Recently, magnetic biochar or biochar obtained during hydrothermal carbonization was used to assess the efficiency for BPA removal from water. Wang and Zhang (2020) tested biochar prepared from discarded pomelo peels modified with $FeSO_4$ and $FeCl_3$ solution. Results suggested that magnetic biochar is easy to remove from solution after adsorption of large amounts of BPAs. Heo et al. (2019) enhanced adsorption of BPA and sulphmethoxazole by magnetic $CuZnFe_2O_4$–biochar composite. Wang et al. (2019) examined the adsorption behavior of BPA to peanut shell biochar and effects of cationic, anionic, and nonionic surfactants. Results demonstrated that many of the chemical substances present in wastewaters may affect the adsorption behavior, inhibiting the process of BPA adsorption on biochar sorbents. Sengottian et al. (2020) prepared biochar from *Casuarina equisetifolia L.* and *Wrightia tinctoria* showed that biochars obtained during hydrothermal carbonization have better sorption capacity for PBA compared to activated carbon. This phenomena was also, previously described by Sun et al. (2011) showing that hydrothermally produced biochars are able to adsorb a wider spectrum of both polar and nonpolar organic contaminants than thermally produced biochar.

3.2 Pesticides

Large group of more than an hundred pesticides widely used in agriculture and households can be listed as potential endocrine disruptors (Mnif et al. 2011). Use of modified biochar for pesticides sorption is widely recognized, showing very promising application of these materials in soil and water remediation. Some of the proposed biochar modification methods are based on the pretreatment of biomass and its loading with different materials (Liu et al. 2018). A good example of such practice is the work of Han et al. (2021), where different ways were identified to efficiently convert biomass wastes into biochar with potential for organic contaminants retention. In this study, $FeCl_3$ and $AlCl_3$ were added to two typical biomass wastes (rice straw and poultry litter) during pyrochar and hydrochar production. Results showed that added metal activators significantly changed the properties of biochar. Al (III) induced the carbonization pyrochar at 250 °C and Fe (III) stimulated the formation of aromatic structures. Applied metal activators increased the stability and adsorption efficiency of both pyrochar and hydrochar for polar and nonpolar contaminants. Yavari et al. (2020) aimed to synthesize chitosan-modified biochar with the objective of producing an efficient biosorbent for removal of imazapic and imazapyr herbicides

in soil. Such improvement resulted in increase of the cation exchange capacity of the material, which evoked 76 and 84% sorption of imazapic and imazapyr, respectively, in case of soil amended with chitosan-modified biochar.

An interesting example of physical modification of biochar is work of Kearns et al. (2019), who tested biochar generated from updraft gasifiers under conditions of simultaneous co-pyrolysis thermal air activation (CPTA). Adsorption of anionic (2,4-D) and neutral (simazine) herbicides from surface water containing dissolved organic matter were investigated. 2,4-D adsorption by ≥ 850 °C CPTA biochar was 10 times more in comparison with biochar generated from a conventional pyrolysis. It was due to the increase in mesopores and removal of pyrolysis tars in CPTA biochar.

Many studies revealed that biochar produced through microwave-assisted pyrolysis may be effective for the remediation of soil contaminated with organic pollutants, including pesticides (Yavari et al. 2015; Lam et al. 2019; Li et al. 2016). Microwave-based technology is an alternative heating method and, thanks to its fast, volumetric, selective, and efficient heating, it has already been successfully used in biomass pyrolysis for biochar and biofuel production (Li et al. 2016). Biochars generated via this method are characterized with high yields (>60 wt%) and BET surface areas (450–800 m^2/g). Clay and Malo (2012) produced maize stover and switchgrass biochar, under the temperature range of 350–670 °C using microwave. Based on their findings, maize stover biochar shows a higher affinity for weak cationic pesticides such as atrazine while the biochar made from switchgrass strongly retained anionic 2,4-D herbicide. A group of Lam et al. (2019) combined a microwave-assisted pyrolysis of palm kernel shells with steam activation and obtained a sorbent with a microporous structure and high surface area (419 m^2/g). The designed activated carbon was then tested as an adsorbent of 2,4-D from surface water in agricultural land, indicating high potential to remove the herbicide.

Klasson et al. (2013) utilized steam activation for preparation of almond shell biochar at 800 °C. The biochar increased its specific surface area to 344 m^2 g^{-1} which resulted in 100% removal of dibromochloropropane from a municipal water well. Removal of thiacloprid and thiamethoxam from water (ultrapure and from natural reservoir in Brazil), using activated and magnetized biochars produced from exhausted husk, and dry tannin from barks of black wattle was done by Matos et al. (2017). The magnetized biochar was obtained by mixing dry input material (dry tannin biomass) with the mixture of FeCl$_3$ and FeCl$_2$, followed by the pyrolysis at 400 °C. The amount of thiacloprid and thiamethoxam adsorbed per gram of biochar was maximum for activated adsorbent (1.02 and 0.97 mg/g, respectively), while for the magnetized biochar it was found to be 0.73 mg/g (thiacloprid) and 0.40 mg/g (thiamethoxam). Baharum et al. (2020) evaluated the adsorption of organophosphorus pesticide—diazinon from aqueous solutions onto chemically activated coconut shell biochar. The carbonized coconut shell biochar (BC1), activated using electrical muffle furnace (BC2), was further chemically modified with phosphoric acid (BC3) and sodium hydroxide (BC4) and tested in batch experiment with diazinon. The modified BC3 and BC4 were reported with maximum diazinon removal at pH 7 (84.55% and 87.93%, respectively).

Deashing of biochar is another popular way of its chemical modification. Wheat and rice biochars prepared at 400 and 600 °C and their deashed counterparts were tested as potential sorbents of sulfonylurea herbicide-pyrazosulfuron-ethyl (Manna et al. 2020). This chemical modification of both types of biochar, based on reaction with a mixture of 10% HF 1 M HCl (v/v), resulted in enhanced and effective herbicide adsorption by a factor of 2–3. Zhang et al. (2018) elucidated the sorption affinity of biochar for neonicotinoid pesticides (midacloprid, clothianidin and thiacloprid) on sorption mechanisms of 24 biochar samples, which were further deashed with acids. This treatment increased the relative percentage contents of organic carbon, bulk oxygen content, aromaticity and O-containing functional groups, surface area, and pore volume of biochar. As a result, they efficiently adsorbed the studied neonicotinoids and multiple mechanisms were involved in sorption, indicating that the ash can bind neonicotinoids by specific interactions playing a negative role in the sorption process. Cederlund et al. (2016) studied the ability of thermally treated and magnetized wood-based biochar produced by slow pyrolysis to adsorb bentazone, chlorpyrifos, diuron, glyphosate, and MCPA to assess its potential use as a filter material to prevent point source pollution in agriculture. They modified the biochar by its heating (450 °C) which resulted in an increase of the specific surface area and the wettability of the biochar, at the same time increasing the adsorption of bentazone and MCPA. Additional treatment with iron salts, which partially coated the biochar with an iron oxide (particularly, with magnetite), decreased the specific surface area of the tested sorbent, but increased the adsorption of glyphosate. Mixing the modified biochar fractions allowed to optimize the sorbent properties and improved its sorption abilities toward the studied agrochemicals.

Al Bahri et al. (2012) designed a sorbent fabricated in conventional wet, chemical impregnation method of grape seeds with phosphoric acid and applied it for the adsorption of diuron from water. In terms of physical properties of biochar the best results (surface area of 1139 m^2 g^{-1} and mesopore volume of 0.24 cm^3 g^{-1}) were obtained for grape seeds to phosphoric acid ratio of 1:3 and a carbonization temperature of 500 °C. Its utility to adsorb diuron was high and comparable to the one of powdered activated carbon. Modification of biochar via slow pyrolysis of ammonium di-hydrogen phosphate (ADP) pretreated biomass from corn straw was the subject of the studies of Zhao et al. (2013). They compared ADP-pretreated biochar with the same one produced conventionally, and observed the enhancement of specific surface area, porosity, and the micropore volume of the modified biochar, which significantly increased atrazine sorption.

3.3 Triclosan

Triclosan (TCS) is a broad-spectrum antibacterial agent present as an active ingredient in some personal care products such as soaps, toothpastes, and sterilizers. It is an endocrine-disrupting compound and its increasing presence in water resources

as well as in biosolid-amended soils used in farming, its potential for bioaccumulation in fatty tissues and toxicity in aquatic organisms are of concern to human and environmental health, mainly due to its probable role in breast and hepatic tumourigenesis (Olaniyan et al. 2016). Biochar application for triclosan removal from aqueous phase was tested showing better efficiency for triclosan removal by biochar obtained during high-temperature pyrolysis and preconditioning of biochar using inorganic acids. Using such modified biochar, maximum adsorption of 872 µg triclosan/g biochar was achieved using biochar pyrolyzed at 800 °C, at pH between 5 and 9 (Tong et al. 2016). Kimbell et al. (2018) tested biosolid–biochar columns that demonstrated high efficiency of triclosan removal from water and wastewaters solutions, however, contaminant removal was reduced in the presence of other organic pollutants and inorganic nutrients (ammonium and phosphates) in the solution. This finding can limit the carbonaceous materials application for wastewater treatment. Use of municipal biosolids in agriculture present a concern with potential uptake and bioaccumulation of pharmaceutical compounds from biosolids into agronomic plants. Bair et al. (2020) studied the effects of biochar application to minimize triclosan uptake by lettuce and carrots, showing even 67% reduction of triclosan in carrot roots after soil amending with 100 t/ha walnut shell biochar. However, the results of Phandanouvong-Lozano et al. (2018) determined that biochar application to soil can reduce the bioavailability of triclosan to soil microbes, inhibiting biodegradation process of the contaminant, which is an undesired mechanism during soil remediation.

4   Organic Solvents and Dyes

Trichloroethylene (TCE), representing chlorinated hydrocarbons, has been widely used as a solvent in industry, dry cleaning, and food processing, but also as an ingredient in printing dyes, household care products like degreasers, spot removers, mold release agents, paints and as a general anesthetic or analgesic (Bakke et al. 2007). TCE is one of the most hazardous volatile organic (VOCs) compounds which has been proven to be carcinogenic and mutagenic (Shukla et al. 2014). For the remediation of contaminated soil or groundwater with TCE, biotic and abiotic methods have been employed, however, abiotic methods like sorption seem to be more efficient. Biochar has been recently tested as TCE sorbent from wastewaters showing an increase of sorption capacity with increased temperature of pyrolysis (Dong et al. 2017). As nanoscale zero-valent iron (NZVI) has been widely used for the degradation of trichloroethylene (TCE) in contaminated water, NZVI impregnated biochar is described as a win–win solution enhancing TCE adsorption from wastewaters mitigating the problem of NVZI aggregation due to its high surface energy and magnetic interaction in solution (Lawrinenko et al. 2017; Li et al. 2017). Siggins et al. (2020) studied pristine biochars (spruce wastes, herbal pomace and oak bark) pyrolyzed at >600 °C. The results demonstrated that waste-derived biochars were capable of

adsorbing >99.5% TCE, however, the efficiency of the process increases when very fine biochar material is utilized in this process.

Similarly, to other ECs, high-temperature biochar is more effective in removing TCE (Ahmad et al. 2014; Zhang et al. 2015; Puppa et al. 2020). The fate of TCE in the environment depends on the medium (air, soil, or water) into which it is released. TCE is not easily biodegradable and hydrolyzed as a hydrophobic substance. However, different groups of microorganisms have been recently found to participate in TCE biodegradation in soil (Shukla et al. 2014) and bioremediation strategies seem to be more effective in contaminant removal than standard applications of adsorbents. That is why trichloroethylene sorption studies on biochar in soil are rare. Sorption of hydrophobic organic compounds in soil is depended on organic matter (OM) content and probably (there is no study on the topic) biochar application, especially to soils poor in OM will enhance TCE sorption process. Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry, leather tanning, food technology, or cosmetics production. Due to large wastewater yield, high concentrations of aromatic pollutants, dark color, weakly biodegradable components, alkaline properties, and a variety of complex substances, the dyeing industry wastewater caused serious water pollution (Forgacs et al. 2004). Due to its high surface area and proper microporous structure, biochar proved to be an effective adsorbent for both cationic and anionic dyes. Electrolytes in solution effectively neutralized the negative charge of biochar and induced the dimerization of cationic dyes, thus enhancing the adsorption of both ionic forms of dyes by biochar (Qiu et al. 2009). Fan et al. (2016) studied methylene blue adsorption by municipal sewage sludge and tea waste biochar. The results demonstrated that biochar adsorption capacity for dyes increased with the pyrolysis temperature and many different mechanisms were involved in adsorption process, such as electrostatic interaction, ion exchange, surface complexation, physical diffusion, and others, suggesting the use of biochar as very promising for dyes removal from wastewaters. Similar findings were described by Sumalinog et al. (2018) testing the efficiency of methylene blue adsorption on biochar obtained from the slow pyrolysis of municipal solid waste (MSW), suggesting that dye adsorption occurs mainly due to chemical reactions on biochar surface in a wide range of pH values. Finally, Zhang et al. (2020b) presented green biochar/iron oxide composite as an effective adsorbent for dye substances removal from industrial effluents, showing that modified biochar has very good dye removal capacity.

5   Nitrogen and Phosphorus Contaminants

Various agricultural chemicals, such as fertilizers are being used to increase the output of crops. The risk posed by the contamination of water with excessively posed phosphorus and nitrogen from agricultural runoff is of great concern (Salimova et al. 2020). Also, wastewaters containing high concentrations of inorganic salts, organic compounds including nitrogenous molecules (urea), and other metabolic

waste components became a source of N, P, K in the environment. Agricultural runoffs and natural surface water contamination with wastewaters lead to the process of eutrophication, causing depletion of drinking water supplies. Numerous studies have shown the applications of biochar for nutrient (ammonia and phosphate) recovery from aqueous solutions and urine. Nutrient extraction from human urine is a sustainable option for waste disposal and an economically feasible way to produce soil conditioner/fertilizer (Masrura et al. 2020). Raw materials and pyrolysis conditions can influence different biochar properties, however, the affinity of pristine biochar for the removal of oxyanions is relatively low due to the electrostatic repulsion by negatively charged BC surface. Biochars activated by metals have a significantly higher capacity to adsorb nitrate and phosphate than their unmodified counterparts. For oxyanions such as NO_3^- and PO_4^{3-}, mainly positively charged metal oxides, increasing the number of active sites in biochar and its surface charge, are responsible for their sorption (Wang et al. 2020a, b). Its mechanism occurs mainly via ion exchange and interactions with oxygen-containing functional groups on biochar surfaces and is related to the catalytic action of the composite material (Wang et al. 2020a, b; Zhang et al. 2020a).

5.1 Nitrates

For NO_3^-, the sorption mechanisms are governed by multiple interactions. Electrostatic attraction and ionic bonds with exchangeable cations from the biochar is postulated as a primary route of nitrates retention. Biochar is a potentially effective sorbent for NO_3^- in water treatment and soil applications. Fidel et al. (2018) evaluated nitrates sorption rates to acid-washed biochar produced from red oak and corn stover at different pyrolysis temperatures and pH range. Additionally, they quantified NO_3^- sorption, as well as Cl^- displacement for corn stover biochar to examine the sorption mechanisms. Nitrates sorption was the maximum (1.4–1.5 mg N g^{-1}) at 600 °C and pH of 3.5–4. NO_3^- displaced Cl^- from previously $CaCl_2$-saturated corn stover biochar, which supports the predominance of ion exchange mechanisms. Viglašová et al. (2018) fabricated a biochar/montmorillonite composite, using bamboo as raw material and tested its utility in the adsorption studies for removal of nitrates from aqueous solutions. Montmorillonite was distributed across the biochar surface which resulted in enhancement of the maximum adsorption capacity of the composite to 9 mg of NO_3^- per gram of the sorbent.

A variety of different activating agent solutions (HCl, NaCl, KCl, $MgCl_2$, $ZnCl_2$, $AlCl_3$, $FeCl_3$, $MgCl_2$ with HCl) were added to the pristine corncob biochar, to study its utility to remove NO_3^- in wastewaters (Long et al. 2019). Among the studied variants, $FeCl_3$ modified biochar with the highest positive surface charge was further tested to remove nitrates from aqueous solutions. Through the formation of iron nitrate hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) on the biochar surface, higher nitrate adsorption, than that of pristine biochar, was achieved. In the study of Hafshejani et al. (2016), chemically modified biochar (developed from sugarcane bagasse) was

used for the nitrate removal from aqueous solution. The results showed that the maximum percentage of NO_3^- adsorption was achieved at equilibrium pH of 4.64, after 60 min of contact time and with an adsorbent dose of 2 g L^{-1}. Additionally, competing anions (carbonate and chloride ions) have shown maximum and minimum influence on the NO_3^- adsorption of the studied BC.

5.2 Phosphates

Effective and economical phosphate removal from wastewater can be very often achieved by magnetic modification of biochar. Precipitation by metal oxides in BC is the primary mechanism for PO_4^{3-} removal. Ajmal et al. produced magnetically modified biochar by co-precipitation of Fe(II) and Fe(III) ions in their presence, from wood and rice husks. Its utility as PO_4^{3-} sorbent in wastewaters was tested to be twice as efficient (25–28 mg g^{-1}) than that of the unmodified biochar. According to the results, the driving PO_4^{3-} sorption mechanism on magnetic biochar is simultaneously the electrostatic attraction, surface precipitation, and complexation, while for the original biochar, the sorption mainly depends on electrostatic attraction. Sometimes, however, the input material itself can exhibit properties enabling it to efficiently sorb the destined pollutant. One such example is sewage sludge that after pyrolysis acts as an excellent PO_4^{3-} sorbent (the maximum sorption capacity of 303.5 mg g^{-1}) in the wide pH range of the studied eutrophic waters (Yin et al. 2019). This ideal adsorption ability was mainly due to the abundance of metal oxides and functional groups in sewage sludge that are capable of effectively removing phosphates. Magnetic modification of biochar was also used to study the phosphates adsorption mechanisms in soil, under field conditions. Wu et al. (2019) pyrolyzed peanut shells and modified them with MgO. Such activation of biochar resulted in 20% increase in phosphates adsorption than unmodified biochar. Electrostatic attraction, precipitation, and exchangeable anions contributed to the adsorption of phosphate and MgO-modified biochar, which possessed the greatest adsorption capacity and its application in soil increased the available P content and resulted in higher rice yields in the field experiments. Iron-modified corn straw biochar was used as an adsorbent to remove phosphorus from agricultural runoff (Liu et al. 2015). The surface of the activated biochar was covered by small iron granules, which were identified as Fe_3O_4. The tested biochar was packed in a column and the agricultural runoffs with a total phosphorus concentration of 1.86–2.47 mg L^{-1} were applied with a hydraulic retention time of 2 h. The efficiency to remove the phosphorous from effluent was 99% and its concentration was less than 0.02 mg L^{-1}. At the studied biochar-to-soil rate (5%), the stem, root, and bean of broad bean plants demonstrated increased growth rates of 91%, 64%, and 165%, respectively.

Chemical modification of biochar with the use of polyethyleneimine (PEI) was conducted to test the efficiency of amine-functionalized biochar to remove phosphates (Li et al. 2020). Biomass pyrolyzed in the study was bamboo. PEI was successfully grafted onto biochar which enhanced P adsorption. The most optimal

conditions for P adsorption were pH 3, low ionic strength, and low concentration of coexisting ions, such as HCO_3^-, SO_4^{2-}, NO_3^-, and Cl^-. The electrostatic interaction between P and surface functional groups of PEI-modified biochar served as the primary mechanism controlling the adsorption process.

Ramola et al. (2021) prepared a biochar–mineral composite by using rice husk and calcite as raw materials. Prepared biochar–calcite composite was an optimized adsorbent for phosphate with maximum removal of 87.3% and adsorption capacity of 1.76 mg/g. The optimized conditions of pyrolysis were—700 °C, 2.3 h, and 4.2:1 (w/w) of rice husk and calcite ratio. Introduction of calcite increased the efficiency of biochar for phosphate removal that was mainly controlled by adsorption onto the surface of biochar–mineral composite and electrostatic interactions. However, the presence of other ions in the solution, reduced the amount of phosphate removal by biochar–mineral composite.

The cosorption of both oxyanions: NO_3^- and PO_4^{3-} was evaluated by Yin et al. (2018) in the studies assessing the effectiveness of eutrophic waters remediation by magnetically modified BC with different Al contents (i.e., 5, 10, 15, and 20 wt %). Biochar with 15% Al content exhibited optimal NO_3^- adsorption capacity (the maximum sorption capacity of 89.58 mg g^{-1}), whereas for PO_4^{3-} it was the highest for 20% Al amendment (57.49 mg g^{-1}). pH = 6 and pH < 6 were advantageous to NO_3^- and PO_4^{3-} adsorptions, respectively, which occurred mainly through chemisorption. Li et al. (2016) also tested modified biochar for NO_3^- and PO_4^{3-} removal from water. They produced biochar from wheat straw in low-temperature pyrolysis (450 °C), activated with hydrochloric acid (HCl), and coated with different amounts of iron ($FeCl_3 \cdot 6H_2O$). Activation with HCl and coating with iron significantly increased biochar adsorption capacity at the optimal ratio of iron to biochar for iron-coated biochar (0.70). The active substance of the optimal-modified biochar (OMB) was amorphous FeOOH. The maximum adsorption capacities were 2.47 at pH 3 and 16.58 mg g^{-1} at pH 6, for nitrates and phosphates, respectively.

5.3 Ammonia

Ammonium (NH_4^+) is one of the common forms of reactive nitrogen (N) in water and wastewater. As biochar usually carries negative surface charge, its adsorption capacity for NH_4^+ cations is high. NH_4^+ adsorption depends more on oxygen functional groups and sorbent porosity and low-temperature biochar seems to be more efficient in ammonium removal. Non-modified, low-temperature biochar (<400 ℃) can adsorb 60–79% of ammonia and up to 60% of phosphorus from aqueous solution (Chen et al. 2011; Xie et al. 2015). Oxygen-containing functional groups such as C=O, –COOH, and –COC– contribute substantially to NH_4^+ adsorption because of hydrogen bonds and electrostatic interaction between NH_4^+ and biochar (Cai et al. 2016). Nitrogen recovery efficiency by biochar increased with solution pH from 7 to 12. At high pH, the zeta potential of biochar decreased leading to enhanced adsorption of positively charged ions (Yang et al. 2020). Tang et al. (2019) tested digested sludge

biochar and demonstrated that the final amount of adsorbed ammonium increased significantly ($p < 0.001$) as the initial pH increased from 2 to 6, and decreased slightly ($p = 0.6$) when pH increased to 8. These results also show that at acidic conditions, ammonium removal capacity is low, mainly due to the competition between H^+ and NH_4^+ in the solution for adsorption to biochar surface functional groups. Significant reduction of ammonia adsorption capacity was observed when pH reached 10, which is due to the effects of pH on the form of ammonium, i.e., it converts to NH_3 (Vu et al. 2017). Designing a proper material for ammonia removal—type of biomass, biochar production temperature, and residence time on NH_4^+ adsorption are significant. Salimova et al. (2020) demonstrated that orange tree biochar has a strong ability to remove ammonia from water, while tea tree biochar did not develop proper properties during the same pyrolysis temperature and efficiency of this material for NH_4^+ was very low. Similar findings were described by Xue et al. (2019) testing seven types of food waste-based biochar (meat and bone, starchy staples, leafy stemmed vegetables, nut husks, fruit pericarp, bean dreg, and tea leaves) achieving even 92.6% of ammonia nitrogen removal, depending on raw material. Raw materials like fruit pericarp and nut husk indicated better effective adsorption, but starchy staples, meat, and bone were least effective. Similarly with the increase of pyrolysis temperature the adsorption capacity of biochar decreased. The efficiency of biochar for ammonium adsorption also depends on initial ammonium concentration. Biochar deashing and acid modifications with inorganic acids seems to be a sufficient method of enhancing biochar sorption capacity for ammonium (Vu et al. 2017).

6 Microplastic

Although microplastic (MP) is not yet on the list of emerging contaminants, its wide occurrence in aquatic and terrestrial ecosystem brings concerns about possible impacts of this microcontaminant on living organisms, including human beings. Biochar application for wastewater and water purification from microplastic seems to be a good strategy to find cost-effective and efficient MP sorbent. The advantage of MP removal is that the main mechanisms are based on physical sorption on the porous structure of adsorbent and it is not necessarily important to obtain materials with high surface area or large number of oxygen functional groups which makes the biochar-based—microplastic sorbent production less expensive and easier to obtain in standard pyrolysis reactors. Siipola et al. (2020) described low-cost spruce and pine bark-derived biochar as good adsorbent for microplastic removal in water purification process. As MPs is adsorbed mainly on biochar micropores, this microporosity can be obtained during steam activation or ball-milling. The more micropores are generated on biochar surface, the more efficient MPs removal is. Similarly, observation was described by Wang et al. (2020a, b) using biochar samples produced at three different temperatures from corn straw and a hardwood biochar to compare retention of spherical microplastics. Results of the study showed that removal efficiency was higher than 95% when microporous biochar were used for trapping MPs.

Limitations

Although biochar has proven to be one of the most efficient adsorbents in removing ECs, certain disadvantages are making it a less attractive option for many applications. Numerous sorption mechanisms, mostly tested under very controlled conditions in pure solutions or batch experiments will not be sufficient to extrapolate on real soils and natural waters conditions. That is why obtained results should be handled with care and further investigation are necessary to predict the efficiency of biochar for the removal of EC in natural systems.

There is a lot of uncertainty about optimum parametric conditions of the process, e.g., pH of medium, adsorbent dose, pharmaceutical concentrations, contact time, or temperature. There are also doubts about the use of proper biomass for adsorbent production as the amount of the biochar necessary to clean wastewaters are estimated in million tons. Finally, what to do with spent biochar waste? How to separate biochar from soil or solution? These are the questions with no answer at this moment. Pretreatments or post-treatments of biochar will be necessary in most of the cases to enhance the adsorption capacity. However, these procedures may significantly increase the cost of biochar use for wastewater treatment. High costs due to the activation process, lack of biodegradability of adsorbed ECs by microbes, and high regeneration cost are some of the limitations of biochar used in this process.

7   Conclusions and Future Prospects

As the problem of emerging contaminants released to the environmental media occurs globally with an unknown effect to human health, there is an urgent need to develop new, cost-effective, and ecological-friendly methods of water and soil treatment to mitigate potential risk related to presence of ECs in the food chain. In this context, the presented review highlights the wide application potential of biomass waste to become a precursor of biochar, i.e., highly efficient material for the removal of emerging contaminants from wastewaters. The number of scientific papers describing efficiency of different biochars for ECs removal from wastewaters and aqueous solutions is gaining a growing interest for this material as an emerging contaminant adsorbent. Designing a proper sorbent should ensure immobilization of high concentrations of contaminants present in media. Therefore, adsorption capacity and affinity to micropollutants molecules should be enhanced by biochar surface modifications.

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Engineered Biochar as Soil Fertilizer

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Abstract Biochar, a heterogeneous carbonaceous material, has multifaceted application potential for environmental management. Biochar has been commonly used for contaminant removal from soil and water systems, soil quality improvement, soil C-sequestration, inoculant carrier, etc. Surface area, pore space, surface functional groups, pH, cation exchange capacity (CEC), and nutrient contents are a few key properties that determine the potential of biochar application. Raw materials and pyrolysis conditions are the determining factors for these aforesaid properties of biochar. Biochar production from lignocellulosic biomass and biosolids at moderate pyrolysis temperatures (350–600 °C) are commonly recommended for waste management. Despite its multifaceted application potential, biochar utilization at widescale is limited due to certain incompatibilities with the environmental systems. To overcome the incompatibilities between biochar properties and environmental conditions, engineering of biochar by using different additives and modifications in pyrolysis conditions are getting wider attention nowadays. In this chapter, we have explored the potential of engineered biochar as soil fertilizer. A bibliometric analysis was performed to collate the literature and to see the research trend of engineered biochar as soil fertilizer. Studies reported that engineering of biochar leads to improvement in its surface and physicochemical properties. Engineered biochar with improved properties helps in enhancing soil physicochemical, nutrient, and biological properties after amelioration. Improvement in soil properties showed better crop productivity in some pot/laboratory experiments. Overall, we observed that the research on exploring engineered biochar as soil fertilizer is comparatively

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limited as compared to its exploration as contaminant adsorbent and source of energy production.

1 Introduction

Land degradation due to desertification, acidification, salinization, nutrient depletion, erosion, pollution, etc., is the major issue impeding the severity to attain food security and agricultural sustainability. As per the United Nations Food and Agriculture Organization (FAO), about 25% of agricultural lands are "highly degraded," 44% are "slightly-to-moderately degraded", whereas about 10% land has been "recovered from degradation," globally (FAO 2011; Smith et al. 2015; Huang et al. 2017). Intensive agricultural practices such as irrational applications of agrochemicals and irrigation regimes for increasing productivity, land-use changes, industrial activities as well as changing climatic scenarios are considered the major causes of the land degradation (Guo et al. 2010; Carlson et al. 2015). Land degradation leads to the deterioration in soil quality by decrease in soil organic matter (SOM) level, poor hydrophysical properties (e.g., water-holding capacity and aggregate stability), and reduced microbial functioning leading to poor plant growth and declining food production (Ibrahim et al. 2013; Ding et al. 2016). Moreover, massive amount of crop residues (~998 MT yr^{-1}) are generated globally (Copley et al. 2015), out of which a major portion is openly burnt in the field which leads to several environmental issues such as gaseous and particulate emissions, and soil health deterioration (Singh et al. 2020a; Jeyasubramanian et al. 2021). Therefore, minimizing the sole dependence on chemical fertilizers, enhancing SOM levels and microbial functioning of degraded/low-fertility soils, crop residue management, and reducing atmospheric CO_2 levels are critically needed for improving soil fertility and sustainable crop productivity (El-Naggar et al. 2019; Dai et al. 2020; Dissanayake et al. 2020). The sustainable methods such as soil amendments, which are abundant and biodegradable, and have ability to overcome the above-mentioned problems with minimal/no side effects on the environment, are the need of the hour (Kuppusamy et al. 2016; Rinklebe et al. 2016). Biochar, a by-product of biomass pyrolysis, has been considered as a promising tool to address these challenges (Khajavi-Shojaei et al. 2020; Panahi et al. 2020).

Biochar production by using crop residue biomass via pyrolysis is a sustainable process and its application as soil ameliorant not only improves soil properties and SOM levels, but also helps in managing crop residue burning, and reducing environmental pollution and CO_2 emission (Chen et al. 2019; Das et al. 2020; Leng et al. 2021). Depending on the biomass source and pyrolysis conditions, biochar has been characterized as a heterogeneous material having partially or completely carbonized, crystallized or non-polyaromatic C-forms and mineral matters (Keiluweit et al. 2010;

Spokas et al. 2012; Das et al. 2020). Moreover, biochar has higher porosity and cation exchange capacity (CEC), larger surface area, and long-term stability in the soil (Chabi et al. 2020; Jeyasubramanian et al. 2021). These properties of biochar help in improving crop growth and productivity by enhancing soil fertility, microbial activity, SOM storage and nutrient retention, modulating soil pH and water conditions, and aggregate formation after soil amelioration (El-Naggar et al. 2018; Dai et al. 2020; Das et al. 2020). Overall, the multifaceted application of biochar in soil quality improvement, C-sequestration, contaminants sorption and removal from soil and water systems, mitigating the emission of greenhouse gases (GHGs), as energy source, and waste management has resulted in gaining wider attention by the scientific and industrial communities (Lehmann and Joseph 2015; Singh et al. 2015; Dissanayake et al. 2020).

Though, biochar has multifaceted benefits as soil ameliorant; however, the sole application of traditionally produced biochar has been reported to have several challenges, viz. low nutrient contents as compared to the inorganic fertilizers, nutrient immobilization and slow-release, poor sorption/adsorption potential for contaminants, etc., which reduces its wider adoption by farmers (Mohamed et al. 2016a). For example, application of biochar with less porosity in hard soils may not result in improved crop productivity, and even application of inappropriate biochar in soil may lead to increased GHG emissions by modulating the soil physicochemical and biological properties (Panahi et al. 2020). Therefore, combined/blended application of biochar with other organic/inorganic materials such as compost, inorganic fertilizers, clay minerals, nanocomposites, etc., has also been suggested nowadays for improving soil fertility and crop performance, particularly in degraded soils (Aggegnehu et al. 2017; El-Naggar et al. 2019; Singh et al. 2019, 2020b; Das et al. 2020). The conventional biochar production systems have little potential to be scaled-up at industrial production level due to low productivity and high production cost (Crombie et al. 2014; Mohamed et al. 2016b). Therefore, researches on biochar production by using different additives during the production or post-production upgradation of biochar properties and minimizing the production costs have been getting wider attention (Abdeljaoued et al. 2020).

1.1 Engineered Biochar: Definition and Need

Though biochar preparation from waste biomass is a sustainable approach; however, the properties of conventionally prepared biochar (viz. pristine biochar) can be further improved for its multifaceted applications (Akhil et al. 2021). For example, pristine biochar has low pore size and surface area which limits its potential to be used for the removal/remediation of several contaminants and nutrients which are smaller in size (Khajavi-Shojaei et al. 2020; Akhil et al. 2021). Improved pore size and surface area help in improving contaminant removal/nutrient retention potential after soil amelioration (Weber and Quicker 2018; Leng et al. 2021). For such improvements in biochar structural (surface and physical) and chemical properties, several novel

methods and modifications have been evolved. The modification at the molecular or micromolecular levels to enhance the surface, physical and chemical properties (e.g., surface area and surface functional groups, porosity, pH, and CEC) of biochar with desired properties for specific applications in the fields of environment, energy, agriculture, and chemistry is referred to as biochar engineering (Wang et al. 2017; Abdeljaoued et al. 2020; Panahi et al. 2020).

Details about biochar engineering and the physicochemical properties of engineered biochar have been elaborated in different chapters of this book. In this chapter, a detailed insight has been given on exploration of the role of engineered biochar as a soil fertilizer. To observe the research trend on engineered biochar as soil fertilizer, a bibliometric analysis was performed using popular literature databases. Moreover, a brief account on the limitations of engineered biochar application as soil amendment has also been presented at the end of the chapter.

2   Bibliometric Analysis for Research on Engineered Biochar as Soil Fertilizer

Biochar has received greater attention of research communities in the last two decades due to its multifaceted application potential. Recently, engineered biochar with improved (surface/physicochemical) properties as compared to their pristine biochar counterparts are getting wider attention. In order to observe the trends in research concerned with engineered biochar and soil fertilizer or soil amendment during the last 20 years (2001–2021), we performed a bibliometric analysis on 27th July, 2021, using different search queries in the Scopus and Web of Science databases. These two databases are the largest indexing and regularly updated databases covering a wide range of peer-reviewed journals (Abdeljaoued et al. 2020; Singh et al. 2021). The initial search query was: (TITLE-ABS-KEY ("engineered biochar") AND PUBYEAR > 2000). The query results in a total number of 182 and 190 documents published during the last 20 years (from 2001 to present, 27th July, 2021) in Scopus and Web of Science databases, respectively. Results were further refined by ("soil fertility" OR "soil amendment") by searching within the first search query which resulted in total 68 and 19 documents in the Scopus and Web of Science databases, respectively.

The year-wise growth of the research on the topic was considered along with country-specific research outputs. Though, we searched from 2000 onwards, but we found research publications on this topic since 2013 only. Starting with merely one paper on the topic in the year 2013, the year 2020 observed a total number of 26 documents published within a single year (Fig. 1a). Interestingly, a total of 18 documents have already been published in the year 2021 (till 27th July). The results signified that the field is still emerging and recently getting much attention from the scientific community. Further, country/territory-, institute/affiliation-, subject/research area-, source/journal-, author- and publication type-wise distribution of research on the
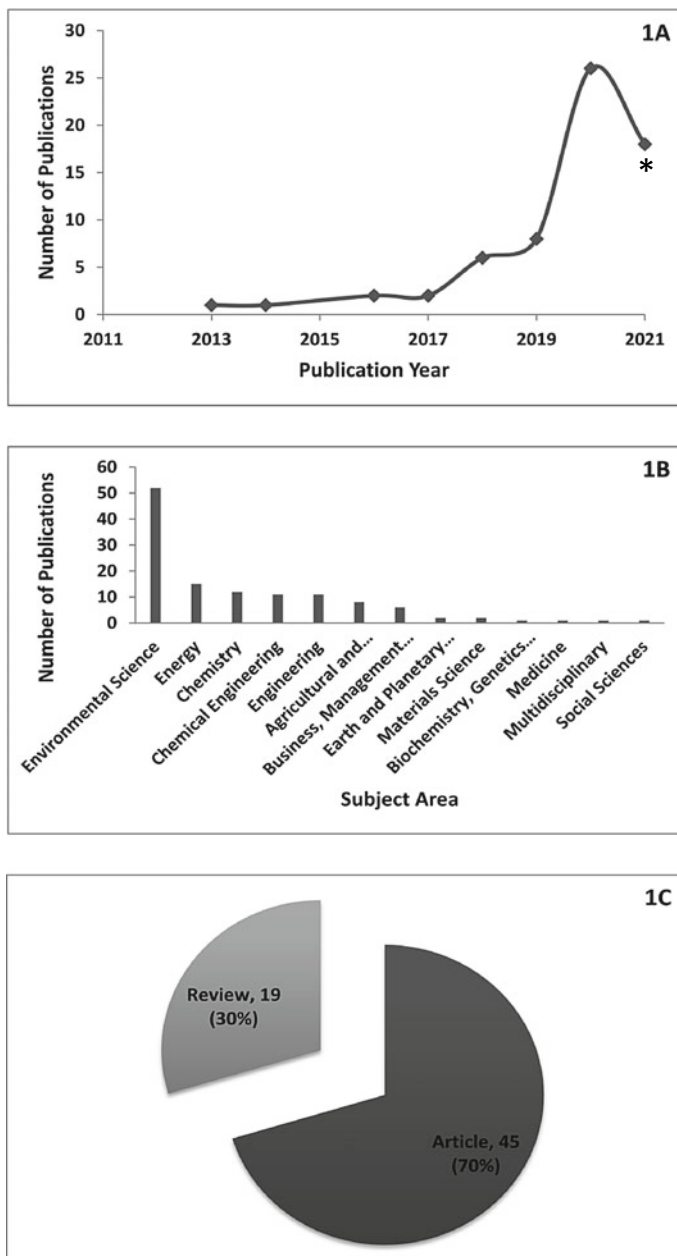
Fig. 1 Bibliometric analysis results showing **a** year-wise publication growth, **b** subject area-wise distribution, and **c** article type-wise publications for the search query "engineered biochar AND soil fertility" (*Source* Scopus database, 2021). *denotes incomplete dataset for the year 2021

topic was also analyzed. China emerged as the largest contributors of papers under country/territory-wise publication category with 33 documents. South Korea and Hong Kong ranked second and third by producing 25 and 19 papers each, while India stood at 6th rank with 7 papers published during the same period (Table 1). These observations revealed that research on engineered biochar as soil fertilizer is getting wider attention in Asian countries as compared to other countries/continents. Since most of the Asian countries are agrarian and facing the problem of massive waste management, such research trends hold crucial importance for future agricultural development. Among the research institutes and universities globally, Hong Kong Polytechnic University produced the maximum number of papers (19), followed by Korea University with 18 papers published during the last 10 years (Table 1). Out of the total 64 publications (Fig. 1b), more than 43% fall under the research areas of environmental sciences followed by engineering (18%), energy (12%), chemistry (10%), and agriculture (8%). This signified that the interdisciplinary researches are increasing on the topic and focus on environmental and engineering research is given optimal importance. Author-wise analysis results revealed Ok YS, Tsang DCW, Hou D, Gao B, and Rinklebe J, as the five most productive authors publishing 20, 19, 8, 7, and 6 papers during the last 10 years on the topic (Table 1).

Science of the Total Environment (7), Journal of Cleaner Production (6), Journal of Hazardous Materials (5), Chemical Engineering Journal (4), and Chemosphere (4) were observed as the major sources which published researches on the topic during the last 10 years (Table 1). These journals have started with the aim to manage and improve the ecosystems health and sustainability by promoting contaminants removal strategies and waste management approaches. Among 64 papers, research and review papers contributed about 70 and 30%, respectively, whereas conference papers, books, and book chapters were not identified (Fig. 1c). The ratio of <3:1 in research and review articles signifies that the topic is getting considerable attention by the research communities in different research dimensions; however, there is ample scope for writing a book chapter (and book) on this topic to reach the graduate and post-graduate reader groups. Based on the Web of Science Keyword-plus datasets, Fig. 2 depicts the focus areas of engineered biochar research in the field of environmental management. It can be seen that removal, adsorption/sorption, aqueous solution/water, pyrolysis, soil/calcareous soil, activated carbon, nitrogen/ammonium, raw material, stability, and low-cost are the top 10 areas of research related to engineered biochar which has been considerably explored in the recent years. In the next section, details about the role of engineered biochar as soil fertilizer have been provided.

Table 1 Bibliometric analysis results showing top 20 countries, top 10 research institutes/affiliations, top 20 authors, and top 10 research journals for the search query "engineered biochar AND soil fertility" (*Source* Scopus database, 2021)

Source category	No. of publications	Source category	No. of publications
Country-wise		*Country-wise*	
China	33	Australia	5
South Korea	25	Canada	5
Hong Kong	19	Taiwan	5
United States	17	Saudi Arabia	4
Germany	7	Finland	3
India	7	Iran	3
Sri Lanka	7	Singapore	3
United Kingdom	7	Belgium	2
Egypt	6	Czech Republic	2
Pakistan	6	Malaysia	2
Affiliation-wise		*Affiliation-wise*	
Hong Kong Polytechnic University	19	Ministry of Education China	7
Korea University	18	Bergische Universität Wuppertal	6
Tsinghua University	9	China Agricultural University	5
University of Florida	8	Foshan University	4
Sejong University	8	The University of Newcastle, Australia	4
Author-wise		*Author-wise*	
Ok, YS	20	Bhatnagar, A	3
Tsang, DCW	19	Chen, Q	3
Hou, D	8	Chen, SS	3
Gao, B	7	Dissanayake, PD	3
Rinklebe, J	6	Fang, J	3
Sun, Y	6	Kwon, EE	3
Igalavithana, AD	5	Peng, Y	3
Shang, J	4	Sarkar, B	3
Vithanage, M	4	Shen, Z	3
Alessi, DS	3	Wang, H	3
Source-wise		*Source-wise*	
Science of the Total Environment	7	Bioresource Technology	3

Table 1 (continued)

Source category	No. of publications	Source category	No. of publications
Journal of Cleaner Production	6	Environment International	3
Journal of Hazardous Materials	5	Biomass Conversion And Biorefinery	2
Chemical Engineering Journal	4	Clean Technologies And Environmental Policy	2
Chemosphere	4	Critical Reviews In Environmental Science And Technology	2
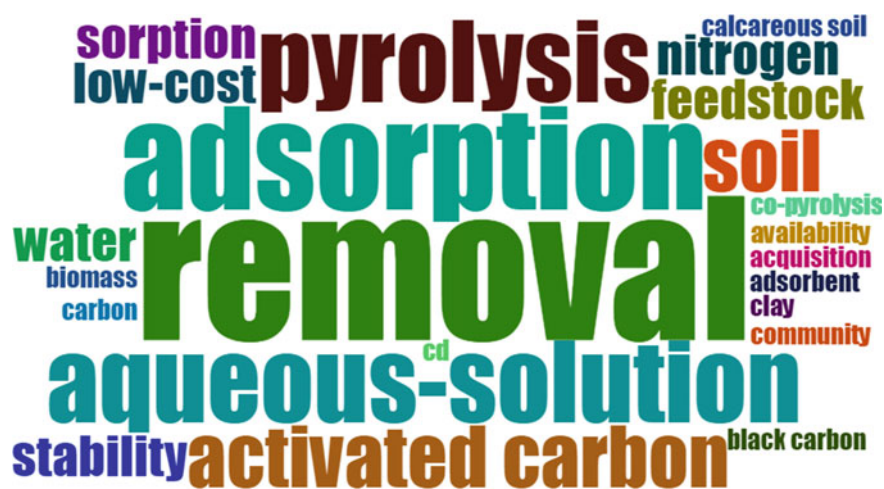
Fig. 2 Representation of application/research focus of engineered biochar for environmental management via word map (size of a word depicts the occurrence frequency in the literature) (*Source* Web of Science database, 2021)

3 Engineered Biochar as Soil Fertilizer

The ability of soil to sustain the crop productivity by providing essential nutrients and water supply to the plants for their survival and growth is referred as soil fertility (El-Naggar et al. 2019). Soil fertility is governed by different physicochemical (e.g., pH, soil N, P, K contents, CEC, and C-sequestration) and biological (e.g., microbial community composition and nutrient cycling) properties (Igalavithana et al. 2016; Panahi et al. 2020). After soil amelioration (Fig. 3), biochar has been reported to improve the physical, chemical, and biological properties of soil as well as improve the nutrient uptake and reduce leaching (i.e., improve nutrient-use-efficiency) in the agro-ecosystems (Wang et al. 2017; Qayyum et al. 2017), particularly in the degraded
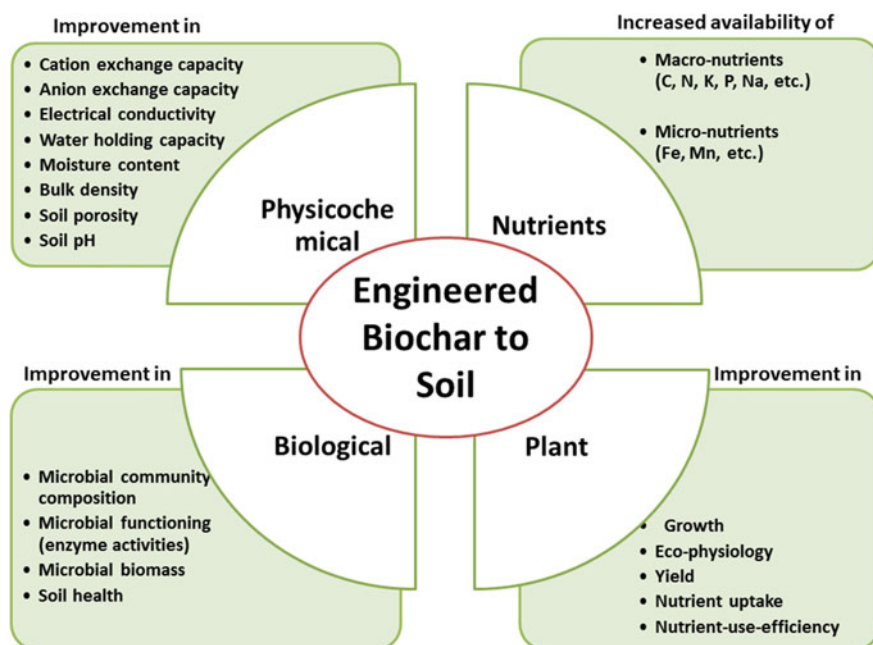
Fig. 3 Varying impacts of engineered biochar application on different soil physicochemical and biological properties as well as plant responses

and low fertility soils (Kuppusamy et al. 2016; Randolph et al. 2017; Panahi et al. 2020). Modifications observed in the soil properties after biochar application might be localized, initially (Quilliam et al. 2013). The impact of biochar amendment to soil could be direct or indirect. For example, application of nutrient-rich biochar directly improve the soil nutrient level, whereas in some cases biochar improve the soil nutrient availability indirectly by improving soil physicochemical properties (Fig. 3) such as water-holding capacity (WHC), soil porosity, water infiltration, pH, CEC, SOM level, etc. (Kuppusamy et al. 2016; El-Naggar et al. 2019; Panahi et al. 2020). Improvement in soil properties after biochar application resulted in enhanced crop production (Laghari et al. 2015; Zhang et al. 2017a). However, the impact of biochar amendment to soil properties and crop productivity mainly depends on biochar properties (e.g., pH, CEC, and C/N ratio) and its production conditions (e.g., raw material, pyrolysis temperature and other modifications), soil type and conditions, crop plant species, and management practices (Zhang et al. 2017a; Singh et al. 2019; Dai et al. 2020; Leng et al. 2021). For example, biochar derived from lignocellulosic biomass has better pore structure and help in improving soil hydro-physical properties after application (Singh et al. 2019), whereas biochar derived from nutrient-rich manure are more beneficial for improving nutrient content and crop productivity in low fertility soils (Jeffery et al. 2017; Dai et al. 2020). The combined/blended application of biochar with other nutrient sources like organic

manure, fertilizer, clay minerals, etc., has shown better soil properties (e.g., nutrient availability) and crop productivity as compared to the sole application of biochar (El-Naggar et al. 2019; Singh et al. 2019). Moreover, engineered biochar has also been now produced for improving soil fertility (Li et al. 2016). Though, as highlighted in the bibliometric analysis section, the field is still emerging and more research attention is needed.

4 Enhanced Properties of Engineered Biochar and Its Impact on Soil Properties

The engineering process of biochar modifies its physicochemical properties making it suitable for industrial application. Engineered biochar differs from pristine biochar in terms of its morphological properties and chemical attributes (Table 2). Engineering of biochar improves its physical (density, particle size distribution, mechanical strength, pore size) and chemical characteristics (C and N content, pH, electrical conductivity, CEC) along with its surface (Fig. 3) properties (Das et al. 2020). The pH of biochar generally varies from 4 to 12; however, most of the biochar have alkaline pH range (von Gunten et al. 2019; Lehmann and Joseph 2021). Presence of different concentrations of oxides, hydroxides, and carbonates of alkali metals in the biochar resulted in higher pH ranges (Lehmann and Joseph 2021). Engineered biochar can enhance adsorption as it can hold both positive and negative charges on its surface. Biochar produced at lower pyrolysis temperature contains higher volatile matter content, low pH (prevents nutrient loss), and more nutrient exchange sites in the form of O-containing functional groups (El-Naggar et al. 2019). Microbial activity is enhanced due to the presence of aliphatic, cellulose-type structures in such biochar. Additionally, on raising the temperature from 350 to 600 °C, available N decreases whereas the content of P and K increases (Zhao et al. 2013). The amount of volatile matter and the residual C mass (ash) determine the stability of biochar in soil (Amonette et al. 2009). As a result, biochar has been reported to improve several soil physicochemical properties (Weber and Quicker 2018). Interestingly, improvement in soil physicochemical properties was more pronounced in the coarse-textured and low fertility soils as compared to the fine-textured and fertile soils (Laghari et al. 2015; Omondi et al. 2016). Biochar has been found to have a major environmental impact. Due to its recalcitrant/stable nature, biochar application has been reported to reduce GHG emissions by modulating soil C and N transformation processes (El-Naggar et al. 2019; Lehmann and Joseph 2021). In addition, biochar produced from lignocellulosic biomass has been reported as an effective agent for sorption of the organic contaminants (Wang et al. 2017). High surface area and pore spaces of the (mineral-treated) engineered biochar provide more adsorption sites for binding of the agrochemicals (Li et al. 2015). Improvement in key soil physicochemical properties after engineered biochar amelioration has been highlighted in the following subsections (also see Table 2).

Table 2 Comparative impact of pristine biochar and engineered biochar on different soil properties after application

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
1	Corn straw	500 °C	0.5%, 1%, 2%, and 4%	Chemical activation (Fe/Al hydroxides)	Calcareous soil	Laboratory (polyethylene containers)	(i) Increased soil pH (increased P precipitation and reduced soluble P) with high stability	Less stable pH compared with engineered system	Peng et al. (2021)
							(ii) Adsorption of excessive P from fertilizers was increased, thereby reducing P leaching while maintaining a saturated P content in soil	Poor P adsorption	Peng et al. (2021)
2	Cow dung	450–750 °C	2%	Chemical activation (MgCl₂ followed by P adsorption)	Acid sandy soil	Pots	(i) Considerably improved soil indexes (soil available P, pH, organic carbon, soil moisture)	Improvement seen to a lesser degree	Chen et al. (2018)

(continued)

Table 2 (continued)

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
							(ii) Basic characteristics of lettuce like plant height, fresh weight, and dry weight increased	More than control, but less than P laden engineered biochar	Chen et al. (2018)
3	*Eichhornia crassipes* (Water hyacinth)	450 ± 5.0 °C	NA	Chemical activation (Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+})	Sandy soil	Samples from agricultural drain planted in pots	(i) Increased water-holding capacity (WHC, by 18.48–22.45%) was observed	Comparatively smaller increase (<18.45%)	Mosa et al. (2018)
							(ii) Higher anion exchange capacity (AEC, by 1.41–1.82%) and cation exchange capacity (CEC, by 3.73–6.35%)	Slight increase in AEC (0.77%) and CEC (3.53%) as compared to soils without biochar	Mosa et al. (2018)
							(iii) Available P and K contents increased upon engineered biochar application. But lesser increase in available N was observed	Higher increase in available N was observed as compared to engineered biochar	Mosa et al. (2018)

Table 2 (continued)

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
							(iv) Improvement in biomass and nutrient concentration of early growth maize seedlings	Poor in comparison to engineered (activated) biochar	Mosa et al. (2018)
4	Switchgrass	300 and 400 °C	1% and 2%	Physical activation (microwave catalysis) + chemical activation (K_3PO_4, clinoptilolite and/or bentonite)	Loamy-sand soil	Laboratory	Biochar prepared by microwave heating showed higher porosity that caused an efficient increase in soil WHC	Conventional heating process is less efficient	Mohamed et al. (2016a)
5	90% beech + 10% oak wood	475 ± 25 °C	0.2%, 0.75%, and 1.5%	Physical activation (steam activated at 900 °C)	Haplic Luvisol (neutral sandy and slightly alkaline silty)	Pots	(i) Elevation in levels of soil available N, P, and C/N ratio with a decrease in nutrient leaching	Lower than the activated biochar	Borchard et al. (2012)
							(ii) Nutrient uptake by plant biomass decreased in case of sandy soil, increased in silty soil	Decrease in both soil types	Borchard et al. (2012)

4.1 Physicochemical Properties

Regardless of soil type, biochar application has been reported to improve soil–water interactions (Omondi et al. 2016; El-Naggar et al. 2019; Dai et al. 2020). Pore structure and volume, specific surface area and surface functional (hydrophilic) groups are the major factors which influence the biochar's ability to improve soil hydraulic parameters such as WHC (Wang et al. 2017; Panahi et al. 2020). However, the hydrophobicity of the biochar surfaces prevent the water adsorption/uptake in the pore spaces (El-Naggar et al. 2019). Altogether, engineered biochar has greater potential to improve soil hydraulic properties which will be beneficial to the plants in the drier or water-limited regions of the world (Mohamed et al. 2016a; Khajavi-Shojaei et al. 2020). In addition to water availability, application of biochar with varying pH range affects the soil pH which further regulates different soil biophysical properties and microbial communities (Palansooriya et al. 2019). Biochar application to soil generally increases soil pH (Dai et al. 2020). However, some (alkaline) soils have pH buffering capacity which did not show significant changes in soil pH after biochar application (Usman et al. 2016). Though application of acidic biochar may reduce the alkaline soil pH and improve the availability of some nutrients (e.g., K and micronutrients) in the soil matrix. Thus, application of engineered biochar (e.g., HCl-treated) has potential to improve the pH condition of alkaline or calcareous saline/sodic soils (Sadegh-Zadeh et al. 2018). Application of alkaline pH biochar is more suitable for acidic soils which improved nutrient bioavailability and crop productivity (von Gunten et al. 2019; Panahi et al. 2020). The changes in pH after biochar application have initial localized effects which further reflected in the whole soil matrix (Wang et al. 2017; Yu et al. 2019; Chen et al. 2021).

Biochar addition has been reported to improve the soil CEC due to high surface area and presence of negatively charged functional groups (e.g., –COOH) which increases the retention of cations on its surface and reduces nutrient leaching (Wong et al. 2016; Dai et al. 2020; Panahi et al. 2020). However, changes in soil CEC depend on biochar properties, soil types, and application rate (El-Naggar et al. 2019; Yuan et al. 2021). For example, biochar prepared at low pyrolysis temperature showed higher CEC as compared to the high-temperature biochar. Further, soil CEC increases with aging of biochar in the soil system (Wong et al. 2016). The improvement in soil CEC after biochar application has been found more pronounced in sandy/low fertility soils (El-Naggar et al. 2019). Overall, engineered biochar have potential to improve various soil physicochemical properties which may further lead to improvement in soil nutrient availability and biological properties (Fig. 3).

4.2 Improvement in Soil Nutrient Contents

Chemical properties of biochar are majorly determined by the amounts of mineral elements (C, H, N, S, O, etc.) present. These elements are found in the form of

biomolecules including cellulose, hemicelluloses, and lignin. They consist of both organic and inorganic linkages. The elemental constitution of pristine and engineered biochar differs considerably. The amounts of C, H, and N in engineered biochar are lower than that in raw biochar. These elements are used to assess the chemical factors of biochar. High pyrolysis temperature leads to the crystallization of amorphous elements and organic salts as insoluble phases. Therefore, they have low nutrient contents (Ding et al. 2016; Zornoza et al. 2016). The content of water-soluble P is dependent on H/C and O/C ratios and negatively linked to pH of biochar and charosphere. Therefore, engineering of biochar increases its suitability as P fertilizer due to enhanced P availability (Chen et al. 2021).

Biochar application to soil has been reported to improve soil fertility by enhancing nutrient retention and use-efficiency by the plants (Randolph et al. 2017; Wu et al. 2020). It reduces the nutrient (NO_3^-–N, NH_4^+–N, and PO_4^{3-}–P) leaching after fertilizer application by adsorbing the nutrients on its surfaces (Brassard et al. 2019; Jeyasubramanian et al. 2021). The results are more pronounced in the low fertility sandy soils (Laghari et al. 2015; Lei et al. 2018; Yuan et al. 2019). Biochar being a rich source of exchangeable cations (such as Na, K, Ca, and Mg) increases their availability in soil matrix (Mohamed et al. 2016a, b; Moon et al. 2017). However, availability of micronutrients and soil P to the plants may reduce after biochar application to the alkaline soils due to changes in soil pH conditions (Gunes et al. 2014; Laghari et al. 2015). As P availability to plants has been found more pronounced at pH 5.5–7.5 range, application of biochar which increases the soil pH above or below this range may change the soil P availability (Andersson et al. 2015; Chen et al. 2021). Application of engineered biochar (e.g., $MgCl_2$-modified and steam activated) has been reported to further improve the nutrient adsorption properties and may act as slow-release fertilizers which reduces the nutrient leaching and increase crop productivity (Zhang et al. 2017b; Khajavi-Shojaei et al. 2020). The changes in soil pH conditions after biochar application affect the soil microbial activities which further modulate different soil biogeochemical processes (Yu et al. 2019). Thus, the impacts of biochar application to soil nutrient availability are governed by the complex interactions of soil–water–plant–microbe nexus in the agroecosystems (Singh et al. 2018, 2019).

Biochar application in soil system regulates the N dynamics by acting as either N-supplier through its own N content directly or as N-improver by increasing N retention after fertilizer application (Randolph et al. 2017; Mia et al. 2019). In general, biochar application mainly acts as N-improver in the soil system (Dai et al. 2020). Biochar properties, soil pH, fertilizer type, etc., regulate the soil microbial functioning related to the N-transformations such as N-fixation, nitrification, and denitrification processes (Panahi et al. 2020). Specifically, surface (e.g., surface area and acidic functional groups) and physicochemical (e.g., pH and CEC) properties of biochar predominantly regulate the N cycling in the soil (Nguyen et al. 2017). Biochar adsorbs the inorganic-N species (e.g., NH_4^+–N and NO_3^-–N) on its surface and release them slowly in the soil system, thus acting as slow-release fertilizers (Haider et al. 2017). In addition, biochar application induces the N-transforming microbial communities which further determine the soil N cycling (Nguyen et al.

2017; Zheng et al. 2013a). However, negatively charged biochar surfaces showed greater affinity to the NH_4^+–N as compared to the NO_3^-–N in soil system (Zheng et al. 2013a). Engineered biochar showed improved efficiency for N-transformations in the soil. For example, biochar prepared after chemical and ultrasonication treatment showed better N (particularly, NH_4^+–N) adsorption capacity as compared to the pristine biochar (Chen et al. 2017; Feng et al. 2019). Steam-activated biochar showed increased retention of NO_3^-–N as compared to pristine biochar (Borchard et al. 2012). The $MgCl_2$-modified biochar release soil nutrients (e.g., NH_4^+–N and NO_3^-–N) more slowly as compared to the pristine biochar and chemical fertilizers (Khajavi-Shojaei et al. 2020). High porosity and surface area with sufficient (O-containing) functional groups and improved soil physicochemical properties are responsible for increased adsorption capacity of nutrients released in the biochar applied soil systems (Panahi et al. 2020; Khajavi-Shojaei et al. 2020). The C/N ratios of soil and biochar and inorganic-N species availability in the soils determine overall N dynamics (Nguyen et al. 2017). For example, application of high (>20) C/N ratio biochar resulted in N-immobilization, whereas low (<20) C/N ratio resulted in N-mineralization (Jeffery et al. 2017; Nguyen et al. 2017; Lehmann and Joseph 2021). Thus, C/N ratio (ranging between 7 and 400) of biochar (and soil) should be taken into consideration, as it regulates the N-availability via mineralization and immobilization processes resulting in N-limitation and poor plant performance. To overcome the challenges related to N-availability, early application of biochar (one month before crop cultivation) and/or along with organic N-sources has been suggested (Dai et al. 2020; Panahi et al. 2020).

Improvement in soil physicochemical properties has been reported to improve P-availability and use-efficiency by plants (Qayyum et al. 2017; Bornø et al. 2018). Biochar application has been reported to improve the soil P-retention and availability (Copley et al. 2015; Glaser and Lehr 2019). Improvement in soil pH by biochar addition is mainly responsible for increased P-availability in soil (Panahi et al. 2020). Like P, biochar application to soil is also reported to improve the soil K-availability (Dai et al. 2020; Panahi et al. 2020). As mentioned earlier, biochar derived from biosolids (e.g., animal manure, poultry wastes, and sewage sludge) has more potential to improve soil P- and K-availability as compared to the lignocellulosic biochar (Zheng et al. 2013b; Igalavithana et al. 2016). For example, better P-availability was observed in neutral and acidic soils, whereas less or no improvement in P-availability was observed in alkaline soils after pristine biochar application (Glaser and Lehr 2019). Application of engineered biochar may help in improving P-availability in alkaline soils (Qayyum et al. 2017). For example, Mg- and Al-modified biochar showed high P adsorption potential which can be utilized as slow-release fertilizer (Wang et al. 2017). Addition of inorganic catalysts such as clinoptilolite, bentonite, and K_3PO_4 during the pyrolysis of biomass improves the physicochemical properties of biochar and their sorption capacity for the available nutrients (Mohamed et al. 2016a). Similarly, acidified biochar application also improved the P-availability in alkaline soils (Takaya et al. 2016; Qayyum et al. 2017). However, acidification of biochar should be adequately done, as higher acidification may not result in improving P-availability (Qayyum et al. 2017). Nanobiochar or MgO-biochar nanocomposites

produced by pyrolyzing anaerobically digested or $MgCl_2$-pretreated lignocellulosic biomass showed considerably high P-sorption capacity as compared to other C-based adsorbents (Zhang et al. 2012; Yao et al. 2013). Moreover, addition of P-laden engineered biochar improved soil moisture, pH, SOM content, and available P content of soil, thus, enhances the soil fertility (Chen et al. 2018).

In addition to the effects on major soil nutrient availability, biochar application also affects the micronutrient (e.g., Fe and Mn) availability in soil matrix by several mechanisms (Das et al. 2020). For example, decrease in pH after biochar amendment in highly alkaline soils results in increased availability of Fe and Mn (Masto et al. 2013). Moreover, excess availability of K in soil after biochar addition has been reported to interfere with the uptake of Mg and Ca by plants, particularly in presence of chemical fertilizers (Das and Awasthe 2018). Overall, biochar has variable impacts on different nutrients in the soil which are majorly regulated by the biochar types and properties, soil conditions, and management practices.

4.3 Soil Biological Properties

Biochar application to soil influences the soil microbial community composition and structure by modulating soil physicochemical and nutrient parameters (Panahi et al. 2020). As described earlier, biochar has a large surface area with high (micro, meso, and macro) pore spaces, high (labile and stable) C content and other nutrients on its surface (Quilliam et al. 2013). These properties provide a suitable habitat conditions (and available nutrients) for the settlement and growth of soil microfaunal diversity such as bacteria, protozoa, fungi, etc. (Lehmann et al. 2011; Gul et al. 2015). Biochar's macropores provide suitable microenvironment for microbial colonization by protecting them from desiccation, predation and other adverse environmental conditions, whereas micro- and mesopores help in storing nutrients for microbial metabolism (Gul et al. 2015; Zhu et al. 2017; Awad et al. 2018; Das et al. 2020). In addition, biochar addition to soil improves soil aeration, water content, and reduces soil compaction which further helps in luxuriant microbial growth (Laghari et al. 2016). Organic C content, pH, and WHC of the biochar considerably affect the soil biological properties such as microbial biomass, N-mineralization/immobilization, and enzyme activities (Li et al. 2019; Das et al. 2020). Similarly, improved macro- and micronutrient availability induces symbiotic and free-living N-fixing bacterial growth, depending on soil–water conditions (Biederman and Harpole 2013; Nguyen et al. 2017). The macropore spaces of the biochar favor fungal (hyphae) growth, whereas alkaline pH range favors soil bacterial growth (Panahi et al. 2020). However, presence of different phenolic and polyphenolic compounds on the biochar surfaces pose negative effects on soil microbial growth (Das et al. 2020). Thus, the impact of biochar on soil biological diversity mainly depends on the soil and biochar properties and application rates.

Various extracellular and intracellular enzymes released from the soil microorganisms play significant role in different biochemical transformation processes

(Panahi et al. 2020). Biochar addition to soil has variable impacts on soil enzyme activities. Biochar application could induce the α-glucosidase, β-glucosidase, β-D-cellobiosidase, aminopeptidase, N-acetyl-β-glucosaminidase, and alkaline phosphatase enzyme activities which are involved in nutrient cycling in the soil matrix (Wang et al. 2015). Improved microenvironmental conditions after biochar application are the primary cause for improved enzyme activities (Nie et al. 2018). Biochar produced from animal manure increased the alkaline phosphomonoesterage activity, whereas reducing the acid phosphomonoesterase activity in different fine-textured soils (Batool et al. 2015). High surface area and surface functional groups bind the extracellular enzymes, thus interfere with their activities (Das et al. 2020). Teutscherova et al. (2018) reported decrease in some hydrolytic enzymes (viz. β-glucosidase, β-glucosaminidase, and phosphatase) activities after biochar application in the Acrisol, possibly due to inactivation of these enzymes after adsorption on the biochar surfaces (Panahi et al. 2020). In a pot experiment study, pristine biochar has been reported to increase the soil catalase and urease activity, whereas Fe-modified biochar decreased these enzyme activities (Wen et al. 2021). Changes in soil pH conditions and different ion/nutrient availability after different biochar application might be the primary cause of variation in enzyme activities (Wen et al. 2021). Moreover, biochar prepared at different pyrolysis temperatures also showed variable impacts on soil enzyme activities (Steinbeiss et al. 2009). Thus, depending on the biochar and soil conditions, the extent of different extracellular and intracellular enzyme activities may vary.

4.4 Crop Responses to Engineered Biochar Application

In general, improvement in soil physicochemical, nutrient, and biological properties (e.g., pH, CEC, hydraulic properties, nutrient availability, and use-efficiency) after biochar application enhances the nutrient uptake and plant growth conditions which further improve the crop productivity, in general (Das and Avasthe 2015; Dai et al. 2020; Panahi et al. 2020; Qayyum et al. 2017). However, crop responses to biochar application may be regulated by different factors such as biochar properties, soil conditions, climatic conditions, and experimental types (Hussain et al. 2017; Dai et al. 2020). Application of P-laden biochar considerably improved the plant growth (height and weight), ecophysiological (water use-efficiency) characteristics and productivity (Chen et al. 2018; Das et al. 2020). Biochar application (having high ash/mineral content) to sandy soils improve the plant productivity (Dai et al. 2020). Improvement in soil pH after biochar application is considered as the most important factor influencing the plant growth owing to the direct impact of pH on soil microbial functioning and nutrient cycling (Dai et al. 2017). Application of acid-treated biochar to the alkaline soils may improve crop productivity by modulating soil pH conditions (Sadegh-Zadeh et al. 2018). Fe-modified biochar application in continuously flooded soils showed more grain production as compared to alternative

flooded system (Wen et al. 2021). Application of MgCl$_2$-modified biochar as slow-release fertilizer to maize crop grown in a pot experiment increased plant growth (height, shoot and root dry weight), eco-physiological (chlorophyll content and leaf area) properties, and plant N-use-efficiency (Khajavi-Shojaei et al. 2020). However, there is no conclusive remark on the impacts of engineered biochar on plant growth due to lack of understanding of the mechanisms operating in soil–plant system after biochar application to soils (Xiao et al. 2019; He et al. 2020; Akhil et al. 2021).

5 Limitations Related to Engineered Biochar Use as Soil Fertilizer

Although (engineered-)biochar has multifaceted application potential for environmental management, its application as soil fertilizer directly as well as after contaminant adsorption should be considered based on the following risk assessments:

1. Application of engineered biochar produced from contaminant-loaded raw material may lead to the distribution and movement of tiny contaminants and particles (e.g., nanobiochar) in the water and air systems (Ramanayaka et al. 2020; Huang et al. 2020)
2. Since the particle size of engineered biochar is very small (e.g., biochar-nanocomposite), their application to soil may result in bioaccumulation or biomagnification after some time (Panahi et al. 2020)
3. Application of nanobiochar as soil fertilizer may induce cytotoxic, genotoxic, or ecotoxic effects to crop plants (Cifuentes et al. 2010)
4. Nanobiochar showed higher activity in alkaline medium; thus, presence of nanobiochar to the water system may influence the humans and animals at different (e.g., ingestion, dermal contact to cell and tissue damage) levels (Chen et al. 2010; Ma et al. 2019)

6 Conclusion and Future Prospects

Biochar engineering leads to the enhanced surface area and pore structure, and nutrient retention capacity. Application of engineered biochar with improved properties modulates different soil properties such as pH, CEC, soil nutrient availability, and microbial activities (and enzyme activities) which resulted in improvement of soil fertility and crop productivity. Engineered biochar showed better potential to be used as soil ameliorant as compared to the pristine biochar. Surface area, pore spaces, surface functional groups, pH, and CEC of the biochar play a major role in determining their potential as soil fertilizer. However, most of the studies are limited to lab or pot scales. Further research should focus on:

1. Combined application of engineered biochar with other soil additives such as organic manure for further improvement in soil fertility and crop performance
2. Impact of engineered biochar application on changes in soil biological (micro- and macrofaunal) diversity and activity for achieving the sustainability in agriculture
3. Risks associated with engineered biochar application to soil should be thoroughly studied before its wider application to plot and field scales

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Engineered Biochar: Sink and Sequestration of Carbon

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Abstract The concentration of carbon dioxide in the atmosphere have been increasing mainly due to large scale emissions from anthropogenic activities, causing global warming and climate change. The carbon emissions can be reduced by capturing and storing it for long term in soil, oceans, vegetation (afforestation), and geological formations, which is broadly termed as carbon sequestration. The conversion of waste biomass into biochar (contains recalcitrant carbon) through pyrolysis and its application for soil carbon sequestration is documented in the prior art. Biochar utilization as a sorbent for carbon dioxide capture from sources of emissions is also widely researched method. However, the pristine biochar sorbent effectiveness is limited due to poor textural and surface characteristics. Therefore, recent research studies investigated the development of engineered biochar sorbents with better textural and surface characteristics such as high surface area, pore volume, and enrichment of nitrogen related and hydroxyl functional groups. The present chapter outlines the performance of engineered biochar sorbents produced through various physical and chemical modification methods and raw material for carbon dioxide capture. Limitations and future prospects of engineered biochar production and application for carbon sequestration has also been provided to facilitate the research advancement.

Keywords Engineered biochar · Carbon capture · Adsorption capacity · Soil carbon sequestration

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1 Introduction

Carbon dioxide (CO_2) is a major greenhouse gas and it negatively affects the global climate due to global warming. The concentration of CO_2 in atmosphere has shown an unprecedented surge in last few centuries. The atmospheric CO_2 concentration that happened to be 287 ppm in year 1750 has increased to level of 415 ppm in present times (Marescaux et al. 2018). It has been predicted by the International Panel on Climate Change (IPCC) to surpass 570 ppm by year 2100, which can lead to increase in global mean surface temperature by 1.9 °C (IPCC 2014). This would drastically affect the global environment, causing droughts, changes in rainfall patterns, extreme heat events, glaciers melting, and rising sea levels. Every year plants absorb and capture a major quantity of carbon from the atmosphere, but when these plants die the carbon is returned back to the atmosphere, resulting in little net change. Burning of the residual biomass from these plants (mostly from agriculture and plantations) also add carbon dioxide directly to the atmosphere. For example, burning of agricultural wastes from rice and wheat in Punjab, India contributes approximately 140 MT of CO_2 to atmosphere annually (Punia et al. 2008). Therefore, it is necessary to control atmospheric carbon dioxides levels through different carbon sequestration methods such as utilization of green sustainable technologies for reducing the emissions, capture and long-term storage of carbon in soil, oceans, vegetation (afforestation), and geological formations. Crop rotation, reduced tillage, conversion to perennial grass and crops; and manure-compost addition are some of the methods for soil carbon sequestration.

Recently, conversion of biomass (e.g., agro-residues) into biochar through pyrolysis and its application in soil has been studied for soil carbon sequestration. In contrast to biomass that due to decay and burning releases carbon in the environment, carbon present in biochar is more recalcitrant and hence can be stored for long term in soil. Soil carbon sequestration through addition of biochar has proven its worth as a mitigation strategy to capture and store atmospheric carbon. Biochar is biologically unavailable and sequesters fixed carbon in the soil. Different studies have shown that the application of biochar in soil leads to significant reduction in emission of GHGs such as CO_2, N_2O, and CH_4 (Jia et al. 2012; Sun et al. 2014). Thus, it provides a tool to absorb net carbon from the atmosphere and hence serves as a sink for carbon.

Biochar has also been investigated as sorbents to capture CO_2 prior to its emissions from different sources i.e., pre-combustion, post-combustion and oxy-fuel combustion capture systems (Shafawi et al. 2021). It is also eco-friendly as it is produced from waste biomass, which can be easily procured. Due to sufficient availability of raw material, biochar is almost ten times cheaper than other CO_2 adsorbents. Moreover, biochar is stable with an average carbon half-life of about 105 years (Punia et al. 2008). Due to its potentially large storage capacity when mixed in soil, it has been considered as a major carbon storage method for mitigating climate change (Verma et al. 2014). It has been reported that up to 12% of anthropogenic CO_2 emissions can be reduced by the storage of biochar in soil (Lehmann et al. 2006). Biochar

produced from different raw materials such as sugarcane bagasse and hickory wood raw material etc. showed potential adsorbent for CO_2 capture (Creamer and Gao 2016). The International Biochar Initiative (IBI) has advised the technical advisory body of the United Nations Framework Convention on Climate Change (UNFCC) to incorporate biochar within the work program for mitigation (refers to addressing causes of climate change) in the agricultural sector (IBI 2013).

The limitation of using pristine biochar sorbents is its low CO_2 adsorption capacity and capture compared to other adsorbents such as zeolites, hydrotalcite, activated carbons, and metal–organic frameworks (Choi et al. 2009; Shafawi et al. 2021). This is mainly due to the low surface area, and micropore volume. Hence, to maximize the CO_2 capture capacity, recent research studies are focused on the development of engineered biochar with better textural properties (high surface area and pore volume) and surface chemistry through different physical and chemical modification methods. These engineered biochar are produced by modification of simple/pristine biochar through different physical, chemical and biological methods (Wang et al. 2018). The present chapter outlines the performance of engineered biochar adsorbents produced through various physical and chemical modification methods and raw material for carbon dioxide capture. Limitations and future prospects of engineered biochar production and application for carbon sequestration have also been provided to facilitate the research advancement.

2 Relevant Characteristics of Biochar for CO_2 Capture and Sequestration

The characteristics of biochar depend on the type of raw material and the thermochemical production conditions. Potential of biochar for carbon sequestration predominantly depends on its specific characteristics such as the surface area, pore size, pore volume, presence of surface functional groups, presence of alkali and alkali earth metals, hydrophobicity, polarity and aromaticity. These aspects are important and considered for the production of engineered biochar with improved characteristics and better capacity for CO_2 capture and sequestration (Shafawi et al. 2021).

2.1 Physical Properties

The adsorption of CO_2 occurs through van der waals forces between gas molecules and the biochar that varied based on the specific surface area, pore size, and pore volume of the biochar (Sungyup et al. 2019). The specific surface area of biochar can be defined as the ratio of its total surface area and total mass of the biochar (You et al. 2017). A larger surface area provides more sites for physical adsorption that increases

the CO_2 adsorption capacity (Creamer and Gao 2016). The specific surface area of biochar mostly depends on the raw material type and properties. Biochar produced from plant materials (e.g., oak wood, and pine needles) exhibit higher surface areas than the biochar produced from animal manure and biosolid waste (Ahmad et al. 2014; Liu et al. 2018). The surface area of the biochar also increases with increasing pyrolysis temperature and residence time, possibly because of the release of volatile matter, which increases the pore volume (Ahmad et al. 2014).

The pore volume and pore size can affect the CO_2 adsorption capacity of biochar. The CO_2 capture capacity of porous carbon strongly depends on the presence of micropores with a diameter of less than 1 nm (Zhang et al. 2013; Sevilla and Fuertes 2012). However, studies have revealed that pores with a diameter of 0.5 nm or less contribute more to CO_2 adsorption at low partial pressures, whereas pores with a diameter smaller than 0.8 nm make a higher contribution to CO_2 uptake at 1 bar pressure (Chiang and Juang 2017). The micropore and total pore volume of the biochar generally increases, when the temperature increases from 400 to 500 °C and a reverse trend is observed when the temperature goes above 500 °C (Dissanayake et al. 2019).

2.2 Chemical Properties

The adsorption of CO_2 onto the biochar surface is also affected by the chemical properties of the biochar such as alkalinity, mineral composition, presence of surface functional groups, hydrophobicity, and non-polarity (Xu et al. 2016; Zhang et al. 2013). The CO_2 adsorption capacity of biochar can be enhanced by increasing the alkalinity of the biochar surface (Lahijani et al. 2018). Basic surface functional groups are also important for the CO_2 adsorption by biochar because of their contribution to surface basicity, which enhances the affinity of the biochar for CO_2 (Shafeeyan et al. 2012). The presence of alkali and alkaline earth metals (e.g., Na, K, Ca, Mg, and Li) enhances the formation of basic sites with a strong affinity for CO_2 that itself is a Lewis acid (Xu et al. 2016). The CO_2 adsorption capacity may be reduced under humid environments due to the high affinity for H_2O (Nugent et al. 2013; Gao et al. 2015). Biochar with hydrophobic and non-polar characteristics may facilitate the CO_2 adsorption capacity by limiting the competition of H_2O molecules.

3 Engineered Biochar Potential for Carbon Capture and Sequestration

The CO_2 adsorption capacity of pristine biochar is generally low, but engineered biochar (Table 1) produced through different methods has enhanced CO_2 adsorption capacity. Therefore, the engineered biochar application could have more potential

Table 1 Engineered biochar (BC) capacity for CO_2 capture and sequestration

Adsorbent	Raw material	Pyrolysis temp (°C)	Biochar modification	CO_2 adsorption capacity (mg/g)	References
Nitrogen doped BC	Chicken manure	450	Treatment of biochar with NH_3 and HNO_3, reaction with sodium-L-gulopyranuronate to form beads	446.6	Nguyen and Lee (2016)
Nitrogen enriched BC	Cotton stalk	600	Treatment with CO_2 and NH_3 at 900 °C	72–96	Zhang et al. (2014)
Metal incorporated BC	Walnut shell	900	Impregnation of metal nitrate salts like sodium nitrate, magnesium nitrate hexahydrate	82.04	Lahijani et al. (2018)
Activated BC	Whitewood	500	Physical activation through steam and CO_2. Chemical activation using KOH	59–78	Shahkarami et al. (2015)
Nitrogen doped microporous BC	Soybean straw	500	Thermal treatment with CO_2 and NH_3 at 900 °C	63–80	Zhang et al. (2016a, b)
Activated char	Almond shell	600	Conventional activation using CO_2 at 750 °C for 2 h	118.83	Plaza et al. (2010)
Activated BC	Olive stone, Almond shell	600	Conventional physical activation using CO_2 at different temperature	425.04–604.56	Plaza et al. (2011)
Ammonia modified BC	Olive stone, Almond shell	600	Treatment of biochars with ammonia at 800 °C for 2 h	232.76–312.4	Plaza et al. (2011)
Activated BC	Olive stone, Almond shell	600	Single step activation using CO_2 at 750–800 °C for 2 h	118.83–136.43	Gonzalez et al. (2013)
Steam modified BC	Cellulose fiber	600	Steam assisted pyrolysis resulting into direct activation	102.54	Gargiulo et al. (2018)
Activated carbon	Palm kernel shell	600	Direct activation using CO_2 at 950 °C for 60–120 min	110.03	Rashidi and Yusup (2020)
Activated carbon	Date seed	800	CO_2 activation at 900 °C for 1 h	141.14	Ogungbenro et al. (2018)
Waste based hydrochar	Olive mill	350	Hydrothermal carbonization followed by CO_2 activation at 850 °C for 1 h	129.61	Gonzalez and Manya (2020)
Activated BC	Vine shoot	600	Physical activation using CO_2 at 800 °C for 1 h	117.51	Manya et al. (2020)

Table 1 (continued)

Adsorbent	Raw material	Pyrolysis temp (°C)	Biochar modification	CO_2 adsorption capacity (mg/g)	References
Activated BC	Wheat straw	500	Physical activation using CO_2 at 800 °C for 1 h	107.38	Manya et al., (2020)
Sustainable porous carbon	Eucalyptus sawdust	230–250	Hydrothermal carbonization followed by activation using KOH under N_2 at 600 °C for 1 h	212.00	Sevilla and Fuertes (2011)
Microporous carbon	Palm shell	600	Activation using KOH under N_2 at 850 °C for 1 h	193.64	Ello et al. (2013)
Hetero-atom doped porous carbon (O-doped, N-doped)	Lignin	300	Hydrothermal carbonization followed by KOH and adenine treatment at 90 °C for 10 h with activation under N_2 at 700 °C for 1 h	211.25	Demir et al. (2018)
Microporous carbon	Cashew nutshell	500	Chemical activation using K_2CO_3 treatment followed drying in oven at 105°C for 24 h	273.60	Garg and Das (2020)
Biochar derived carbon	Coffee grounds	400	Ammoxidation using melamine and physical activation using KOH at 400–600 °C for 2 h	117.51	Liu and Huang (2018)
Biomass based carbon	Black locust	650	Activation using KOH under N_2 at 830 °C for 1 h. Added treatment with ammonia in solution	222.25	Zhang et al. (2016a, b)
Steam activated BC	Pine sawdust	550	Purging steam at 550 °C in biochar for 1 h	32.13	Igalavithana et al. (2020)
Activated biochar	Coconut shell	400	Catalytic pyrolysis followed by activation using KOH treatment under N_2 at 700 °C for 3 h	198.05	Du et al. (2020)
Porous carbon	Rice husk	400	KOH impregnation of rice husk before pyrolysis followed by activation using KOH under N_2 at 780 °C for 30 min	183.08	Li et al. (2015)
Biomass derived activated carbon	Camellia japonica	250	Hydrothermal carbonization followed by activation using KOH and thermal activation under N_2 at 700 °C for 1 h	220.05	Coromina et al. (2015)
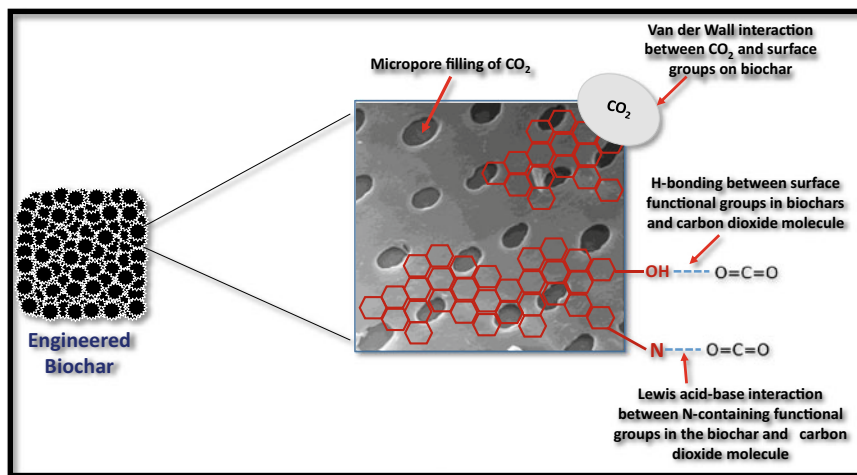
Fig. 1 Mechanism for CO_2 adsorption by engineered biochar

for climate change mitigation (Wang et al. 2012). Modification of biochar can be done by various processes such as use of activation conditioning, precursors and additives by physical–chemical modification and impregnation with elements. Many studies suggested that the addition of basic nitrogen functional groups would enhance the basic sites on biochar and increases the uptake of acidic CO_2 (Nguyen and Lee 2016). The CO_2 adsorption potential can be increased with nitrogen doping, amine functionalization and alkaline metal/metal oxide (i.e., Mg, Al, Fe, Ni, Na) impregnation into biochar (Shafawi et al. 2021).

The CO_2 capture by the biochar sorbent involves different mechanisms (illustrated in Fig. 1) i.e., micropore filling, hydrogen bonding, Van der Waals attractions, and acid–base interactions between CO_2 and surface functional groups of the biochar. The type of mechanism for CO_2 capture by biochar is very much dependent on its physical, structure and surface chemistry. Micropore filling effect has been suggested as the major physisorption process behind the CO_2 adsorption by the biochar, both in pristine and engineered forms (Klasson et al. 2015). Size of the pores is an important factor that drives the sorption process. Micropores of size—0.3–0.8 nm are considered most suitable for CO_2 adsorption and micropores with size below 0.5 nm are considered most effective for carbon capture (Igalavithana et al. 2020). Generally, biochar has large surface area due to dominant porous structure. Engineered biochar with enhanced porosity can be produced with different modification processes including physical (Shahkarami et al. 2015) and chemical activation (Zhang et al. 2016a, b) along with additional thermal treatment. These methods increase the micropore volume and overall surface area, which results into better CO_2 adsorption (Liu et al. 2020).

Carbon capture by engineered biochar is also assisted by specific functional groups bearing oxygen i.e., –OH (hydroxyl) and –COOH (carboxyl). Due to difference in

electronegativity between O and H attached to it, H tends to attract electronegative O, which results in hydrogen bonding i.e., O–H–O=C=O (Liu and Wilcox 2012; Liu et al. 2013a, b; Xing et al. 2014; Jeyasubramanian et al. 2021). Though this is considered as a weak hydrogen bond compared to H-bond linked with more electronegative atoms (F, O and N), but they found effective in binding CO_2. The CO_2 adsorption through H-bonding is limited by presence of other gases, particularly water vapor as H_2O that is more polar than CO_2 (Liu and Wilcox 2012). Biochar mainly contains condensed aromatic structures formed during pyrolysis of cellulose and hemicellulose (Tomczyk et al. 2020). These aromatic structures are very large and they tend to facilitate CO_2 adsorption onto their surface through Van der Waals attraction (Shafeeyan et al. 2012; Igalavithana et al. 2020).

One of the most important mechanisms that mediate CO_2 adsorption onto engineered biochar involves the interaction between the basic N-containing functional groups and acidic CO_2 molecules, which can be also considered as a Lewis acid–base reaction (Plaza et al. 2010). As most of the N-containing functional groups are lost due to pyrolysis reaction above 400 °C, therefore chemical modifications using N-precursors are required to introduce the basic N- containing functional groups (Sajjadi et al. 2019). N-containing functional groups such as pyridone, pyridine and pyrrole highly affect CO_2 adsorption (Liu et al. 2013a, b; Lim et al. 2016). Among them, pyridone and pyrrole are also able to develop H-bond with CO_2 as they have hydrogen attached to N (electronegative). As per the Lewis acid–base interaction, N-atom in given functional group has a lone pair of electrons which makes it electron-rich and thus mediates binding of acidic CO_2 to biochar surface (Liu et al. 2013a, b; Chiang et al. 2019). The pyridone group relatively bond strongly with CO_2 due to the H-bonding and Lewis acid–base reaction combined (Lim et al. 2016). It was followed by Pyridinic-N and Pyrrole-N (H-bonding and Lewis acid–base interaction was weakest). Earlier experimental studies (Liu et al. 2013a, b; Fan et al. 2013; Chiang et al. 2019) also reported that biochar with pyridone, pyridine and pyrrole functional groups have strong interaction with CO_2.

Engineered biochar with higher carbon retention and sequestration are produced by different modification methods. Rock phosphate blending with maize residue produced biochar composite with improved retention of carbon up to 43% (Tumbure et al. 2020). Similarly, co-pyrolyzing rock phosphate with rape straw also increased carbon retention up to 27.5% (Gao et al. 2019). Biomass pretreated with potassium salt (KOH) produces engineered biochar with 45% higher carbon sequestration potential (Masek et al. 2019). If the carbon composition of biochar is $\geq 60–80\%$, then it is equivalent to $\geq 2.20–2.94$ CO_2 sequestrated ton^{-1} biochar (Verma et al. 2014). The CO_2 emission can be reduced by 12–84% if biochar is added into the soil (Gaunt and Lehmann 2007). When biomass is converted into biochar and is applied to soil, C can be stored for more than 1000 years (Kuzyakov et al. 2014). As per the research study of Purakayastha et al. (2015), total soil carbon at end of the year of carbon mineralization increased from 41 to 65% in biochar treated Inceptisol of Delhi. It was predicted that in India about 309 million tons of biochar, which is equivalent to 154 mt of biochar carbon could be produced yearly. This might offset about 50% of carbon emissions (i.e., 292 Tg C yr^{-1}) (Lal 2005). The soil application of biochar

can sequester about 1 Pg C yr^{-1} (Sohi et al. 2009; Gaunt and Lehmann 2007). Woolf et al. (2010) evaluated that maximum sustainable potential of biochar in the world is 2.27 PgC year^{-1}. Overall, biochar application in soil may remain for centuries and sequester carbon for long term.

4 Limitations

Existing research on engineered biochar mostly explored physical and chemical modifications methods, but the underlying mechanisms are rarely studied in detail. The diverse characteristics of engineered biochar due to use of different raw materials and production methods also pose serious challenge to compare and identify between them the best one with highest CO_2 sorption capacity. There is lack of information about the life cycle, regeneration capacity, and reusability of the exhausted engineered biochar sorbents of CO_2. Pilot and large-scale production of engineered biochar for carbon capture are also not studied. Application of engineered biochar in soil is not yet investigated, and its effectiveness in reducing carbon emissions and sequestration is not known. In addition, the long-term stability of the carbon sequestered by the engineered biochar in soils is also not researched in the prior art, which is crucial to know the practical feasibility of engineered biochar compared to pristine biochar. The economic benefits of carbon sequestration by engineered biochar through carbon emissions trading has also not yet evaluated and ascertained.

5 Conclusions and Future Prospects

The CO_2 emissions can be prevented by the application of engineered biochar sorbents prior to its release in the atmosphere. The engineered biochar exhibited higher CO_2 sorption capacity because of suitable characteristics such as surface functionalities, high surface area and pore volume. Engineered biochar prepared by surface functionalization with nitrogen related and hydroxyl groups can be suitable for that. However, research studies emphasize on the tailoring of textural and surface chemical properties of engineered biochar to further enhance the CO_2 uptake capacity. Future research on engineered biochar can be directed toward the highly selective uptake of CO_2 from real gases mixture emissions from different industrial sources. Methods for regeneration of exhausted engineered biochar need to be researched. The application of exhausted engineered biochar sorbent in land, and the release and stability of captured CO_2 from it under real environmental conditions need to be investigated. Future research should also extensively investigate the impact of engineered biochar on greenhouse emissions, along with physico-chemical and biological properties of soil. In addition, it is also very important to study the influence of different soil conditions and biota specifically microorganisms on the

recalcitrant carbon of engineered biochar to know its long-term carbon sequestration potential.

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Engineered Biochar as Gas Adsorbent

Duy Anh Khuong and Hong Nam Nguyen

Abstract From the 1100 s B.C to the present, biochar and adsorption technologies have been constantly evolving with a remarkable history. Biochar as a gas adsorbent is a biomass-derived material that has satisfactory properties for gas adsorption application. Since then, the mechanism, kinetics, and thermodynamics of gas adsorption have been investigated with the development of a series of novel models. Gas adsorption models are evaluated based on experimental adsorption isotherm, from which surface parameters of biochar can be derived. The surface and physicochemical characteristics of engineered biochar are ultimately determined by the type of the raw material and methods of char making including carbonization, physical activation, and chemical modification. Morphology, pH, total surface area, pore-volume, porosity, and surface functional groups are decisive factors for the gas adsorption capacity. Until now, biochar for gas adsorption is engineered for universal application to some gases such as CO_2, H_2S, CH_4, and N_2O, which are the main components of greenhouse gas emissions. Previous studies have shown the high efficiency of using engineered biochar as a gas adsorbent. However, it is still undeniable that this type of material still has certain limitations related to technical, economical, and environmental problems due to the knowledge gaps of mechanism, large-scale system, or regeneration process. Thus, in response to the current industrialization situation, it is mandatory to develop modern appropriate techniques to actualize the use of biochar as a gas adsorbent in the market.

Keywords Gas · Adsorption · Biochar · Modification · Structure · Adsorbent

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1   Introduction

1.1   History of Gas Adsorption

Gas adsorption is a surface mass transfer process, in which the gas molecules transfer and attach to the liquid or solid surfaces by physical or chemical forces (Artioli 2008). In reality, the natural adsorption phenomenon was coined and studied very early, with the first experiment being carried out by Gideon since 1100 B.C. century (Giles 1962). As reported, dew, otherwise known as the humidity of the air, was tested to be adsorbed on the fleece of wool fibers. Up to the fifteenth century, an architect named L. B. Alberti explained well about the adsorption of water, but it was not until 1773 that C. Scheele simultaneously J. Priestley and A. Fontana started to find a way to measure adsorption capacity systematically (Robens 1994).

The development of research in sorptometry technology has gone through a long history from 1100 BC to the end of the 20th century (Table 1), and is still ongoing at the present (Robens 1994; Kodama et al. 1987; Robens and Jayaweera 2014). Various methods to survey the adsorption have also been studied, such as hygrometry, thermogravimetry, calorimetry, thermoporometry, etc. However, sorptometry is the most preferred method because it gives high accuracy in the surface properties and adsorption capacity of a solid substance. Therefore, this chapter will emphasize the investigation of biochar as a gas adsorbent by sorptometry (gas adsorption apparatus).

1.2   Origin of Biochar Applications

Biochar, originally from charcoal, has been a commonly used material since ancient times. Despite the unknown first person who made charcoal, there are pieces of evidence as arrowheads fixed to their shaft with wood tar from the charring process, that were in use even as far back as 6000 years ago (Emrich 1985). The uses of charcoal are recorded to recover iron and metals from ores in Europe around 1100 BC, or for several different purposes in China since the Bronze Age (Chen et al. 2019). Over 2000 years ago, Amazonians in Brazil perhaps utilized biochar to fertilize their nutrient-poor tropical soils to feed a great agricultural civilization (King 2013). Through a lengthy historical period, modernization has led to the innovation of biochar applications from small-scale to industrial scale.

1.3   Adsorbent—Application of Adsorption Technique on Biochar

Over the decades, with the target to remove contaminants from gases economically and effectively, many kinds of adsorbents have been invented which are divided into

Table 1 Sorptometry development history until the 20th century

Investigation time	Method/Discovery	Inventor/Scientists
Around 1100 BC	First awareness of the adsorption (dew on fiber)	Gideon
1450	First gravimetric adsorption instrument	German cardinal Nicolaus Cusanus
End of 15th century	Inclination balances for atmospheric humidity measurement	Leonardo da Vinci
1773–1777	First recorded scientific adsorption measurements of water vapor (humid air) Used mercury to introduce a glowing charcoal piece into a reversed glass cylinder for adsorption measurement	Carl Scheele Priestley, Abbé Fontana
Around 18th century	Thin molecular layers on surfaces	Benjamin Franklin
1833	Thermogravimetry with 39 thermobalances for measuring water content of Chinese silk	Talabot
1881	Differ "adsorption at a surface" from "absorption in the interior"	Kayser, Du Bois Reymond
1886	First adsorption balance	Warburb and Ihmory
End of 19th century	First study about gas adsorption isotherms	Mitcherlich, Chappuis, Kayser
1912	First vacuum microbalance with electromagnetic compensation	Emich
1915	Thermobalance	Honda
1984	Measure standard weights in vacuum (high accuracy)	Japanese Researchers
1916–1918	Modern work on adsorption, Langmuir model	Langmuir
1938	BET theory	Brunauer, Emmet, Teller
1949	Application of gravimetric apparatus for surface area and pores investigation	van Nostrand
20th century	Volumetric apparatus (sorptometer) for simple gas, nitrogen adsorption isotherm	Chappuis, Emmett, Nelson and Eggertsen
1970–1999	The adsorption of gas (liquid-ike adsorbate) is calculated as a function of gas pressure at a fixed temperature	Sing, Gregg, Dabrowski, Rouquerol
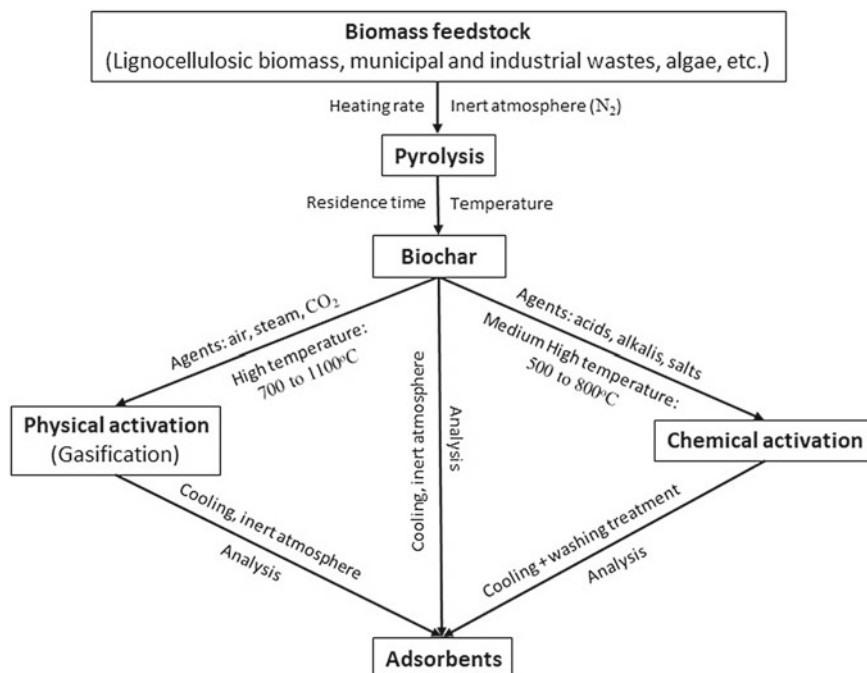
Fig. 1 The schematic of the procedure to make gas adsorbents from biomass

three main groups: carbon-based sorbents, silica-based sorbents, and metal–organic frameworks (MOF) (Bamdad et al. 2018). Nevertheless, carbon-based one, which is derived from biochar, is the most common due to its easy-to-find raw material, low cost, high efficiency and meets the demand for renewable materials (Fig. 1).

2   Principle of the Gas Sorption

2.1   Mechanism of Gas Adsorption and Desorption Processes

Adsorption is a phenomenon where gas molecules assemble on the adsorbent surface based on the mechanism of surface-based exothermic.

Otherwise, desorption is a reverse process of adsorption, in which molecules of the adsorbate are released from the adsorbent surface. The scheme of the adsorption/desorption process is represented in Fig. 2a. Depending on the interactions between the molecules of the gas compound and the surface of the adsorbent, adsorption could be defined as two types: "physisorption" and "chemisorption" (Rouquerol

Fig. 2 **a** The schematic describing the adsorption and desorption processes. **b** The illustration about two ways of adsorption (physical and chemical)
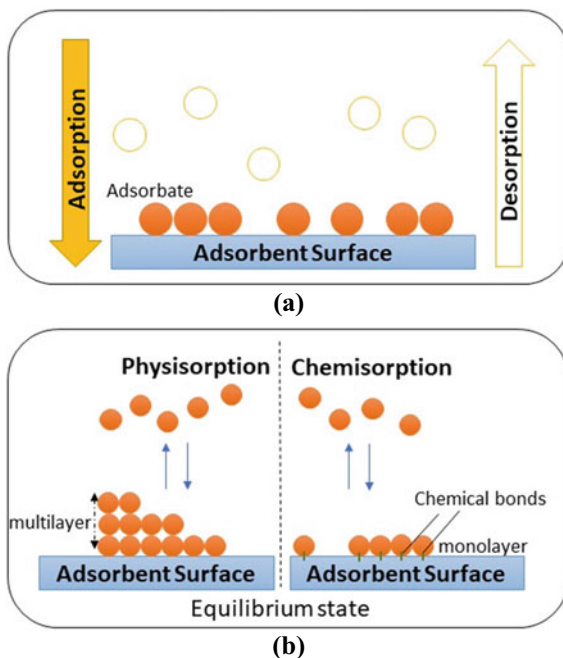
et al. 1999a). Physisorption or physical adsorption occurs by the physical weak forces including electrostatic interactions and Vander Waals force.

Physisorption can happen quickly, reversibly with no activation energy at low temperature, which usually forms multilayers of adsorbate molecules on the adsorbent surface. Meanwhile, chemisorption or chemical adsorption takes place slowly by the covalent bonds between the surface and molecules, irreversible with activation energy and high temperature required. It specifically involves the formation of the monolayer on the adsorbent surface (Dąbrowski 2001). Figure 2b shows the schematic explanation of the adsorption/desorption process and multi/monolayer of adsorbate molecules in the physical and chemical adsorption.

2.2 Isotherm of Gas Adsorption

International Union of Pure and Applied Chemistry (IUPAC) classified 6 types of adsorption isotherms (Fig. 3) (the gas adsorption) on the solid surface (Donohue and Aranovich 1998).

Type I is achieved from monomolecular gas adsorption on porous surfaces in a limited void volume. Meanwhile, unrestricted mono-multilayer adsorption without

Fig. 3 Different types of
adsorption isotherm
classified by IUPAC
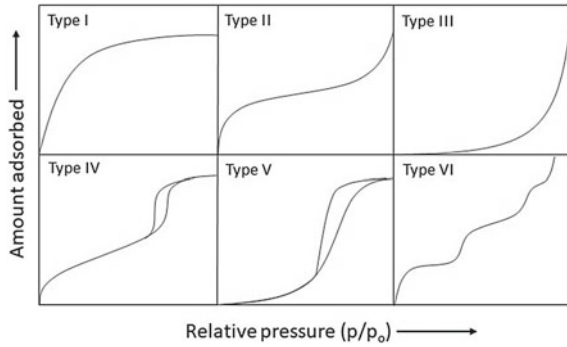
any saturation point is illustrated by the type II isotherm. It expresses the gas adsorption in the macroporous adsorbents. Type III isotherm indicates the weak interactions between adsorbent and gaseous adsorbate. Both Type II and Type III are for the nonporous or microporous adsorbent. Type IV isotherm has two parts: the first part represents mono-multilayer adsorption as Type II and the hysteresis loop is explained by capillary condensation in mesopores, which causes the progressive addition and withdrawal of adsorbate molecules on the adsorbent surface. Because Type V isotherm contains a hysteresis loop, this indicates the existence of mesopores. Type VI isotherm delineates the stepwise formation of multilayers of gas molecules on a uniform non-porous surface (Donohue and Aranovich 1998; Yahia et al. 2013).

Some popular models were invented to analyze the information about the gas–solid interface from the isotherm curves. A short explanation of these models is provided in Table 2.

2.3 Kinetics of Gas Adsorption

For a gas adsorption system, three common steps occurred during the process: (a) molecular mass transfer to the adsorbent surface, (b) internal molecular diffusion on the active sites, and finally (c) equilibrium state. In the case of uniform surfaces, the phenomenological kinetics of the sorption process is determined as the following equation (Zhdanov 2001):

$$\frac{d\theta}{dt} = k_a P - k_d \theta \tag{1}$$

where θ is the coverage, P is the sorption pressure, k_a and k_d are the rate constants representing the dependence between coverage and adsorption/desorption. The two parts of Eq. (1) $k_a P$ and $k_d \theta$ will be equal when the adsorption and desorption are at

Table 2 Description of some famous adsorption isotherm analysis models

Model	Equation	Assumptions	Reference
Langmuir	$\frac{C}{q} = \frac{1}{K_L q_{max}} + \frac{C}{q_{max}}$ C (mg L^{-1}): adsorbate molecules concentration at equilibrium state q (mg g^{-1}): the capacity of adsorbed molecules at any time q_{max} (mg g^{-1}): the maximum adsorption capacity K_L (L mg^{-1}): Langmuir constant	Adsorption at specific binding sites; all adsorption sites are similar; monolayer of molecules covers the adsorbent surface; no interaction at the gas–solid interface	(Langmuir 1918)
Freundlich	$q = K_F + C^{\frac{1}{n}}$ K_F (mg g^{-1}): Freundlich exponent n: Freundlich constant	Heterogeneous multilayer adsorption	(Freundlich H 1911)
Temkin and Pyzhev	$q = \left(\frac{RT}{b}\right)\ln(AC)$ T (K): adsorption temperature R (8.314 Jmol^{-1} K^{-1}): ideal gas constant b (J mol^{-1}): Temkin constant A (L mg^{-1}): equilibrium adsorption constant—maximum adsorption energy	Adsorption heat decreases linear with the covering molecules layer	(TEMKIN 1940)
Harkins–Jura	$\left(\frac{1}{qe^2}\right) = \left(\frac{B_{HJ}}{A_{HJ}}\right) - \left(\frac{1}{A_{HJ}}\right)\log C$ B_{HJ} and A_{HJ}: Harkins–Jura constants	Multilayer adsorption process with heterogeneous pore distribution	(Harkins and Jura 1944)
Halsey	$t = 0.354\left[\frac{-5}{\ln(P/P_o)}\right]^{1/3}$ t: the thickness of adsorption layer on the nonporous silica surface	Same as Harkins–Jura	(Halsey 1948)
BET	$\frac{1}{X[(\frac{P_o}{P}-1)]} = \frac{1}{X_m C} + \frac{C_{BET}-1}{X_m C_{BET}}\left(\frac{P}{P_o}\right)$ X: the number of adsorbed gas molecules at a relative pressure P/P_o X_m: the number of adsorbed gas molecules formed a monolayer C_{BET}: a heat adsorption second-parameter	Multilayer adsorption of the molecules to the adsorption surface	(Brunauer et al. 1938)
BJH	$\log\frac{P}{P_o} = \frac{2\gamma V_M}{rRT}$ P/P_o: relative pressure in equilibrium γ: surface tension of liquid nitrogen V_M: molar volume of liquid nitrogen r (cm): radius of capillary	The pores shape is cylindrical; physisorption on the pore walls; capillary condensation inside the capillary volume	(Barrett et al. 1951)

(continued)

Table 2 (continued)

Model	Equation	Assumptions	Reference
DFT	$N_{exp}\left(\frac{P}{P_o}\right) =$ $\int_{D_{min}}^{D_{max}} N_{QSDFT}\left(\frac{P}{P_o}, D\right) f(D) dD$ $N_{exp}(P/P_o)$: experimental adsorption isotherm (number of moles adsorbed at a pressure P) $N_{QSDFT}(P/P_o, D)$: theoretical isotherm in pores series D: pore size (width) f(D): pore size distribution function D_{min} and D_{max}: minimum and maxmium pore size	Pores are the slit-shaped type	(Seaton et al. 1989; Landers et al. 2013)

equilibrium. Another elucidation of this phenomenon is the same chemical potential of adsorbed and gas-phase particles. However, to access in-depth the adsorption kinetics on the non-uniform surface, it is necessary to apply some adsorption systematic models. The first-known important model is the pseudo-first-order model of Lagergren (1898) with the given equation:

$$\frac{dq_t}{dt} = k_1(q_o - q_t) \tag{2}$$

where q_t is the gas adsorbed amount (mg g^{-1}) at any time t (min), q_o is adsorbed amount at equilibrium, and k_1 is the rate constant of the first-order process (min^{-1}). Following this model, the adsorption happens only on the specific site of the adsorbent surface, with no interaction between gas molecules and surface, the adsorption energy is independent with the molecular layer formation and the adsorption rate is managed by the Eq. (2).

The developed version from the first model is pseudo-second-order (Ho and McKay 1999), which is exposed by Eq. (3):

$$\frac{dq_t}{dt} = k_2(q_o - q_t)^2 \tag{3}$$

This model is supposed to give a great correlation of the experimental data from some systems, though the assumptions made are identical to the previous version except for the model rate (k_2).

Besides, the intraparticle diffusion model proposed by Weber and Morris (1963) is also widely applied for describing the adsorption process, where the diffusion of the adsorbate on the adsorbent surface is the rate-limiting step.

$$q_t = k_3 t^{0.5} \qquad (4)$$

where k_3 is the intraparticle diffusion constant rate.

2.4 Thermodynamics of Gas Adsorption

The understanding of the thermodynamics principle was enhanced thanks to the study of Rouquerol et al. (1999b, 2014) about the adsorption at the gas–solid interface. Their thermodynamic quantities investigation is highly effective to process as well as interpret the experimental isotherms and data, especially the effect of temperature on the adsorption process. Based on some thermodynamic parameters as enthalpy, Gibbs energy, and entropy, the behavior sorption process can be forecasted. The transformed Gibbs energy (G), which is also called the thermodynamic potential of adsorption at equilibrium, is calculated as:

$$G = F + pV + \gamma A \qquad (5)$$

where F is Helmholtz energy, p, V are adsorption pressure and volume of adsorbed gas respectively, γ is surface tension and A is the solid adsorbent's surface area. One usual method to excess differential enthalpies ($\Delta_{ads}\dot{h}$) from the adsorption isothermal data is the Isosteric Method.

$$\Delta_{ads}\dot{h} = -\frac{RT_1T_2}{T_2 - T_1} ln\frac{p_2}{p_1} \qquad (6)$$

By measuring a series of adsorption isotherms at different temperatures and applying Eq. (6), the differential enthalpy or isosteric heat of adsorption would be determined as a function of equilibrium pressure P_1, P_2, and temperature T_1, T_2. The differential standard entropy ($\Delta_{ads}\dot{s}$) can also be inferred as:

$$\Delta_{ads}\dot{s} = \Delta_{ads}\dot{h} - Rln[p] \qquad (7)$$

For determining the isosteric heat of adsorption, some other methods were also proposed as gas adsorption calorimetry, immersion calorimetry, and chromatographic methods. The characteristics of the adsorption process are defined by the differential Gibbs energy and enthalpies. The adsorption process is considered to be spontaneous when the ΔG value is negative and be endothermic when the $\Delta_{ads}\dot{h}$ value is positive (Kecili and Hussain 2018).

3 Changing Biochar Properties by Modification

The microporosity of biochars was demonstrated to be promoted and dominated by CO_2 activation, while steam activation helps develop the meso- and macroporous structure as well as a larger pore size distribution. However, due to the intimate relationship between ascending porosity and descending degree of burned-off char, the industrial process for modified biochar would have a limitation for a yield of about 40 wt% activation (Rodríguez-Reinoso 2001). As reported, steam activation nearly doubled the surface area of biochar produced from *Miscanthus* while degrading functional groups, which led to weakening the polarity (Shim et al. 2015). The surface area and pore volume of biochar derived from teak sawdust by vacuum pyrolysis method were sanitated, from approximately 611 m^2 g^{-1} and 0.27 cm^3 g^{-1} to 1150 m^2 g^{-1} and 0.37 cm^3 g^{-1}, by steam activation (Ismadji et al. 2005). In a very recent study, the bamboo residue char had a dominant microporous structure with a specific area of 2150 m^2 g^{-1} after being activated by CO_2 gas (Khuong et al. 2021a). By air oxidation, a great amount of oxygenated functional groups as carboxylic, lactonic, and phenolic were generated on the surface of biochar (Bardestani and Kaliaguine 2018). However, air activation at the high temperature has a challenge with the controlling step due to its sensitivity and high reactivity with carbon, which can lead to burn-off char, a high percentage of macropore but poor porosity (Sajjadi et al. 2019). Physical activation deforms the surface structure of biochar differently from using the alternative pyrolysis method to modify the char.

Figure 4 shows the morphologies at the same scale ($\times 1000$) of the residue bamboo-derived pyrolyzed at 800 °C, pyrolyzed at 900 °C, and activated by CO_2 at 800 °C for 6 h. As can be seen, the increase of 100 °C in pyrolysis stretched the shape or shattered the edge boundary between macropores, instead, CO_2 activation disrupted most of the capillary structure.

Depending on the selected category of agents, the single-step activation or two-step activation will have certain beneficial effects. For H_3PO_4 activation, a single-step process was demonstrated to be higher effective, whereas the char products were more amorphous, possessing an applicable porous structure with high adsorption capacity (Oginni et al. 2019). A two-step activation was proved to be more advantageous for KOH activation, which modified biochar derived from rice straw in a superior way, high BET specific area, and low ash content (Basta et al. 2009). In the research of activated carbon produced from seed shells, $ZnCl_2$ was considered to be a more effective agent than H_3PO_4 due to its higher adsorption capacity product despite a lower yield (Nsi et al. 2016). Apart from a dependency on activation methods and activating agent types, the impregnation ratio between the material and agent, and the concentration of agent also extremely impacts the growth of porosity. The previous investigation showed that the increment of the concentration as well as the ratio of H_3PO_4 or $ZnCl_2$ led to enlarging pores and surface area, for instance, the BET surface area of activated biochar from *Oreganum* stalks increased from 497 m^2 g^{-1} to 730 m^2 g^{-1} when the H_3PO_4 concentration raised from 40 wt.% to 120 wt.% (Timur et al. 2006). Additionally, some other chemical modification methods such as using
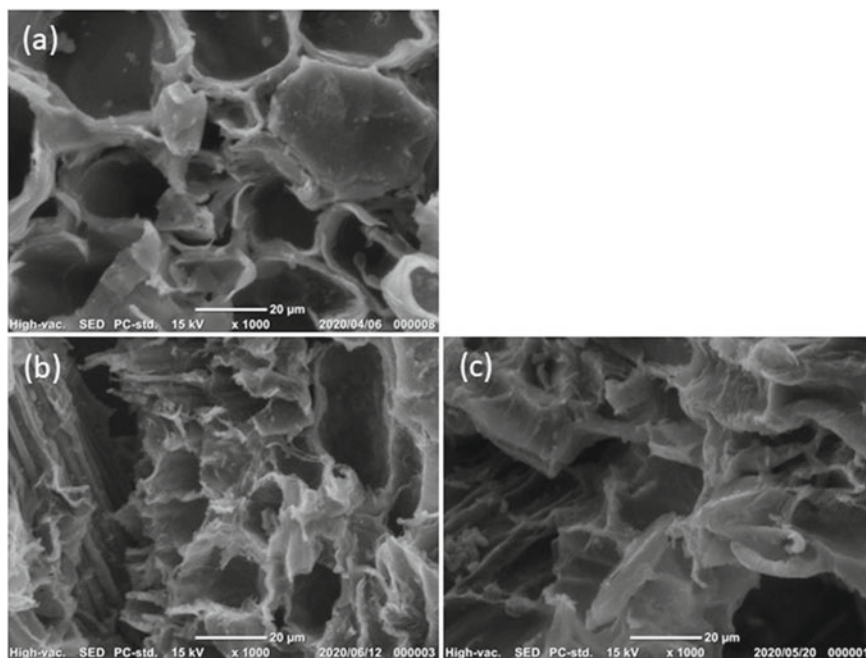
Fig. 4 The morphologies measured by SEM technique of the samples (**a**) pyrolyzed at 800 °C; (**b**) pyrolyzed at 900 °C; (**c**) CO_2 activated at 900 °C

salts, ammonium hydroxide (NH_4OH), ammonia (NH_3), hydroxylamine (NH_2OH), carbamide—urea ($CO(NH_2)_2$), iron, amines, triethylenetetramine—TETA, etc., with heat treatment are applied in biochar to functionalize the surface properties for higher uptake capacity, especially CO_2 uptake (Petrovic et al. 2021). The physical activation allows the narrow pore size distributions with low packing densities, while the chemical process grants the biochar with lower weight loss, high packing densities, and elevated mesoporosity (Prauchner and Rodríguez-Reinoso 2012).

4 Studies of Engineered Biochar as Gas Adsorbent

Over the past few decades, the gas adsorbents derived from biochar were employed, modified, and developed due to the rapid development of society that required clean gas application for environmental regulations (Menéndez-Díaz and Martín-Gullón 2006). Except for nitrogen (N_2), which is used majorly for discovering the porous parameters of adsorbents, the main adsorbate gases being studied at present are acidic gases such as CO_2, CH_4, H_2S, N_2O. Each adsorbate has a different adsorption mechanism on the surface of the adsorbent.

4.1 CO_2 Adsorbents

As aforesaid, the capacity of adsorption compromises with the adsorption conditions as well as the characteristics of biochar-derived adsorbent, which is largely determined by the raw material and the method of modification. Table 3 mentions the CO_2 uptakes recorded from multiple reports that used various materials and techniques.

The activated vine shoots sample in Table 3 is a typical case for the temperature and atmosphere dependence of adsorption capability, that is, an increase in temperature and decrease in pressure led to the decrement in CO_2 uptake. Another study considered that the physisorption adjusted the CO_2 adsorption of biochar, whereas physical adsorption generates 5 to 40 kJ mol^{-1} and chemical adsorption produced 40 to 800 kJ mol^{-1} of adsorption heat (Creamer 2017). From the table, it is clear that the CO_2 capture ability is governed by the unique structure and surface properties of modified biochar. Sawdust without activation or modification has the CO_2 uptake of only 18 mg g^{-1} at 25 °C and 20.7 bar, and this number increased to 44.8 mg g^{-1} at 30 °C when the material was modified by monoethanolamine. Cellulose fiber activated by steam could access higher CO_2 capacity than bamboo activated by CO_2 at the same adsorption condition, although the specific surface area of activated cellulose was lower than activated bamboo. Other samples including Eucalyptus wood, Rambutan peel, African palm shell, sea mango, Miscanthus yielded very promising CO_2 adsorption results. These samples were especially surface-functionalized with different methods to improve the CO_2 uptake.

The presence of basic functional groups has helped to retain the CO_2 gas molecules in pores instead of letting them slide out when approaching equilibrium. Some nitrogen-containing functional groups as amide, pyridinic, imide, pyrrolic, lactam groups, can be contributed to the biochar surface by N-containing reagents as ammonia, amines, nitric acid, or any N-containing precursors (Dissanayake et al. 2020). It was also demonstrated that the CO_2 uptake is attributed to many factors: surface area, nitrogenous groups, pore structure, size, micropore surface area, and volume (Khandaker et al. 2020). Hence, the mechanism of CO_2 adsorption should be evaluated according to the experimental case.

4.2 Other Gas Adsorbents

Recently hydrogen sulfide (H_2S) and methane (CH_4) have also been studied. To investigate the H_2S or CH_4 adsorption capacity of adsorbents, the breakthrough curves must be defined, constructed and analyzed. A breakthrough curve is known as a technical plot that shows the correlation between the concentration of adsorbate and the testing time interval. The adsorbate amount is measured through the capacity of the bed of the adsorbent, where the effluent stream of a mixture of fluid (air and

Table 3 Some reported biochar modification methods and their CO_2 adsorption capacity

Raw material	Modification methods	S_{BET} (m^2 g^{-1})	Adsorption condition	CO_2 uptake	Reference
Sawdust	Pyrolysis at 650 °C; nil	~ 200	25 °C–300 psi (20.7 bar)	18 mg g^{-1}	Ghani and Silva (2014)
Vine shoots	Pyrolysis at 600 °C; KOH activation at 700 °C	1671	25 °C–1 bar 0 °C–1 bar 0 °C–15 kPa	2.46 mmol g^{-1} 5.40 mmol g^{-1} 2.25 mmol g^{-1}	Manyà et al. (2018)
Cellulose fiber	Pre-pyrolysis at 200 °C; steam activation at 800 °C	863	25 °C–1 bar	3.78 mol g^{-1}	Heo and Park (2015)
Bamboo	Pyrolysis and CO_2 activation at 800 °C	952	25 °C–1 bar	3.4 mmol g^{-1}	Khuong et al. (2021b)
Eucalyptus Wood	H_3PO_4 activation at 450 °C; NH_3 modification at 800 °C	2079	30 °C–1 bar	3.22 mmol g^{-1}	Heidari et al. (2014)
Rambutan peel	Pyrolysis at 900 °C; $Mg(NO_3)_2$ modification at 800 °C	~ 505	30ºC–75 ml min^{-1} CO_2	75.58 mg g^{-1}	Zubbri et al. (2020)
African palm shell	$CaCl_2$, H_3PO_4 and CO_2 combination activation at 900 °C; NH_4OH modification at 75 °C	634	0 °C–1 bar	333 mg g^{-1}	Giraldo et al. (2020)
Sea mango	Pyrolysis at 200ºC; H_3PO_4 activation at 500 °C (absence of any gases); deep eutectic solvent modification	~ 436	15% CO_2 in 5 ml/min	9.685 mg g^{-1}	Zulkurnai et al. (2017)
Miscanthus	Pyrolysis at 700 °C, low-frequency ultrasound and TEPA activation; EDC and HOBt functionalization	532	70 °C–0.1 atm	2.89 mmol g^{-1}	Chatterjee et al. (2020)
Cottonwood	Metal (Al) oxyhydroxide composites modification at 600 °C	367	25 °C–50 ml min^{-1} CO_2	71.05 mg g^{-1}	Creamer et al. (2016)
Sawdust	Pyrolysis at 850 °C, Monoethanolamine (MEA) modification	3.17	30 °C–100 ml min^{-1} CO_2 70 °C–100 ml min^{-1} CO_2	44.8 mg g^{-1} 25.2 mg g^{-1}	Madzaki et al. (2016)

vapor in this case) enters until reaching the saturation state (Marsh and Rodríguez-Reinoso 2006). The mechanism of the H_2S adsorption is based on several processes with equation expressed as follows (Shang et al. 2013):

H_2S gas molecules adsorb on the adsorbent surface.

$$H_2S_{gas} \xrightarrow{K_H} H_2S_{ads} \qquad \text{(Reaction 8)}$$

H_2S dissolves in a water film made from the moisture of the adsorbent.

$$H_2S_{ads} \xrightarrow{K_S} H_2S_{ads-liq} \qquad \text{(Reaction 9)}$$

H_2S adsorbate dissociates in the water film.

$$H_2S_{ads-liq} \xrightarrow{K_a} HS^-_{ads} + H^+ \qquad \text{(Reaction 10)}$$

Anion element of dissociation reacts with adsorbed oxygen (O_2) and forms sulfur (S) or sulfur dioxide (SO_2).

$$HS^-_{ads} + O^*_{ads} \xrightarrow{K_{R1}} S_{ads} + OH^- \qquad \text{(Reaction 11)}$$

$$HS^-_{ads} + 3O^*_{ads} \xrightarrow{K_{R2}} SO_{2ads} + OH^- \qquad \text{(Reaction 12)}$$
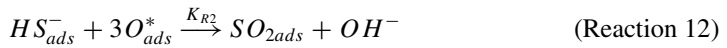
SO_2 is oxidized to H_2SO_4 in the water created from the adsorption.

$$H^+ + OH^- \rightarrow H_2O \qquad \text{(Reaction 13)}$$

$$SO_{2ads} + O^*_{ads} + H_2O_{ads} \xrightarrow{K_{R3}} H_2SO_{4ads} \qquad \text{(Reaction 14)}$$
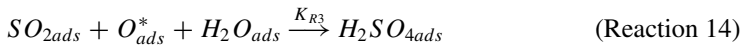
The *gas, ads, ads-liq* are noted for the phases of elements, for instance, H_2S_{gas} corresponds to H_2S in the gas phase, $H_2S_{ads-liq}$ or H_2S_{ads} stands for H_2S in the liquid phase or adsorbed phase. K_H, K_S, and K_a are the equilibrium constants for the adsorption process, gas solubility process, and dissociation process, respectively. K_{R1}, K_{R2}, and K_{R3} are the surface reaction constants. There are some individual investigations on H_2S, with 3 case studies listed in Table 4. These studies indicated that the surface characteristics and pH of biochar rule the mechanism as well as the capacity of the adsorption. The rational use of the raw material and modification methods have brought potential results. Rice husk char achieved a high breakthrough capacity of 382.7 mg g^{-1} in an H_2S environment. Each gram of Maple sawdust with Fe-impregnation can adsorb 15.2 mg of H_2S in a biogas flow. In addition to agriculture residue, activated food waste and sludge could also adsorb a great amount of H_2S, 66.6 mg g^{-1} in gas matrices.

Table 4 Some approach for engineered biochar as H_2S gas adsorbent

Raw material	Modification methods	pH	Adsorption condition	Breakthrough capacity ($mg\ g^{-1}$)	Reference
Camphor	Pyrolysis at 400 °C; nil	9.55	Room temperature–40 ml min^{-1} H_2S	109.3	Shang et al. (2013)
Rice husk		10.56		382.7	
Bamboo		10.21		336.7	
Corn stover	Pyrolysis at 500 °C	10.2	Room temperature–100 mL min^{-1} biogas	0.5	Choudhury and Lansing (2021)
	Pyrolysis at 500 °C and Fe-impregnated	9.10		1.5	
Maple sawdust	Pyrolysis at 500 °C	2.80		2.0	
	Pyrolysis at 500 °C and Fe-impregnated	6.97		15.2	
Wood pallet	Pyrolysis at 700 °C	7.3	Room temperature–0.18 L min^{-1} gas matrices	0.04	Hervy et al. (2018)
	Pyrolysis at 700 °C; Oxygenation at 280ºC	7.6		1.81	
	Pyrolysis at 700 °C; steam activation at 850 °C	9.0		12.92	
Food waste and coagulation flocculation sludge	Pyrolysis at 700 °C	9.6		0.22	
	Pyrolysis at 700 °C; Oxygenation at 280ºC	9.6		0.12	
	Pyrolysis at 700 °C; steam activation at 850 °C	9.8		66.60	

Different from H_2S, the adsorption mechanism of CH_4 is self-diffusion, in which the isosteric heat ranges from 8.715 to 11.746 kJ mol^{-1} at 233.15–363.15 K (40 °C–90 °C) (Wang et al. 2020). Sadasivam and Reddy. (2013, 2014, 2015) applied batch and column adsorption testing methods on biochar derived from woody biomass to explore the transport and adsorption of methane collected in landfills. The adsorption capacity of activated biochar from a mixture of pine and fur wood was found to be up to 3333.3 mL kg^{-1} at 10% CH_4 headspace concentration (Sadasivam and Reddy 2013). At the dry condition, the biochar derived from a type of wood waste (CE-WP1) had a calculated value of CH_4 adsorption capacity 0.21 mol kg^{-1} from the Langmuir model. This value decreased to 0.11 mol kg^{-1}, still higher than that of granular activated carbon (0.06 mol kg^{-1}) when the corresponding water holding capacity was 25% at room temperature (Sadasivam and Reddy 2015). Wood pellet biochar produced from pyrolysis 500 °C had a much higher extent of methane diffusion than that of granular activated carbon (Sadasivam and Reddy 2014).

Likewise, the simultaneous adsorption of gaseous adsorbates is crucial for engineering effective biochar. The selectivity of CO_2, H_2S, and CH_4 gases during the adsorption has been surveyed on some biochar derived from perilla, oak, and soybean stover (Sethupathi et al. 2017). For biochar mentioned in the literature, when adsorbing singular gas, CO_2 was the most adsorbed with adsorption capacity up to 2.312 mmol g^{-1}. Nonetheless, when simultaneous adsorption occurred, H_2S dominated over CO_2 adsorbate, and CH_4 was barely adsorbed. This phenomenon can be explained by the fact that the small CO_2 and H_2S molecules with 3.3 Å and 3.6 Å kinetic diameters, respectively, permeate all the porous structures, even in ultra-micropores, which prevents the CH_4 molecules with the large kinetic diameter of 3,8 Å from being adsorbed on the adsorbent surface (Cui et al. 2004; Scholes et al. 2010; JALON 2017). The breakthrough capacities of H_2S and CO_2 were recorded as 0.208 mmol g^{-1} and 0.126 mmol g^{-1} respectively in the 700 °C-pyrolyzed perilla. It was also disclosed that the biochar from perilla possessed a high adsorption capacity of H_2S and CO_2, which was followed by soybean stover and oak biochar (Sethupathi et al. 2017).

Different from the above mentioned gases, nitrous oxide (N_2O) exists in soils and oceans as a byproduct of nitrification and denitrification ((Machida et al. 1995). Therefore, the application of N_2O adsorption is in biochar-amended soil to suppress its emission in the atmosphere (Solaiman and Anawar 2015). The mechanism of N_2O removal by biochar can be explained by the "electron shuttle", a redox system that easily switches between states and facilitates electron transmissions to microorganisms (Cayuela et al. 2013). It is also noted that the biochar N_2O adsorption capacity is strongly influenced by soil texture, soil pH, and the chemical form of N-fertilizer (Cayuela et al. 2014). The physicochemical treated pecan shell, maple wood, and pinewood could adsorb 4.3 - 21 mmol N_2O per kg, while Lockwood soil or peat could adsorb only 0.13 mmol N_2O per kg at the same low relative pressure condition (Xiao et al. 2018). By adding hardwood-derived biochar in sandy loam soil at a rate of 28 Mg ha^{-1}, N_2O emissions were suppressed 91% of the total amount (Rittl et al. 2021).

5 Limitations

Biochar as gas adsorbent is an attractive topic that is broadly approached in recent years, especially for CO_2 capture application. Biochar is an eco-friendly and low cost product (10 times cheaper than other CO_2 adsorbents) (Chatterjee et al. 2018). However, biochar-based gas adsorbents are still constrained by numerous challenges related to technical, economical, and environmental aspects.

There are many studies on the enhancement of gas adsorption capacity after biochar modification, however, the stability and durability of products have not been clarified for the long-term assessment (Dissanayake et al. 2020). Most studies concentrated only on certain gases or a combination of predetermined gases. Nonetheless, for greenhouse gas emissions (GHG) containing multiple gaseous agents, the removal mechanism is indeed complicated (Solaiman and Anawar 2015), which requires a comprehensive understanding of the effect of each gas on one other during the adsorption process. Besides, the adsorptive characteristics of biochar can be degraded during long-term cyclic sorption, which should be taken into account in the technical issues for biochar production (Zhelezova et al. 2017). So far, the data related to the operation in the continuous flow system as well as the regeneration capacity of modified biochar has not been elucidated (Rosales et al. 2017).

In the case of the economical aspect, Gwenzi et al. (2021) suggested some present knowledge gaps including the lack of studies on the applications of biochar as a gas adsorbent on a large-scale or industrial scale, the scarcity of socio-economic feasibility research, and the competition from existing biochar production technologies. Perhaps, the treatment process of modified biochar is not as cost-effective as bio-oil technology, which also utilized bio-waste or biomass as the raw material.

Although biochar supports the mitigation of GHG emissions, its production produces a relatively large quantity of polycyclic aromatic hydrocarbons (PAHs) and dioxins that cause human and ecological risks (Hale et al. 2012). Furthermore, the amended biochar from wastewater sludge or possibly other residues might accommodate a high level of heavy metal as Zn, Pb, Ni, Cu, Cd (Hossain et al. 2011), which raises difficulties of spent biochar disposal. Without proper control and treatment, the biochar may also migrate in soil that induces negative influences on the ecosystem as well as human lives (Genesio et al. 2016).

In addition to the above rationale, policy and regulatory framework for enhancing biochar as gas adsorbent is also a challenge that needs to be dealt with (Gwenzi et al. 2021). Due to a lack of understanding of technological components, setting development policies will be a big question for future research.

6 Conclusions and Future Prospects

Up to now, a number of studies on the gas adsorption application of biochar have been accomplished and yielded positive results. The physicochemical properties and porous structure of biochar including pH, constituent elements, porosity, morphology, and surface functional groups are the decisive factors for gas adsorption performance. Therefore, to ameliorate the gas adsorption capacity, the characteristics of char products from pyrolysis should be boosted by physical and chemical modifications. Previous findings of modified biochar have shown its superiority in adsorbing gases in the environment, helping to mitigate GHGs, which include mainly CO_2, H_2S, CH_4, N_2O. However, the lack of knowledge in many aspects has posed plenty of challenges for bringing biochar into the potential market of gas adsorption technologies. With the current increasing rate of gaseous pollutants from burning fuels, greenhouse gas emissions, and industrial constructions, novel techniques for gas adsorption application on biochar should be focused on the development of the capacity, regeneration, and reuse features for the industrial scale.

Based on the challenges mentioned above, it is necessary to establish certain strategies to solve those difficulties. Conducting research to solve the technical problems that include the gas mixture adsorption and regenerative long-term techniques should be promoted. Besides, studies on other technologies related to biomass also need to be done, especially economic analysis, to find ways to bring biochar as a gas adsorbent to consumption in the actual market. Above all, a complete database on biochar production and adsorption capacity of a combination of multiple gases should be created to maximize char performance, minimize environmental problems, and set forth new appropriate policies.

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Engineered Biochar as Supercapacitors

Toshiki Tsubota

Abstract Most of the applications of biochar are mainly focused on agriculture and environmental sectors. These traditional applications can be achieved by conventional technologies, and usually do not require advanced technology. However, nowadays the use of biochar is getting attention in the field of engineering as high-performance functional material. Many research studies for the development of electric power storage device have been carried out in the field related to material science. The storage of electric energy is one of the key technologies for eco-friendly society (effective use of natural energy, distributed energy system, etc.) for next generation. For the aforesaid reasons, supercapacitor has been one of the hottest topics. At a glance, natural resource such as plants might not be recognized as a suitable raw material for advanced functional industrial material. However, biochar is a suitable material as it is widely used as an electrode of supercapacitor. The biochar derived from plant-based biomass are eco-friendly and cost-effective that contain different types of pores which can be utilized in different applications of supercapacitors. In this chapter, the outline of supercapacitor is explained and recent research papers of supercapacitor prepared from biochar are classified and listed.

Keywords Activated carbon · Electric double layer capacitor · Electric power storage device · Carbon material · Activation · Electrochemistry

1 Introduction

Supercapacitor, or electric double layer capacitor (EDLC) stores electric energy by dielectric polarization in an electric field. In the case of supercapacitor, the electric double layer (EDL), which is a physical phenomenon, is used for the occurrence of capacitance (As for EDL, it is mentioned in Sect. 2.1 of this chapter.) Most of capacitors are mainly used in electric circuit as an electric component. In the case

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Table 1 Comparison between supercapacitor and battery

	Supercapacitor	Battery (such as lithium-ion battery)
Energy density [Wh kg^{-1}]	0–10	10–100
Power density [kW kg^{-1}]	several hundreds to several thousands	several hundreds
Charging time and discharging time	several tens of seconds	several tens of minutes to several hours
Charge/discharge cycle life	several tens of thousands to several hundreds of thousands	several hundreds to thousands

of supercapacitor, they are often used as electric power storage device because the amount of the stored electric power is much larger than other types of capacitors.

Becker and Ferry (1957) who belonged to General Electric Company, presented the capacitor that has porous carbon electrode and electrolyte. This invention was probably the first proposal of supercapacitor. Boos et al. (1972) who belonged to The Standard Oil Company Cleveland, Ohio, tried to improve the device of supercapacitor and presented the capacitor which has paste type electrode. In Japan, Matsushita Electric Industrial Co., Ltd. (now Panasonic Corporation) and Nippon Electric Company, Limited (now NEC Corporation) were the pioneers that commercialized "supercapacitor" in 1978. So far, super capacitor has been recognized as the device related to electricity and electronics, and the market of supercapacitor has been well established in the world.

The comparison between supercapacitor and battery is listed in Table 1. The differences in the properties are derived from the principle of mechanism for electric power storage. In the battery, because the faradaic chemical reactions are the origin of the function, the electric energy is stored in "volume". Thus, the electric energy of the battery is large. However, since the charging and discharging time, and the current density are affected by the chemical reaction rate, these values are small. The unstable current during the charging process is harmful for the battery. Furthermore, the life of this cycle is not long as the undesirable side reactions occur during the process. In supercapacitor, the electric energy is stored on "surface" via EDL. Therefore, the advantage of supercapacitor is not its energy density but its power density. Large power density means quick release of electric power, that is, high current emission. Moreover, quick charging and long-life cycle are also the advantages of supercapacitor.

The main applications of supercapacitor are listed in Table 2. The electric energy stored in supercapacitor is rather smaller than in the battery such as lithium-ion battery, which stores the electric energy via chemical reaction. Therefore, in the case of only "the usage of stored electric energy", batteries are better. However, some fields require high performance of other properties, such as large power density, rather than large electric energy density. The applications of supercapacitor are well established in these fields.

Table 2 The main applications of supercapacitor

	Applications
Small device	– Power supply for backup in consumer electronics – Auxiliary power unit for quick starting in office automation equipment (copier, printer, etc.) – Power supply for flashlight of digital camera and smartphone
Large device	– Protective equipment for instantaneous voltage drop in factory (semiconductor, pharmacy, etc.) – Electric power storage device of energy regeneration system in construction machinery, gantry crane, elevator, etc.

Nowadays, there is huge interest in electric vehicle (EV) around the world. The prime contender for the electric power storage device of EV are the batteries including lithium-ion battery because of the large electric energy density. Nevertheless, supercapacitor is still one of the candidates for power source of EV due to resistance against instable charging during energy regeneration at breaking and large power density for start of driving. If high permeance (large electric energy density with large electric power density) is realized for capacitor, the improved supercapacitor is suitable for EV.

The classification of "supercapacitor" is shown in Fig. 1. As the similar technologies to "electric double layer capacitor", there are "pseudocapacitor (redox capacitor)" and "hybrid capacitor". The "pseudocapacitor" stores the electric power not only by electric double layer but also by faradaic electron charge transfer. The electrode of "pseudocapacitor" contains the material for redox reaction, such as ruthenium oxide (RuO_2), and conducting polymer (polypyrrole, etc.). The "hybrid capacitor" is hybrid of EDLC and battery, that is, asymmetric electrodes. There are two

* "Supercapacitor" is also called "ultracapacitor".
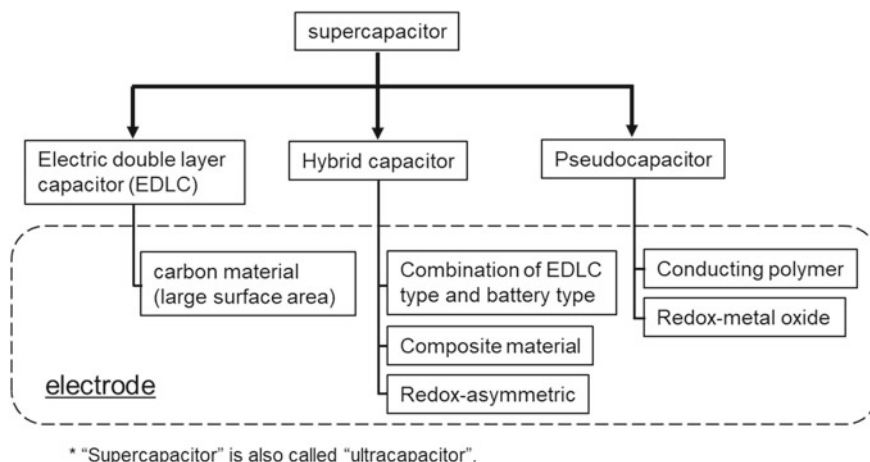
Fig. 1 The classification of "supercapacitor"

types of combinations (i) cathode is activated carbon and anode is non-carbon material such as $Li_4Ti_5O_{12}$ and (ii) cathode is non-carbon material such as NiOOH and anode is activated carbon.

The terms "supercapacitor", "ultracapacitor", and "electric double layer capacitor" are often confusing as the name of the electric power storage devices. The principle of "electric double layer capacitor" is the storage of electric power in electric double layer on porous electrodes. In some cases, the "supercapacitor" and the "ultracapacitor" are used as the alternative name of "electric double layer capacitor", and in other cases these are called as pseudocapacitor, which stores the electric power not only by electric double layer but also by faradaic electron charge-transfer. In hybrid capacitor, one of the electrodes is same as the battery. In these capacitors, the faradaic electron charge transfer for the electric power storage is performed by metal oxide, such as RuO_2, and conducting polymer. As these substances are far from the scope of biochar, in this chapter only the "supercapacitor" is explained as electric double layer capacitor.

2 Principle of Supercapacitor

2.1 Electric Double Layer (EDL)

When the voltage is applied between two electrodes of same material inserted in an electrolyte, containing ion species in solvent, the electrical potential is generated (Fig. 2). Water and other organic compounds that can dissolve ion species can be the solvent for the electrolyte. The potential drops generate only at the interfaces between the electrode and electrolyte, i.e. region of electrolyte near to the surface of the electrode. The phenomenon of the origin of this potential drop is called "electric double layer" (EDL). Some models (Helmholtz, Gouy-Chapman, Stern, Grahame, Bockris/Devanathan/Müllen (BDM)) have been proposed and improved for the explanation of the phenomenon. The BDM model (Bockris et al. 1963), which is said to be close to real situation, is shown in Fig. 3. In this model, there is a strongly held and oriented layer of the solvent molecules that are attached on the electrode because of strong interaction between the charged electrode and the dipole of solvent molecule. This layer can also include some specifically adsorbed ions which are partially solvated because of competitive adsorption. The locus of the centers of these specifically adsorbed ions is called "inner Helmholtz plane" (IHP). The ion species which have opposite charge against the electrode exists on this layer being solvated by the solvent molecules. The locus of the centers of these solvated ions is called "outer Helmholtz plane" (OHP). The region next to OHP is called "diffuse layer", and in this layer, the concentration of the ion species which have opposite charge as the electrode is higher than that of the ion species which have the same charge as the electrode. The electrical pair of the electrode surface and the

Fig. 2 Formation of electric
double layers
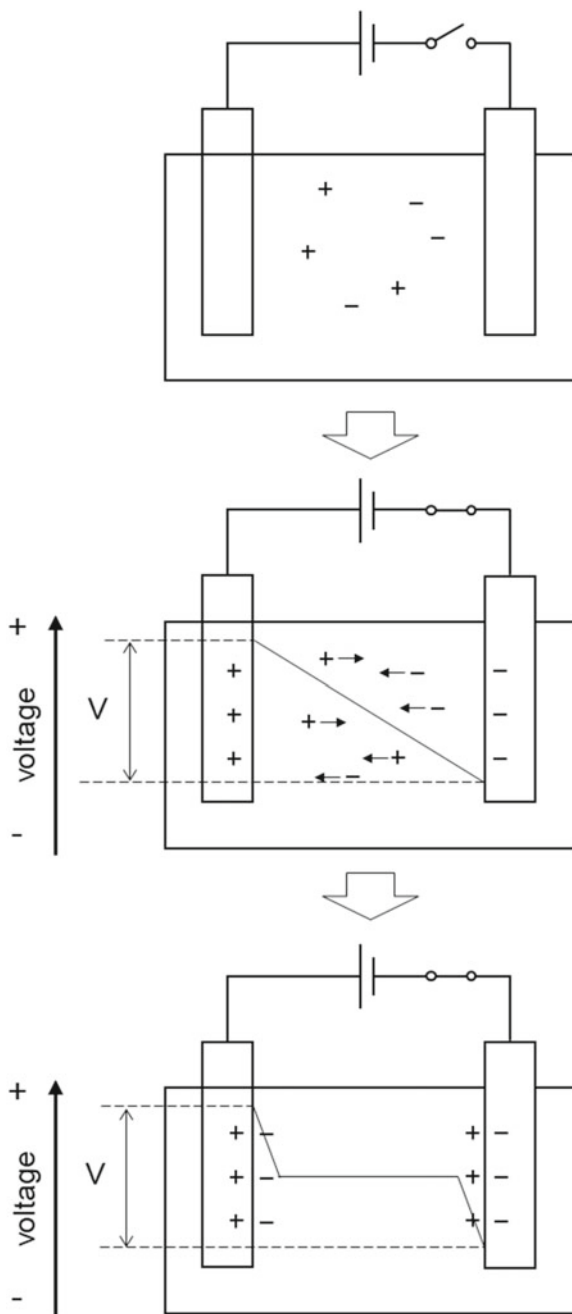
Fig. 3 BDM model for
electric double layer

IHP   OHP   diffuse layer
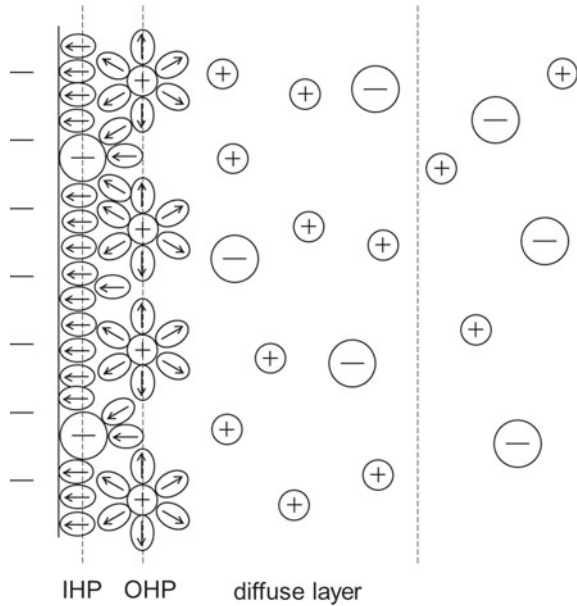
inner region of diffuse layer act as electric double layer (EDL). This EDL is used for
the electric power storage in supercapacitor.

The thickness of EDL depends on the concentration of electrolyte, valence of ion
species, and dielectric constant of the solution (Bohinc et al. 2001). The order of
thickness is considered to be 0.1–1 nm on the electrode of supercapacitor.

2.2 Performance of Supercapacitor

The electric power stored in supercapacitor device, E [J], can be calculated as follows,

$$E = 1/2C\ V^2 \tag{1}$$

where, C [F] is capacitance, and V [V] is the voltage applied between the
electrodes. Therefore, large capacitance value is one of the most important prop-
erties for supercapacitor. The capacitance value of the device depends on the
charging/discharging condition. It is affected by the combination of the constituent
materials of components. Moreover, the construction of the components also affects
the capacitance value of the device.

For the estimation of the performance of materials, the capacitance value can be
measured by using two electrode cells, the components of which are basically the
same as the device, or three electrode cells, which has the reference electrode for the
evaluation of the voltage against standard hydrogen electrode (SHE).

3 Components of Supercapacitor

The fundamental structure of supercapacitor is shown in Fig. 4. In this structure, there is electrolyte, separator, current collectors, and polarizable electrode as the fundamental components.

3.1 *Separator*

The role of separator is avoiding the contact of the electrodes with each other while keeping the movement of ion species. Therefore, porosity to ion species and electrical insulation is required as the property of separator. Moreover, thin membrane (a few hundred of a millimeter) is better because the distance between the electrodes should be close for the decreasing the internal resistance. In addition, wettability against the electrolyte and chemical inertness in the operating conditions are also required for the material of separator. In general, the paper of cellulose is an inexpensive common product that is used as a material for the separator. Some other expensive products used for high performance are nonwoven porous polymeric films (polyacrylonitrile, polyimide film), woven glass fibers, and porous woven ceramic fibers are also used for the separator.
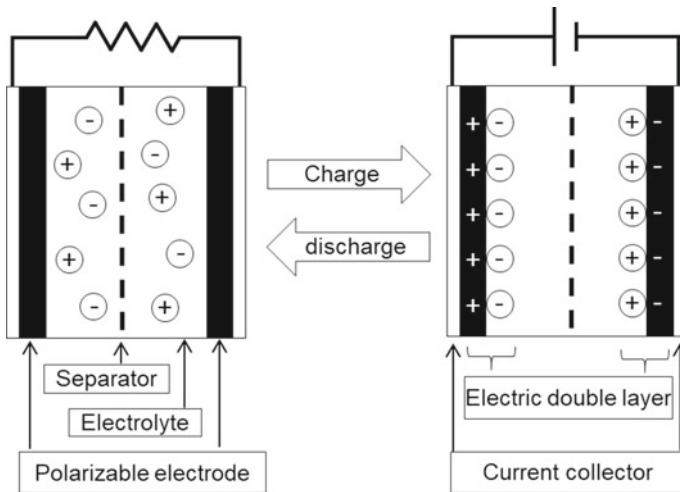
Fig. 4 The model of electric double layer capacitor (EDLC)

Table 3 The comparison between water electrolyte and organic electrolyte

	Water electrolyte	Organic electrolyte
Solvent	water	acetonitrile, propylene carbonate
Salt	H_2SO_4, KOH	tetraethylammonium tetrafluoroborate, triethyl (metyl) tetrafluoroborate
Electrical conductivity [S m^{-1}]	10–100	1–6
Applied voltage per cell [V]	1.2	2.5

3.2 Electrolyte

The electrolyte of supercapacitor is classified by the type of solvent, i.e. water and organic compounds. The comparison between water electrolyte and organic electrolyte is listed in Table 3.

The voltage applied to the electrodes must be less than the voltage for electrolysis of the electrolyte. Organic compounds such as acetonitrile and propylene carbonate have larger voltage for electrolysis than water. Thereby, higher voltage can be applied to supercapacitor using organic electrolyte. The electric power stored in capacitor is expressed as Eq. (1). The increment of the applied voltage is effective in the increase of the stored electric energy because the stored electric power is proportional to the square of voltage. Hence, the supercapacitor using organic electrolyte has advantage as they can store large electric energy. Since large electrical conductivity can contribute to small internal resistance, the supercapacitor of water electrolyte is suitable for high power application. Moreover, the device fabrication of water electrolyte is more moderate than that of organic electrolyte because the small amount of contamination of water from atmosphere is acceptable. Nevertheless, almost all commercial supercapacitors contain organic electrolyte. Most of electric circuits, at least in Japan, work at voltage of 5 V or 3.3 V. As the capacitance value of capacitor decreases in series connection, the smaller number of series connection is better for the application in electric circuit. Therefore, the higher voltage per cell of organic electrolyte is suitable for the application. Actually, the detailed components depend on the real products.

3.3 Current Collector

In general aluminum foils are used for most of the commercial products, i.e. organic electrolyte. For research work using water electrolyte, platinum plates or platinum meshes are often used as the current collector. There are mainly two methods for the setup of the polarizable electrode, which is the powder of porous carbon material on the current collector. One of the methods is the attachment of the sheet prepared from polarizable electrode, conduction supporting agent, and binder on the current

collector. Another method is the coating of the mixture of polarizable electrode, conduction supporting agent, and binder on the current collector.

3.4 Polarizable Electrode

For high performance of supercapacitor, the properties required for polarizable electrode are large surface area, high electric conductivity, and chemical stability against electrolyte during operation. For practical use, inexpensiveness is one of the important factors. Moreover, harmless and no use of miner elements such as rare-earth metals are preferable. There are few materials which have both large surface area and high electric conductivity. The porous carbon material has the potential of simultaneous realization of these properties. From the viewpoint of the creation of new high-performance material, different types of carbon material have been synthesized (Frackowiak and Beguin 2001; Pandolfo and Hollenkamp 2006; Ghosh and Lee 2012; Simon and Gogotsi 2008; Noked et al. 2011). However, these synthesized materials are far from the practical use because of their high prices. In practical use, the so-called "activated carbon" is used for polarizable electrode. Activated carbon has large surface area (in general, more than 1000 $m^2\ g^{-1}$ in BET specific surface area) with many micropores which makes it an ideal candidate.

3.5 Style and Construction of Supercapacitor

In general products, the appearance of supercapacitor is as a cylindrical case or rectangular case. In the cylindrical case, there is a rolled pair of the electrodes. In rectangular case, there are the stacks of the pairs of flat electrodes. Actually, the detailed structures depend on the real products.

4 Preparation of Biochar for Electrode Material of Supercapacitor

As mentioned in Sect. 3.4, activated carbon is used as the polarizable electrode of supercapacitor. The raw materials of activated carbon are coal, synthetic resin, and biomass. Activated carbon can be prepared by using different activation reactions. The activation reactions are classified into two groups, i.e. physical activation and chemical activation. In physical activation, gaseous species are used as activator, which reacts with raw material of activated carbon for enhancing the surface area of the product. In chemical activation, chemical reagents are used as activator. Some reviews summarize the reported work related to the preparation of activated

carbon from biomass (Zhou et al. 2021; Patra et al. 2021; Panwar and Panwar 2022; Heidarinejad et al. 2020; Sevilla et al. 2021; Danish and Ahmad 2018; Yahya et al. 2015; Gonzalez-Garcia 2018; Ioannidou and Zabaniotou 2007). There are also some reviews for the activation using microwave (Ao et al. 2018; Hesas et al. 2013; Yuen and Hameed 2009). The activation using microwave is not mentioned in this chapter. As the review paper about the preparation of activated carbon from biomass (Heidarinejad et al. 2020) summarized the proposed activation mechanisms in detail, only the fundamental points are mentioned in this chapter.

4.1 Physical Activation

Steam (vapored H_2O), CO_2, and O_2 can work as the activator of physical activation. The chemical reaction of steam activation is endothermic, and the process is performed at more than 750 °C. The CO_2 activation is also endothermic, and the process is performed at more than 850 . The O_2 activation is exothermic, and the reaction rate is too rapid to control easily. Actually, the mixture of gases generated during the heating treatment for activation are employed in practical process.

4.2 Chemical Activation

H_3PO_4, $ZnCl_2$, and KOH are the main chemical activators for commercial activated carbon. The chemical reaction of activation depends on the kind of activator. As for H_3PO_4 and $ZnCl_2$ activation, the activator is mixed with the raw material before carbonization, and in general, the suitable temperature is around 500 °C. For KOH activation, KOH is mixed with the carbonized material, and in general the suitable temperature is around 800 °C. The properties related to the performance as polarizable electrode, such as surface area, pore size distribution and electric conductivity, rely on the kind of activation and the activation conditions. In order to control these properties, many research studies have been carried out for the improvement of preparation of activated carbon.

5 Biochar as Supercapacitor Electrode

So far, much research work has reported the supercapacitor electrode being derived from biomass and biochar. Different biomass are tested to be used as the raw material of supercapacitor electrode. Some reviews have been already published for use of biochar as the electrode of electric double layer capacitor, hybrid capacitor, or pseudo capacitor (Fic et al. 2018; Dubey et al. 2020). This chapter is focused on "electric

double layer capacitor". The biomass as raw material is roughly categorized into agricultural waste, crops, fruits, nuts, vegetable, food, plant, grass, and tree.

In general, the agricultural products (crops, fruits, vegetables, tree, etc.) are produced in farm fields, and then these are collected via harvest. Most of these collected products are separated. Thereafter, the generated wastes are collected. The conversion of waste into valuable product is preferable if the conversion system is economically feasible. Automatic collection of waste is convenient for regular and undisturbed supply of the raw material from the viewpoint of the product manufacturing process. Moreover, if the waste has some specific points which are preferable as the raw material of supercapacitor electrode, the distinctive material can be produced for high performance. The microstructure including special pore structure derived from plant tissue is advantageous as it can be valuable for the supercapacitor electrode. The chemical structure of protein contains N atoms in the peptide bond. The introduction of the heteroatoms (N, S, etc.) in carbon material is one of the strategies for enhancing the capacitance value of the electrode of supercapacitor.

In order to increase the surface area of biochar, activation is necessary for the preparation of high-performance material for supercapacitor electrode. Conventional activation process can work against most of biomass for the enhancement of surface area of biochar. Moreover, combination of activation process has been used for the improvement of the performance as supercapacitor electrode.

Biochar is a sustainable product since its preparation is a carbon negative process (Shalini et al. 2021). It can sequester soil carbon, reduce the emission of greenhouse gases in the atmosphere, remediate inorganic and organic pollutants from the environment and also used for geo-engineering purposes (Ramola et al. 2020, 2021; Wani et al. 2021). Modified biochar has several advantages such as presence of fiber structure, layered structure (Xu et al. 2020), and carbon skeleton structure (Wang et al. 2017a, b), high surface area, porosity, and very good conductivity (Li et al. 2018a, b). All of these properties make modified biochar as an excellent candidate for electrode materials for supercapacitors. A detailed listing of different biochar used for supercapacitors are given in Table 4.

6 Conclusion

The demand for sustainable energy has increased owing to the fast depleting resources of renewable energy. Supercapacitors are getting attention for energy purposes since they have high conductivity and power density, high operational temperature, very good capacity of charge–discharge and very high stability. Also, biochar has emerged as an eco-friendly and cost-effective precursor for making electrode. Modification of biochar can induce high porosity and surface area, and other structural properties that make it more advantageous.

Table 4 Different biochar used for supercapacitor

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Agriculture waste	Argan shells	KOH	(Biochar 700 °C):KOH = 1:4, 850 °C for 1 h	2251	0.5 M K_2SO_4 aq	Three electrode	179 (at 0.1 A g^{-1})	Boujibar et al. (2019)
Agriculture waste	Bagasse	K_2CO_3	Bagasse:K_2CO_3:urea = 2:1:4, 800 °C for 2 h	1644	1.0 M $MgSO_4$ aq	Three electrode	315.0 (at 1.0 A g^{-1})	Zou et al. (2019)
Agriculture waste	Bagasse	$CaCl_2$	Bagasse:$CaCl_2$:thiourea = 1:2:2, 800 °C for 2 h	835.9	6.0 M KOH aq	Three electrode	349.0 (at 1.0 A g^{-1})	Tan et al. (2018)
Agriculture waste	Coffee grounds	KOH	Coffee grounds:KOH:$MgSO_4$ = 4:4:1, 800 °C for 1 h	1079	6 M KOH aq	Two electrode	240 (at 1 A g^{-1})	Ma et al. (2018)
Agriculture waste	Coffee waste	$ZnCl_2$	[(Biochar 800 °C):$ZnCl_2$ = 1:2, 800 °C for 3 h]:cysteine = 1:0.3	743	6 M KOH aq	Three electrode	71.3 (at 1 A g^{-1})	Hong et al. (2020)
Agriculture waste	Coffee grounds	KOH	[Hydrothermal treatment (180 °C for 12 h) with 1 M H_2SO_4 aq., and then 600 °C for 2 h]:KOH = 1:4, 800 °C for 1 h	2906 ± 19	PYR13-TFSI	Two electrode	178.0 ± 12.0 (at 50 A g^{-1})	Biegun et al. (2020)
Agriculture waste	Cotton fibers	$Zn(NO_3)_2$	Cotton fiber in 1.0 M $Zn(NO_3)_2$ aq., 1273 K for 30 min	1390	1 M Et4NBF4/PC	Three electrode	126 (at 0.05 A g^{-1})	Sagisaka et al. (2018)
Agriculture waste	Japanese distilled liquor waste	KOH	[(Biochar 600 °C):KOH = 1:1, 800 °C for 1 h], plasma at 240 V in 0.01 M KOH aq	–	0.5 M KOH	Three electrode	211 (at 10 mV s^{-1})	Tashima et al. (2020)
Agriculture waste	Japanese distilled liquor waste	KOH	(Biochar 700 °C):KOH = 1:2, 900 °C for 1 h	2434	1 M TEABF4/PC	Two electrode	152 (at 0.1 mA cm^{-2})	Eguchi et al. (2020)

(continued)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Agriculture waste	Loofa sponge	KOH	(Biochar 600 °C):KOH = 1:4, 800 °C for 1 h	1819	1 M NaCl aq	Three electrode	93.0 (at 5 mV s^{-1})	Feng et al. (2018)
Agriculture waste	Oil palm kernel shell	KOH	(Biochar 500 °C):KOH = 1:4, 500 °C for 4 h	730	1 M H_2SO_4 aq	Two electrode	74.76 (at 0.3 A g^{-1})	Misnon et al. (2019)
Agriculture waste	Olive residue	KOH	(Biochar 300 °C):KOH = 1:2, 840 °C for 2 h	1626	1 M H_2SO_4 aq	Two electrode	224 ± 3 (at 250 mA g^{-1})	Elmouwahidi et al. (2017)
Agriculture waste	Papaya leaves	NaOH	(Biochar 400 °C):NaOH = 1:2.5, 720 °C for 1 h	2664	1 M Na_2SO_4 aq	Three electrode	98.47 (at 1 mV s^{-1})	Dulyaseree et al. (2017)
Agriculture waste	Silk	$ZnCl_2$	Silk:$ZnCl_2$:$FeCl_3$ = 3[g]:30[g]:2.5 M, 850 °C for 1 h	1285.31	1 M H_2SO_4 aq	Three electrode	178 (at 0.5 A g^{-1})	Zhang et al. (2018a, b, c, d)
Agriculture waste	Silkworm cocoon	KOH	(Biochar 400 °C):KOH = 1:2, 800 °C for 2 h	2723	6 M KOH aq	Three electrode	287 (at 0.5 A g^{-1})	Song et al. (2018)
Agriculture waste	Soybean waste	steam	(Soybean waste, pH 1, hydrothermal treatment 200 °C for 24 h), 800 °C for 1 h	1321	1 M Na_2SO_4 aq	Two electrode	220 (at 0.1 A g^{-1})	Sun et al. (2020)
Agriculture waste	Soybean waste	KOH	(Biochar 300 °C):KOH = 1:2, 800 °C for 2 h	1837.26	6 M KOH aq	Three electrode	321.1 (at 1 A g^{-1})	Zhou et al. (2018)
Agriculture waste	Straw cellulose waste residue	NaOH	(Biochar 500 °C):NaOH = 1:2.5, 750 °C for 1 h	2776.3	1 M H_2SO_4 aq	Three electrode	358 (at 0.5 A g^{-1})	Chen et al. (2019)
Agriculture waste	Tea-leaves	$ZnCl_2$	Tea-leaves:$ZnCl_2$ = 1:2, 700 °C for 2 h	1143.9	2 M KOH aq	Three electrode	296 (at 0.5 A g^{-1})	Ma et al. (2017)

(continued)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [m² g⁻¹]	Electrolyte	Cell	Best capacitance value [F g⁻¹]	Reference
Agriculture waste	Waste sugar residue	KOH	(Biochar 600 °C):KOH = 1:3, 700 °C for 2.5 h	1953	6 M KOH aq	Two electrode	273.31 (at 40 mA g⁻¹)	Hao et al. (2017)
Agriculture waste	Wheat gluten	KOH	(Wheat gluten, hydrothermal treatment 200 °C for 12 h):KOH = 1:3, 700 °C for 1 h	1805	6 M KOH aq	Three electrode	350 (at 0.5 A g⁻¹)	Xu et al. (2018)
Agriculture waste	Wine reside	KOH	Wine reside:KOH = 1:2, 1073 K for 1 h	1325	H₂SO₄ aq	Two electrode	260 (at 200 mA cm⁻²)	Guardia et al. (2019)
Agriculture waste	Wine residue	KOH	(Wine residue, hydrothermal treatment 523 K for 3 h):KOH = 1:2, 1073 K for 2 h	1861	1 M KOH aq	Three electrode	134 (at 1 A g⁻¹)	Alcaraz et al. (2020)
Crops	Corncob	KOH	(Biochar 400 °C):KOH = 1:3, 600 °C for 1 h	800	1 M H₂SO₄ aq	Three electrode	390 (at 0.5 A g⁻¹)	Karnan et al. (2017)
Crops	Corncob sponge	-	(Corncob sponge:EVA:CNT:CTAB = 0.2[g]:0.05[g]:0.05[g]:0.05[g]), 850 °C for 2 h	140.43	6 M KOH aq	Three electrode	213.4 (at 0.5 A g⁻¹)	Fang et al. (2019)
Crops	Corncob	KOH	(Corncob, citric acid, hydrothermal treatment 200 °C for 6 h):KOH = 1:(unclear), 700 °C for 2 h	952	1 M Na₂SO₄ aq	Three electrode	452 (at 10 mV s⁻¹)	Zhang et al. (2018a, b, c, d)
Crops	Corn straw	KOH	(Biochar 450 °C):KOH = 1:4, 800 °C for 1 h	2790	6 M KOH aq	Two electrode	327 (at 0.2 A g⁻¹)	Qiu et al. (2018)

(continued)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\,g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\,g^{-1}$]	Reference
Crops	Corn husk	KOH	(Biochar 500 °C):KOH = 1:2, 750 °C for 1.5 h	1109	seawater	Two electrode	144 (at 0.5 A g^{-1})	Raj et al. (2021)
Crops	Cornstalk core	KOH	[(Biochar 800 °C):rGO = 1:1]:KOH = 1:6, 800 °C 1 h	1281.8	6 M KOH aq	Two electrode	278 (at 1 mV s^{-1})	Liu et al. (2019a, b)
Crops	Ground grain hulls	KOH	(Biochar 800 °C):KOH = 1:4, 800 °C for 2 h	1376	1 M Na_2SO_4 aq	Two electrode	313.3 (at 0.5 A g^{-1})	Pang et al. (2020)
Crops	Rice husk	KOH	(Biochar 500 °C):KOH = 1:4, 700 °C for 1 h	2804	gel electrolyte (NaCl)	Two electrode	214.3 (at 0.2 A g^{-1})	Na et al. (2018)
Crops	Rice husk	KOH	(Rice husk, conc. H_2SO_4, 160 °C for 3 h):KOH = 5[g]:10[g], 900 °C 5 h	1855	(Tetrapropylammonium bromide):(Ethylene glycol) = 1:5 (mol ratio)	Two electrode	100 (at 0.1 A g^{-1})	Sathyamoorthi, et al. (2018)
Crops	Rice straw	KOH	(Biochar 800 °C):KOH = 1:3, 800 °C for 2 h	476.52	1 M Nacl aq	Three electrode	36.83 (at 5 mV s^{-1})	Wu et al. (2020)
Crops	Rice straw	KOH	(Biochar 500 °C):KOH = 1:(unclear), 750 °C for 30 min	1330	0.5 M H_2SO_4 aq	Three electrode	93 (at 10 mV s^{-1})	Nam et al. (2018)
Crops	Rice straw	KOH	(Biochar 600 °C): KOH = 1:3, 600 °C 1 h	1007	1 M H_2SO_4	Three electrode	332 (at 0.5 A g^{-1})	Sudhan et al. (2017)
Crops	Rotten potate	KOH	(Rotten potate, hydrothermal treatment, 200 °C for 8 h):KOH = 1:1, 750 °C for 1 h	960	6 M KOH aq	Three electrode	269 (at 1 A g^{-1})	Chen et al. (2016)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Fruits	Banana peel	KOH	[(Banana peel, 0.5 M H_2SO_4, 160 °C for 12 h]:KOH = 1:1, 900 °C for 1 h	1362	1 M $NaNO_3$ aq	Three electrode	115 (at 0.5 A g^{-1})	Fasakin et al. (2018)
Fruits	Boat-fruited sterculia seed	KOH	[(Boat-fruited sterculia seed) + (urea), hydrothermal treatment, 180 °C for 12 h]:KOH = 1:1, 800 °C for (unclear)h	1382	6 M KOH aq	Three electrode	337 (at 1 A g^{-1})	Wang et al. (2017a, b)
Fruits	Durian shell	KOH	(Biochar 400 °C):KOH = 1:4, 800 °C for 1 h	2535	6 M KOH aq	Three electrode	321 (at 0.5 A g^{-1})	Cai et al. (2020)
Fruits	Durian peel	KOH	[Upper part of [(durian peel) + (85 wt% H_3PO_4), 200 °C for 5 h]]:KOH = 3:2, 700 °C for 2 h	1809.32	6 M H_2SO_4 aq	Three electrode	364 (at 1 A g^{-1})	Zhou et al. (2020)
Fruits	Japanese citron	KOH	(Biochar 600 °C):KOH = 1:3, 800 °C for 1 h	2514	1 M H_2SO_4 aq	Three electrode	157 (at 1 mV s^{-1})	Tsubota et al. (2020)
Fruits	Mangosteen peel	NaOH	(Biochar 600 °C):NaOH = 1:3.5, 700 °C for 2 h	2623	6 M KOH aq	Three electrode	357 (at 1 A g^{-1})	Yang et al. (2019)
Fruits	Peach gum	KOH	[[(Peach gum):1,6-hexanediamine = 1:3], hydrothermal treatment, 180 °C 12 h]:KOH = 1:3, 700 °C for 2 h	1279	6 M KOH aq	Three electrode	406 (at 0.2 A g^{-1})	Lin et al. (2019)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\,g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\,g^{-1}$]	Reference
Fruits	Pineapple leaf fiber	KOH	(Biochar, 1 M H_2SO_4 aq., hydrothermal treatment, 150 °C for 12 h):KOH = 1:2, 800 °C for 1 h	1681	1 M H_2SO_4 aq	Three electrode	202 (at 5 mV s^{-1})	Sodtipinta et al. (2017a)
Fruits	Pineapple leaves	KOH	(Biochar, 0.5 M H_2SO_4 aq., hydrothermal treatment, 180 °C for 24 h):KOH = 1:3, 800 °C for 1 h	-	1 M Na_2SO_4 aq	Three electrode	131 (at 5 mV s^{-1})	Sodtipinta et al. (2017b)
Fruits	Pomegranate husk	$ZnCl_2$	[(Pomegranate husk):$ZnCl_2$ = 1:2, 800 °C for 2 h], 4 M urea aq.), hydrothermal treatment, 180 °C for 10 h	1754.8	2 M KOH aq	Three electrode	254 (at 0.5 A g^{-1})	Sun et al. (2017a, b)
Fruits	Pomelo peel	–	[(Biochar 900 °C), (diammonium hydrogen phosphate)aq. for 24 h], 900 °C for 2 h	807	2 M KOH aq	Three electrode	240 (at 0.5 A g^{-1})	Wang et al. (2018)
Fruits	Pomelo peel	KOH	[[(Pomelo peer, 1[g]) + (ammonium persulfate, 1[g])], 500 °C for 2 h]:KOH = 1:(unclear), 600 °C for 2 h	1193	6 M KOH aq	Three electrode	310 (at 0.5 A g^{-1})	Liu et al. (2019a, b)
Fruits	Pomelo peel	KOH	(Pomelo peel, 1 M KOH aq.), 800 °C for 1 h	1360	Na_2SO_4-NaI-KI	Two electrode	334.3 (at 0.5 A g^{-1})	Nguyen et al. (2020)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\,g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\,g^{-1}$]	Reference
Nuts	Chestnut	KOH	(Biochar 800 °C):KOH = 1:3, 800 °C for 1 h	1252.5	6 M KOH aq	Two electrode	173 (at 0.1 A g^{-1})	Januszewicz et al. (2020)
Nuts	Coconut shell	–	Coconut shell, 900 °C for 6 h	1194.4	1 M H_2SO_4 aq	Two electrode	258 (at 5 mA g^{-1})	Sun et al. (2017a, b)
Nuts	Coconut coir pith	NaOH	[(Biochar 650 °C):NaOH = 1:3], 700 °C for 1 h	2056	1 M H_2SO_4 aq	Two electrode	232.3 (at 0.1 A g^{-1})	Sesuk et al. (2019)
Nuts	Groundnut shell (peanut shell)	KOH	(biochar 600 °C):KOH = 1:3, 850 °C for 1 h	1700	6 M KOH aq	Two electrode	220.6 (at 0.5 A g^{-1})	Muthu Balasubramanian et al. (2020)
Nuts	Malva nut	KOH	[(Malva nut, hydrothermal treatment, 200 °C for 18 h), 500 °C for 60 min.]:KOH = 1:3, 700 °C for 90 min	2605	6 M KOH aq	Three electrode	312 (at 1 A g^{-1})	Ye et al. (2020)
Nuts	Peanut shell	NaOH	(Peanut shell, thermal dissolution carbon enrichment, 350 °C for 60mi.):NaOH = 1:2, 700 °C for 2 h	2746	6 M KOH aq	Two electrode	228 (at 1 A g^{-1})	Hu et al. (2020)
Nuts	Peanut shell	$ZnCl_2$ + CO_2	Peanu shell:$ZnCl_2$ = 1:2, 800 °C for 2 h with CO_2 flowing	1483	PVdF-HFP/EMIT/Mg (Tf)2	Two electrode	189 (at 125 A g^{-1})	Yadav et al. (2018)
Nuts	Pistachio shell	$ZnCl_2$ + CO_2 (plasma)	[Pistachio shell:$ZnCl_2$ = 1:, 500 °C for (unclear)h], CO_2 plasma for (unclear)h	1250	1 M KCl aq	Three electrode	118 (at 2.5 mV s^{-1})	Şahin et al. (2020)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Vegetable	Cauliflower	–	Cauliflower, 1000 °C for 3 h	1139	6 M KOH aq	Three electrode	228.9 (at 0.5 A g^{-1})	Du et al. (2018)
Vegetable	Lotus leaves	KOH	(Biochar 500 °C):KOH = 1:3, 700 °C for 3 h	2669.3	6 M KOH aq	Three electrode	343.1 (at 0.5 A g^{-1})	Yang et al. (2020)
Vegetable	Lotus root	K_2CO_3	(Biochar 700 °C):K_2CO_3 = 1:1, 700 °C for 4 h	1400	3 M KOH aq	Two electrode	273 (at 0.34 A g^{-1})	Rajendiran et al. (2019)
Vegetable	Mushroom	$KHCO_3$	(Biochar 500 °C):$KHCO_3$ = 1:3, 900 °C for 2 h	1788.1	1 M H_2SO_4 aq	Three electrode	354.8 (at 1.0 A g^{-1})	Chen et al. (2018)
Vegetable	Onion	KOH	Onion:KOH = 100[g]:4[g], 900 °C for 1 h	1914.9	6 M KOH aq	Two electrode	179.5 (at 0.5 A g^{-1})	Zhang et al. (2018a, b, c, d)
Food	Beancurd	KOH	(Biochar 400 °C):KOH = 1:4, 800 °C	2960	6 M KOH aq	Two electrode	207 (at 0.1 A g^{-1})	Lee et al. (2017)
Food	Beancurd	CH_3COOK	(Biochr 350 °C):CH_3COOK = 1:2, 750 °C for 2 h	1735	1 M H_2SO_4 aq	Two electrode	315 (at 0.1 A g^{-1})	Li et al. (2019)
Food	Beancurd	CH_3COOK	Beancurd + 15wt% CH_3COOK, 750 °C for 2 h	2180	1 M H_2SO_4 aq	Two electrode	355 (at 0.1 A g^{-1})	Li et al. (2018a, b)
Food	Indian Cake Rusk	KOH	(Biochar 450 °C):KOH = 1:3, 750 °C for 3 h	1413	1 M H_2SO_4 aq	Three electrode	381.0 (at 1.7 A g^{-1})	Kesavan et al. (2019)
Plant	Bamboo	KOH	(Biochar 300 °C):KOH:K_3[Fe $(CN)_6$] = 1:1:0.5, 2 h	1360	6 M KOH aq	Two electrode	ca. 150 (at 5 mV s^{-1})	Gunasekaran et al. (2018)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [m² g⁻¹]	Electrolyte	Cell	Best capacitance value [F g⁻¹]	Reference
Plant	Bamboo	KOH	(Biochar 700 °C):KOH = 1:3, 900 °C for 3 h	2221.1	3 M KOH aq	Three electrode	293 (at 0.5 A g⁻¹)	Zhang et al. (2018a, b, c, d)
Plant	Bamboo-cellulose fiber	NaOH	(Biochar 600 °C):NaOH = 1:2.5, 720 °C	2366	1 M Et4NBF4/PC	Two electrode	43 (at (unclear) mA g⁻¹)	Fujishige et al. (2017)
Plant	Bamboo waste	KOH	[[(Biochar 200 °C) in 1 M KOH aq., hydrauli press], 800 °C for 1 h], 900 °C for 2.5 h	1137.86	1 M H_2SO_4 aq	Two electrode	174 (at 1 mV s⁻¹)	Farma et al. (2021)
Plant	Bamboo shoots shell	KOH	Bamboo shoots chell:KOH = 1:1, 700 °C for 2 h	1351	1 M H_2SO_4 aq	Two electrode	223.21 (at 1 A g⁻¹)	Han et al. (2018)
Plant	Bamboo	steam	Bamboo, 940 °C for 240 min	1400	1 M Et4NBF4/PC	Two electrode	67 (at 5 mA cm⁻²)	Kikuchi et al. (2018)
Plant	Bamboo stems waste	$ZnCl_2$ + CO_2	(Biochar 600 °C):$ZnCl_2$ = 1: (unclear), 700 °C for (unclear)h with CO_2 flowing	–	1 M H_2SO_4 aq	Two electrode	154 (at 1 mV s⁻¹)	Taer et al. (2020a, b)
Plant	Bamboo	CO_2	[(Bamboo 20[g] + CH_3COOH 100[mL] + H_2O_2 100[mL]), 85 °C for 8 h], 9wt% guanidine phosphate, 800 °C for 3 h with CO_2 flowing	2001	1 M H_2SO_4 aq	Three electrode	153 (at 1000 mA g⁻¹)	Tsubota et al. (2017)
Plant	Bamboo	KOH	(Biochar 500 °C):KOH = 1:3, 800 °C for 1 h	ca. 1800	1 M H_2SO_4 aq	Three electrode	285 (at 10 mA g⁻¹)	Tsubota et al. (2018)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\,g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\,g^{-1}$]	Reference
Plant	Macroalgae	–	(Biochar 900 °C), 30% HNO_3, reflux 100 °C for 18 h	354	3 M KCl aq	Three electrode	376.7 (at 1 A g^{-1})	Pourhosseini et al. (2017)
Plant	Marine bloom green alga	$ZnCl_2$	Marine bloom green alga:$ZnCl_2$ = 1:4, 600 °C for 3 h	1910.84	1 M H_2SO_4 aq	Three electrode	332.4 (at 0.2 A g^{-1})	Xie et al. (2020)
Grass	Fern	H_3PO_4	Fen:H_3PO_4 = 1:1, 600 °C for 1 h	758	1 M H_2SO_4 aq	Three electrode	ca. 108 (at 1 mV s^{-1})	Trinh et al. (2020)
Grass	Miscanthus	KOH	(Biochar 700 °C):KOH = 1:4, 900 °C for 1 h	3024	1 M Et4NBF4/PC	Two electrode	110.8 (at 0.05 V s^{-1})	You et al. (2018)
Grass	Rose petal	KOH	(Biochar 600 °C):KOH = 1:4, 900 °C for 1 h	3384	5 M lithium bis (trifluoromethane sulfonyl)imide aq	Two electrode	56 (at 0.5 A g^{-1})	Xu et al. (2019)
Grass	Saccharum bengalense	$ZnCl_2$	Saccharum bengalense:$ZnCl_2$ = 1:(unclear), 800 °C for 20 min	2090	1 M Li_2SO_4 aq	Two electrode	102.6 (at 2 mV s^{-1})	Rawal et al. (2018)
Grass	Southern cattail	KOH	[[Southern cattail 4.0[g], KOH (unclear)[g]], graphene oxide 0.2[g]], 700 °C for 3 h	–	6 M KOH aq	Three electrode	277.5 (at 0.5 A g^{-1})	Amiri and Golmohammadi (2019)
Grass	Tassel tree flowers	KOH	(Biochar 400 °C):KOH = 1:4, 800 °C for1h	3310	6 M KOH aq	Three electrode	394 (at 0.5 A g^{-1})	Ma et al. (2019)
Grass	Tremella	KOH	(Biochar 400 °C):KOH = 1:5, 800 °C for 3 h	3760	6 M KOH aq	Two electrode	71 (at 1 A g^{-1})	Guo et al. (2017)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Tree	Auriculiformis bark	KOH	Auriculiformis bark:KOH = 1:1, 700 °C for 2 h	619.5	(unclear)M KCl aq	Three electrode	247 (at 1 A g^{-1})	Momodu et al. (2017)
Tree	Birch sawdust	NaOH	(Biochar 400 °C):NaOH = 1:1.25, 600 °C for 120 min	ca. 1600	4.9 M H_2SO_4	Two electrode	390 (at 0.3 A g^{-1})	Volperts et al. (2017)
Tree	Chinese fir sawdust	Steam, KOH	(Biochar 850 °C for 1 h with steam flowing):KOH = 1:6, 850 °C for 3 h	2395	6 M KOH aq	Two electrode	242 (at 0.5 A g^{-1})	Huang et al. (2017)
Tree	Cotton rose wood	–	Cotton rose wood, 800 °C for 3 h	486	2 M KOH aq	Three electrode	133 (at 10 mA cm^{-2})	Ma et al. (2020)
Tree	Cotton rose wood	–	Cotton rose wood, 800 °C for 3 h	355	2 M KOH aq	Three electrode	161 (at 5 mA cm^{-2})	Ma et al. (2021)
Tree	Eucalyptus bark	$ZnCl_2$	Eucalyptus bark:$ZnCl_2$ = 1:2, 800 °C for 2 h with CO_2 flowing	1721	0.5 M NaTFSI/EMITFSI	Two electrode	155 (at 0.5 mA cm^{-2})	Yadav and Hashmi (2020)
Tree	Eucalyptus leaves	$ZnCl_2$ + KOH	(Eucalyptus leaves + 25wt% $ZnCl_2$):KOH = 1:1, 900 °C for 1 h	2638.8	1 M CH_3COONa aq	Two electrode	208 (at 1.25 A g^{-1})	Jain et al. (2020)
Tree	Loblolly pines	NaOH	(Biochar C):4 M NaOH aq. = 3[g]:40[mL], 800 °C for 2 h	960	6 M KOH aq	Two electrode	74 (at 20 mV s^{-1})	He et al. (2017)
Tree	Metasequoia	KOH	(Biochar 500C):KOH = 1:3, 700 °C for 60 min	1831	6 M KOH aq	Three electrode	326 (at 0.5 A g^{-1})	Jia et al. (2019)

Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\,g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\,g^{-1}$]	Reference
Tree	Moringa cleifera fruit shell	$ZnCl_2$	Moringa cleifera fruit shell:$ZnCl_2$ = 1:2, 800 °C for 5 h	–	3 M KOH aq	Three electrode	130 (at 0.5 A g^{-1})	Palisoc et al. (2020)
Tree	Neem leaves	$ZnCl_2$	Neem leaves:$ZnCl_2$ = 1:2, 800 °C for 2 h	705	1 M LiClO4 in EC/PC	Two electrode	74 (at 1 mA cm^{-2})	Ahmed et al. (2018)
Tree	Pine bark	Mg	Pine bark:Mg = 1:3, 800 °C for 1 h	2055	EMIMBF4	Two electrode	193 (at 1 A g^{-1})	Wang et al. (2019)
Tree	Pine tree	KOH	(Biochar 500C):KOH = 1:3, 800 °C for 1 h	2500	1 M H_2SO_4 aq	Three electrode	190 (at 10 mA g^{-1})	Kalderis et al. (2020)
Tree	Platunus tree bark	ZnO	Platanus bark 8[g] + ZnO 8[g], 800 °C for 2 h	1512	6 M KOH aq	Three electrode	286 (at 0.5 A g^{-1})	Yu et al. (2020)
Tree	Pines of Pinus nigra	KOH	(Pines of pinus nigra, HNO_3 treatment):5 M KOH = 1:(unclear), 1000 °C for 5 h	–	6 M KOH aq	Three electrode	165 (at 3.3 A g^{-1})	Khalid et al. (2020)
Tree	Pinecone	KOH	Pinecone:KOH = 1:4, 800 °C for 1.5 h	1169.31	1 M H_2SO_4 aq	Three electrode	185 (at 0.5 A g^{-1})	Rajesh et al. (2020)
Tree	Pine pollen	$MgCO_3$	850 °C for 2 h	1311.2	6 M KOH aq	Three electrode	419.6 (at 1 A g^{-1})	Wan et al. (2019)
Tree	Pollen cone of Kauri pine	KOH + CO_2	(Biochar 450 °C):KOH = 1:6, 800 °C for 2 h with CO_2 flowing	2314	1 M Na_2SO_4 aq	Two electrode	127–156 (at 0.5 A g^{-1})	Hor and Hashmi (2020)

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Table 4 (continued)

Category	Raw material	Activator	Activation condition	BET specific surface area [$m^2\ g^{-1}$]	Electrolyte	Cell	Best capacitance value [$F\ g^{-1}$]	Reference
Tree	Rubberwood sawdust	KOH	(Biochar H_2SO_4 treatment): KOH = 1:2, 900 °C for 5 h	1932	1.0 M LiTFSI aq	Two electrode	100 (at 0.1 A g^{-1})	Le Calvez et al. (2019)
Tree	Rubber wood wastes	H_3PO_4	Rubber wood wastes: H_3PO_4 = 1:1, 800 °C for 4 h	693	1 M H_2SO_4 aq	Two electrode	129 (at 1 mV s^{-1})	Thubsuang et al. (2017)
Tree	Syzygium oleana leaves	KOH + CO_2	(Biochar 250°C): KOH = 1:3.5, 600 °C (N_2 flow) and then 850 °C for 150 min. (CO_2 flow)	1137.61	1 M H_2SO_4 aq	Two electrode	188 (at 1 mV s^{-1})	Taera et al. (2020a, b)
Tree	Thin bristle fibers of plane tree fruits	NH_3	Thin bristle fibers of plane tree fruits, 900 °C for 50 min. with NH_3 flowing	2254	1 M Et4NBF4/AN	Two electrode	240.5 (at 1 A g^{-1})	Zhang et al. (2020)

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Engineered Biochar as a Catalyst

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Abstract Biochar is a carbonaceous material obtained by thermochemical treatment of biomass. Preparation of biochar for a specific application can be done by changing its physicochemical properties via different modification strategies and selection of raw materials. Biochar is now being developed as an alternative catalyst with many applications, including environmental remediation and energy generation, aiming to substitute conventional catalysts. Biochar is cheaper, has a lower risk of leaching and a wide range of functional groups. Pristine biochar without any previous modification often has limitations for its catalytic potential in terms of its lower surface area, porosity, mineral components, and functional groups. These properties can be enhanced by the modification of biochar via different methods. This chapter discusses the use of modified biochars as catalysts for environmental remediation, viz. advanced oxidation processes, photocatalysis, and energy generation, viz. biogas, biofuel, and syngas.

Keywords Biochar · Metal · Catalyst · Advanced oxidation processes · Photocatalysis

1 Introduction

Biochar is the carbon-containing material obtained by pyrolysis of biomass in oxygen-deficient environments (Lehman and Joseph 2009). Biochar is distinguished from charcoal in that biochar is intended for use in soil application or broader environmental uses (Ender et al. 2012; Lehman and Joseph 2015; Méndez et al. 2013).

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In the last few years, biochar has received great attention as a precursor of new and more advanced materials such as catalysts, adsorbents, or super condensers (Low and Yee 2021; Rawat et al. 2022; Yuan et al. 2022).

In most cases, the production of pristine biochar via pyrolysis, gasification, or other thermal treatments, leads to relatively low surface areas that limit their advanced uses. Modification of biochar can produce carbonaceous materials with optimized properties also referred to as 'engineered biochar' (Duan et al. 2019). Different methods have been proven based on chemical, physical, or biological treatments (Wang et al. 2018a, b; Rajapaksha et al. 2016). Consequently, engineered biochar is defined as the derivative of pristine biochar that is transformed to improve its physicochemical properties such as specific surface area, porosity, cation exchange capacity, surface functional groups, pH, or redox activity (Wang et al. 2018a, b). While biomass-derived activated carbon can be counted as one type of engineered biochar (Fig. 1), the definition of engineered biochar is much broader. Additionally, most of the biochar engineering methods are more convenient or less expensive than those used in the activated carbon preparation processes.

The combination of different properties of modified biochars make them interesting catalysts for a wide range of applications. A brief description is given in the present chapter about their use as a catalyst for environmental remediation, specifically in advanced oxidation processes, photocatalysis; and energy generation (mainly focused on biogas, biofuel, and syngas).

Fig. 1 Properties and applications of biochar as a feasible catalyst
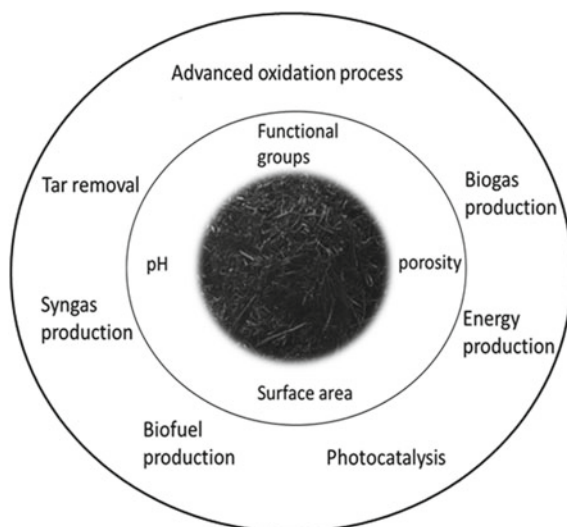
2   Modified Biochar as Catalysts

2.1   Modified Biochar as a Catalyst in Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been traditionally used to remove recalcitrant organic compounds (drugs, dyes, endocrine disruptors, and pesticides) or inorganic pollutants, particularly heavy metals and metalloids from wastewater (Zhao et al. 2021b). This technology involves the use of highly oxidizing molecules such: hydroxyl radical (OH^-*), sulfate (SO_4^-*), hydroperoxyl (HO_2^-*), and superoxide (O_2^-*) (Zhao et al. 2021a), to produce low-risk substances or to directly mineralize pollutants into CO_2 and H_2O (Zhao et al. 2017; Zhao et al. 2021a). Processes, viz. ozonation, ultraviolet (UV) radiation, Fenton reaction, or their combination, are required to produce them.

According to Kumar et al. (2021), although these processes offer a way to remove some pollutants, there are reasons why they are not entirely feasible. For example, ozonation removes recalcitrant organic compounds and odors, and can be used as a pre- or post-treatment, but its implementation is expensive. UV radiation can reduce the color of the sample; however, it requires a large amount of energy. In addition, although the Fenton reaction shows better results (because it favors removing different organic compounds), it can produce intermediate ions that are difficult to remove, requires additional chemicals to control the pH and it works better when coupled with other techniques, which also apply to the above-mentioned processes.

Another shortcoming is the high cost of the catalysts (Anto et al. 2021). Consequently, many research studies have been carried out suggesting alternative catalysts, so that is when pristine and modified biochars become relevant. Biochar is cheaper than any traditional catalyst, captures carbon during its fabrication process, lowers the risk of leaching, and additionally, has a wide range of functional groups (depending on the type of biomass, pyrolysis conditions, and activation process) (Shan et al. 2020; Wang et al. 2021). The sum of these properties promotes the direct binding of pollutants or oxidizing agents to boost its degradation capacity. However, it is very important that both the biochar and the oxidizing agents such (H_2O_2), persulfate (PS), peroxymonosulfate (PMS), and peroxydisulfate (PDS) are activated for this degradation to occur as it increases the adsorption capacity and the subsequent removal of pollutants (Anto et al. 2021). In some cases, since the raw materials have a wide variety of functional groups, the pristine biochar does not need to be modified to activate the oxidizing agent. This can reduce the cost of the process. For example, in case of sewage sludge biochar, the addition of H_2O_2 or PMS removed trichloroethylene (83%) and triclosan (100%) (Wang et al. 2022), respectively.

When the biochar itself does not activate the oxidizing agent, it can be done through:

(1)   Nitrogen doping to make its surface reactive that facilitates electron transfer;

(2) Coupling metals to the biochar, since these are prone to oxidize that favors the activation of either H_2O_2, PMS or PDS;

(3) Elaborating composites with the addition of heteroatoms to the biochar, as well as metals and graphitic materials (Zhao et al. 2021a, b, c).

Each of the previous processes will activate the biochar, thus allowing the oxidizing agent to interact with the surface and produce free radicals, which boost pollutants degradation in the medium (Luo et al. 2021). Wang et al. (2022) reported a particular case of sugarcane biochar doped with Fe. The addition of H_2O_2 following oxidation resulted in obtaining the corresponding free radical that achieved 99.7% removal of the Orange G dye. Table 1 includes a description of different types of biochar, the amount of oxidizing agent, and their removal efficiency for different pollutants.

Currently, research is focusing on the use of sulfur compounds. It has many advantages since the derived radicals (e.g., SO_4^-*) have a longer half-life, are less affected by pH, pose a lower risk to the environment, are more selective, have higher potential as an oxidizing agent, and their use in AOPs guarantees an efficient removal of organic pollutants such as chlorophenol, dioxane, ibuprofen, naphthalene, and organophosphate pesticides (Ushani et al. 2020; Zhao et al. 2021a, b, c). In fact,

Table 1 Biochar-based catalysts as oxidant agents activators

Catalyst	Oxidant (mM)	Pollutant (mM)	Removal efficiency (%)	References
Pine needle biochar	PMS (8.0)	1,4-dioxane (20.0)	90.0	Wang et al. (2022)
Sunflower stalk-derived biochar	PDS (10.0)	p-nitrophenol (0.72)	85.85	
Sludge biochar	PS (1.85)	4-clorophenol (0.039)	92.3	
	PMS (0.8)	Triclosan (0.034)	98.9	Pi et al. (2019)
Soybean residue biochar/alkali activation	PDS (1.0)	Tetracycline (1.13 $\times 10^{-4}$)	77.35	Li et al. (2021)
Sawdust biochar	PDS (10.0)	Clofibric acid (0.10)	97.8	Zhao et al. (2021c)
N-doped biochar	PDS (1.0)	Sulfadiazine (1 $\times 10^{-5}$)	96.2	Wang et al. (2022)
Spent coffee biochar/Co impregnated	PMS (0.6)	Tetracycline (0.2)	97	Nidheesh et al. (2021), Zhao et al. (2021a)
Fe^0 + biochar	PS (1.0)	Acetaminophen (2 $\times 10^{-6}$)	100	Zhao et al. (2021b)
CO_2-activated biochar	PDS (5.0)	Phenol (0.5)	99.5	Wang et al. (2022)

studies such as Cui et al. (2021) suggest that using biochar in tandem with PMS and ferric compounds provide a more powerful and reliable alternative (good results are obtained and it is even possible to reuse the catalyst) to degrade different types of recalcitrant organic pollutants in water. This leads to the subsequent large-scale establishment of these AOPs in water treatment plants to guarantee a higher quality of the resource and reduce the risk to ecosystems and public health.

2.2 Modified Biochar in Photocatalysis of Emerging Pollutants

Photocatalysis by semiconductors has been used for the removal of various environmental pollutants. Biochar can be combined with various nanocatalysts to form hybridized biochar-supported photocatalysts. It can support various nanocatalysts owing to its chemical stability, presence of varied functional groups on its surface, and electrical conductivity (Liu et al. 2015; Xia and Larock 2010; Dutta et al. 2014). In these hybridized nano-photocatalysts, biochar acts as a charge carrier and provides binding sites. Adding biochar also helps to improve the surface area, porosity, ion exchange capacity, binding capacity, photostability, catalytic ability, and recovery (Zhu et al. 2016). Biochar-supported photocatalysts can be synthesized by different methods, viz. sol–gel, ultrasound-assisted, thermal polycondensation, solvothermal, hydrothermal, hydrothermal carbonization, self-assembly, and ball milling. These hybridized photocatalysts are highly efficient for the degradation of various water pollutants such as synthetic dyes, phenols, heavy metals, and pharmaceuticals. Using biochar as a support to photocatalysts increases the photodegradation of several contaminants due to the presence of hydrophilic and hydrophobic surface functional groups, a large number of available pores, aromatic structure, and mineral components. The mechanisms involved in adsorption of organic pollutants are π–π stacking, H_2 bonding, and electrostatic interactions (Wang et al. 2009). Hybridized nano-photocatalyst biochar increases surface area and active sites in comparison to non-hybridized photocatalysts. Biochar acts as a matrix providing uniform dispersion of nanoparticles, which increases the active sites, light scattering, and photodegradation (Lisowski et al. 2017). Biochar promotes storage and transport of electrons. Electron storage is due to the redox activity of quinones present in biochar. Therefore, the more quinone content, the greater its ability to donate an accept electrons. Electrons transfer takes place from the bulk chemical electron donor to the receptor (Yu et al. 2015). This electron transfer between the reactants is mediated by the redox-active moieties and the condensed aromatic ring present in biochar (Xu et al. 2013). The aromatic structure of biochar helps in delocalizing the electron from the active site to the receptors site. In biochar-supported photocatalysts, the efficiency of pollutant degradation is more, due to increased electron transfer that increases the electron–hole separation and thus decreases the electron–hole recombination (Ahmaruzzaman 2021).

2.3   Modified Biochar as a Catalyst in Energy Production Applications

The conversion of different organic wastes into energy is gaining attention in the actual worldwide energy crisis due to their environmental sustainability.

Biogas via anaerobic digestion

Biogas production by anaerobic digestion of different organic wastes is a promising and sustainable management method. Anaerobic digestion is a cost-effective and widely used method to produce biogas from different organic wastes including industrial wastes with higher moisture content to get versatile high-value fuels (Ramola et al. 2020). It is based on a microbial process, where organic wastes are transformed into stable macromolecules by hydrolysis, acidogenesis, acetogenesis, and methanogenesis, which occur sequentially. In some cases, the anaerobic digestion is limited by low methane yields, process instability, and different inhibition problems. In the past years, different studies have revealed the benefits of using different carbon materials such as activated carbons, graphite, or biochar during anaerobic digestion. Among them, biochar is low cost and can be produced from renewable raw materials. In addition, biochar production may include a wide variety of physicochemical properties by controlling feedstocks, pyrolysis operating conditions, and activation processes (Nanda et al. 2016), resulting in "tailor-made biochar" for specific applications. Biochar as an additive in anaerobic digestion systems could improve microorganism metabolism and optimize the structure of microbial communities, alleviate inhibitor stress, and maintain anaerobic digestion process stability (Wang et al. 2018a, b).

Wei et al. (2020) studied the use of corn biochar in anaerobic digestion of primary sludge and found that dosing biochar in ratios of 1.82, 2.55, and 3.06 g/g, total solids increased methane content from 67.5% to 81.3–87.3% and enhanced methane production by 8.6–17.8%. The results demonstrated that biochar provided a strong buffering capacity, alleviated NH_3 inhibition, and increased sludge conductivity. Similar effects were previously observed by Zhang et al. (2019). These researchers studied the impact of different biochar types on the anaerobic digestion of sewage sludge and found that all types of biochar significantly enhanced the methane production but the maximum yield was obtained with biochar having a maximum specific surface area (Zhang et al. 2019). In a similar way, Deng et al. (2021) studied the effect of two biochar samples obtained by pyrolysis of whiskey by-products at different temperatures and found that the biochar obtained by pyrolysis at 700 °C enhanced biomethane yield by 5%. The authors proposed that the capacity of 700 °C derived biochar for enhancing interspecies electron transfer was related to a moderate graphitization degree and a high abundance of surface nitrogen and especially, in the quinone functional group. These authors found that a further increase in the pyrolysis temperature above 700 °C reduced the abundance of surface functional groups on the biochar, which led to the decreased capacity in promoting interspecies electron transfer.

Chiappero et al. (2020) suggested that the effect of biochar addition to anaerobic digestion was related to the following potential mechanisms: increase of the buffering

capacity of the anaerobic digestion system; mitigation of inhibition phenomena or agents; support media for biomass immobilization; promotion of syntrophic metabolism; enhancement of digestate quality; biogas cleaning and upgrading. They concluded that key biochar properties were specific surface area, porous structure, and distribution, nature of surface functional groups, elemental composition, and ash content. Finally, considering the digestate, biochar has been reported to enhance its quality in terms of nutrient retention, increase of the C/N ratio, and reduction of nutrient leaching, and consequently, biochar doesn't need to be separated from digestate (Fagbohungbe et al. 2017).

Energy from biomass

The application of biochar-based catalysts for biomass conversion, such as polysaccharides hydrolysis, biodiesel production, bio-oil upgrading, etc. have been widely studied. During biomass gasification, the formation of tar hinders the process as tar condensation reduces the energy efficiency and results in contamination and blockage of downstream operations. The catalytic transformation of tar possesses the capability of converting the tar to components of syngas, i.e., hydrogen and carbon monoxide.

Biofuel production

Biodiesel is a renewable, nontoxic, and biodegradable substitute for petrochemicals. According to the American Society for Testing and Materials (ASTM), biofuel (mono-alkyl esters of long-chain fatty acids) is a renewable fuel with comparable properties to fossil fuels that can be created from the transesterification of vegetable oils or the esterification of free unsaturated fats with alcohols (Hameed et al. 2009). Two different types of catalysts are used for the transesterification process: homogeneous and heterogeneous. Homogeneous catalysts are in the same phase whereas heterogeneous catalysts are in different phases as that of reactants. Homogeneous catalysts have disadvantages such as difficult separation from reaction mixture, low regeneration, and high-water consumption for purification of biodiesel thus increasing the production costs (Ramos et al. 2019). Heterogeneous catalysts such as $WO_3/ZrO_2/Al_2O_3$, TiO_2/ZrO_2, and Al_2O_3/ZrO_2 have been successfully used for high production of esters with 90% yield at 250 °C and 94% yield at 175 °C. However, these catalysts are expensive (Lee et al. 2017).

Biochar catalysts are used for producing biofuels through transesterification and esterification reactions. Basically, there are two types of biochar catalysts that have been used for biodiesel production, viz. (a) acid-functionalized biochar catalysts and (b) base-functionalized biochar catalysts. Among acid functionalized, sulfonated biochar are the most commonly used heterogeneous catalysts for biodiesel production. The sulfonation of biochar can be easily achieved by impregnating the biochar with concentrated H_2SO_4 at a high temperature or by exposing the biochar to gaseous SO_3, resulting in the immobilization of $-SO_3H$ groups on their surface (Cao et al. 2017). Dehkhoda et al. (2010) have studied the use of sulfonated biochar as a catalyst for transesterification using canola oil, and esterification using waste vegetable oil in the presence of ethanol. These authors showed that catalysts with the maximum surface area and acid density have the maximum catalytic activity for the production

of biodiesel in the presence of methanol as the reagent. Furthermore, the catalyst with the highest surface area indicated the highest transesterification activity among the catalyst with similar acid densities. This concluded that biochar has a tremendous potential to be used in a process converting a high free fatty acid raw material to biodiesel. Lathiya et al. (2018) used sulfonated biochar from the waste orange peel as a catalyst in biodiesel production and achieved 91.68% of conversion under optimum reaction conditions using a catalyst concentration of 5%. Cardoso Bastos et al. (2021) also studied the optimization of biodiesel production using a sulfonated biochar. These authors found that reusing the catalyst with purified jupati oil maintained the catalytic activity of around 80% of ester content until the fourth reaction cycle.

Biochar has been successfully used to convert fats into esters. Some of the commonly used fat raw materials are waste vegetable oil, canola oil, mixture of palmitic, stearic acids, soybean oil, waste cooking oil, sunflower oil, etc. (Lee et al. 2017). The surface area and acid groups of biochar influence its catalytic activities. In this regard, more number of $-SO_3H$ groups, surface area, and high density of acid sites have been shown to yield higher biodiesel (Shu et al. 2010). Some of the advantages of using biochar catalysts for biodiesel production include: its easy preparation, abundant raw material and absence of toxic heavy metals as in case of some of the conventional heterogeneous catalysts. The solid biochar catalysts can be compared with the conventional heterogeneous catalyst in terms of ester yield (Lee et al. 2017).

Some of the disadvantages of using biochar catalysts for biodiesel production is the leaching of $-SO_3H$ functional groups after some uses which cause decreased functional properties of biochar catalysts and thus lowers the reusability chances. Also, impurities present in crude oil such as chlorophylls and phospholipid and some of the impurities present in microalgae biochar such as Cl and P can impair the catalytic activities of biochar (Dong et al. 2015).

More recently, alkali biochar-based catalysts (CaO-biochar, KOH-biochar, or K_2CO_3-biochar) were prepared for biodiesel production. These catalysts showed a high biofuel yield and decent reusability, making them an appealing option in contrast to existing transesterification catalyst frameworks (Vakros 2018). Calcium oxide is a commonly used catalyst because of its vast availability and low cost although it has certain disadvantages such as loss of activity and less surface area.

Syngas production and tar removal by biochar catalysts

Syngas or synthetic gas is a mixture of H_2 and CO. It is produced through the gasification of biomass. Syngas is an initial and/or intermediate feedstock for heat and power generation as well for the production of fuels and chemicals through Fischer–Tropsch synthesis (Bartholomew and Farrauto 2005). The use of biochar as a catalyst has been reported to increase the production of syngas (15–46 wt%) and hydrogen fraction (0–27 vol%) (Ren et al. 2014). Biochar is also used as a catalyst in Fischer–Tropsch synthesis. Yan et al. (2013) used pine wood biochar as a support material for the synthesis of carbon-encapsulated iron nanoparticles that were then used as a catalyst for the conversion of syngas to liquid fuels. About 90% of CO

was converted to liquid hydrocarbon with 70% selectivity and olefins being the most dominant liquid hydrocarbon product.

Tar is made up of aromatic hydrocarbons such as toluene, naphthalene, phenol, styrene, and polycyclic aromatic hydrocarbons (Lee et al. 2017). Tar formation consumes carbon atoms of biomass during gasification and thus reduces the yield of syngas. Condensable tar also blocks pipes and other instruments and contaminates the syngas. The application of tar-contaminated syngas adversely affects its application as combustion of such syngas produces more aerosols and soot particles and thus ends up polluting the atmosphere (Shen et al. 2015). Conventional catalysts suffer from deactivation and poor or no recovery. This calls for the development of a cost-effective catalyst for tar removal during the gasification process.

Several properties of biochar such as surface area, mineral content, and functional groups affect its catalytic activity for tar removal. The presence of inorganics in biochar increases its catalytic activity. However, biochar formation at high temperatures may have decreased catalytic activity due to the reaction of inorganics with metal oxide.

The catalytic activity of biochar for toluene removal is also enhanced by several activation techniques that help increasing the surface area, pore diameter, and pore volume (Bhandari et al. 2014). Loading biochars with metals such as Ni and Fe can increase the catalytic activity for toluene removal. For example, loading 13% Fe on biochar resulted in the complete removal of toluene at 800 °C (Kastner et al. 2015). Similarly, Ni loading on biochar has shown to remove 96% of tar in syngas (Wang et al. 2011). Rice husk biochar-supported Ni/Fe catalyst increased the conversion efficiency of condensable tar to 92.3% from 42% which was achieved without any Ni/Fe loading. Alkaline oxygenated groups also contribute to its catalytic activities, whereas acidic groups disappear at a high temperature and do not contribute to cracking reactions (Klinghoffer et al. 2015).

3 Conclusion and Future Prospects

Studies on biochar-based catalysts are still in early stages and purpose-driven synthesis is required for its wider industrial applications. For better functioning of biochar as a catalyst, it is important to know the effects of pyrolysis conditions and raw materials on the physicochemical properties. Also, it is equally important to know the relationship between the catalytic activity of biochar and its physicochemical properties. The catalytic properties of biochar are affected by its surface area, pore size, and availability of $-SO_3H$ groups. Activation or modification of biochar is often done for its better functioning as a catalyst. Future prospects should also include the co-production of biochar with desired catalytic properties and later its use directly as a catalyst for various functions.

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Engineered Biochar as Construction Material

Diksha Pandey, Monika Chhimwal, and R. K. Srivastava

Abstract Biochar has a broad array of applications and is deployed in a variety of fields, including agriculture, sustainable development, and geoengineering. Various engineering methods have recently been developed and used to widen the application of biochar. One of them is the use of engineered biochar as a construction material. It can be exploited as a material for construction due to properties such as chemical stability, flammability, and low thermal conductivity. This chapter provides an overview of the properties of engineered biochar that make it suitable for the role of construction material. Factors such as pyrolysis conditions specifically, pyrolysis temperature, heating rate as well as pressure, along with various construction material properties have been depicted here. This chapter also highlights the implications of engineered biochar on the physical, mechanical, and durability aspects of building materials. Comprehensively, this engineered biochar is being used as a construction material due to a number of unique and interesting qualities, including the capability to build in a carbon-negative manner in addition to its applicability as an insulating material, biochar-based clay and lime plasters, building bricks, concrete and roof tiles. The chapter also aims to examine engineered biochar's current and future implications in the construction field.

Keywords Engineered biochar · Geoengineering · Adsorption · Pyrolysis · Construction material

1 Introduction

Biochar is a porous substance having various functional groups on the surface and is made from a variety of organic materials. Usually, pristine biochar has lower adsorption capacity than activated biochar, because of its low density and small particle size (Wang et al. 2017). To maximize the adsorption competency of biochar and its application in different areas, different engineering techniques have been proposed

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and used in soil improvement, waste management, geoenvironmental applications in addition to climate mitigation. The creation of an activated or modified form of biochar is called engineered biochar. Engineered biochar is a derivation of pure biochar that has been improved by physical, chemical, and biological means (e.g., properties such as surface area, porosity, cation exchange capacity, surface functional group, pH, etc.) and its adsorption capacity compared to pristine biochar (Yao et al. 2013).

In recent years, engineered biochar has gotten considerable attention as a building material, with a new trend of using it as an additive or replacement in cementitious composites (Restuccia et al. 2020; Belletti et al. 2019). Engineered biochar-containing constructional material provides much higher structural strength and improved permeability in contrast to pristine biochar. These findings suggest that engineered biochar has the capacity to be used as a carbon-sequestering admixture in construction materials and waste recycling methods (Gupta et al. 2017). Besides, the construction industry is expected to emit more greenhouse gases as the population grows and demands for a better-built environment increases, CO_2 emissions rapidly approaching a pivotal point that could result in irreversible climate change. The earth's capacity to neutralize the CO_2 emissions through the natural carbon cycle has been over-stretched. So reducing cement-based material productions could result to bring positive changes in the climate. Engineered biochar holds a lot of potential as a CO_2 absorbent material in construction applications (Akinyemi and Adesina 2020).

2 Properties of Engineered Biochar Suitable for Geoengineering and Advantages

The use of biochar as a material in construction applications is a relatively new area of research. Various raw materials and production processes have been used in various studies with the purpose of improving some properties of the end product via biochar. Pyrolysis temperature, pyrolysis rate, and pressure are regarded to be the most critical factors that determine textural properties among the several approaches that can affect the structure of the modified biochar (Newalkar et al. 2014). Pyrolysis temperature is significant because it is correlated to physical processes during biochar preparation such as volatile emission, char skeleton carbonization, pore creation, and broadening. The pyrolysis rate affects the physical mass transfer of volatiles at a specific temperature (Antal et al. 2003; Boateng 2007). Biochar also undergoes a secondary reaction at high temperatures, which enhances the formation of gas and liquid while decreasing the quantity of char. The physicochemical features of biochar, such as elemental composition, surface functional groups, and surface adsorption are affected by pyrolysis temperature (Shaaban et al. 2013; Yuan et al. 2014). Higher temperatures produced more activation energy, which resulted in more pore formation and enhanced surface area of biochar (Gupta et al. 2017; Ramola et al. 2020). Longer vapor residence time and lower temperature can result in increased biochar yield

(Encinar et al. 1996). Although residence time has little effect on char yield, it does change the composition of bio-oil and gaseous products (Mohamed et al. 2013). The textural properties of biochar are also influenced by pyrolysis pressure. Pyrolysis pressure has an impact on surface area as well as on biochar reactivity. When pressure was raised from 5 to 10 bar, surface area decreased, but it increased when pressure was raised from 10 to 20 bar (Newalkar et al. 2014). Apart from this, high chemical stability, low thermal conductivity, and low flammability are three qualities that make biochar ideal for use as a construction material.

2.1 Chemical Stability of Engineered Biochar

The chemical stability of biochar is mostly determined by the stability of fixed carbon in addition to the existence and abundance of oxygen groups and the presence of reactive oxygen. Moreover, the oxygen to carbon ratio (O: C ratio) is generally reported to estimate a threshold for relative stability of biochar. However, this ratio is not a robust indicator of inertness of carbon in biochar (Ndirangu et al. 2019). Chemical stability can possibly be achieved by incorporating biochar into cementitious materials for various construction applications. Better chemical stability of biochar is proficient when fast pyrolysis at a temperature of 800 °C is used. This is attributable to the fact that at a low pyrolysis temperature of 350 °C, only small amounts of carbon nutrients with low sorptive capacities are formed, that are required for sequestration (Novak et al. 2009; Gundale and Deluca 2006). At higher temperatures, higher carbon contents and aromaticity are produced accompanied by increased surface area needed for sorption while oxygen and hydrogen volume are reduced (Chen et al. 2008; Khanmohammadi et al. 2015). When biochar is blended with cementitious materials, the reactive areas are reduced, resulting in improved chemical stability. Apart from that, the use of engineered biochar diminishes alkali and alkaline base contents in soil amendment through biomass particle pulverization and thermal pretreatment. This aids in the fluidization of the combustion process while also reducing the biomass polymer structure (Kambo and Dutta 2015).

2.2 Low Thermal Conductivity

Low thermal conductivity is contributed by the involvement of a broad range of numerous nanopores, mesopores, and micropores on the surface of biochar particles; each with various sizes, shapes, and orientations which affect their performances differently (Askari et al. 2015) However, the distribution of pores depends on the raw material used and pyrolysis temperature (Brewer et al. 2014). Pores present in biochar prevent heat bridging inside the concrete, resulting in better building insulation. This is critical for lowering energy usage in building heating and cooling.

Depending on the temperature of biochar production, pores in biochar have different tendencies. When pyrolysis is carried out at a higher temperature, the volume of the pores normally expands (Bird and Ascough 2012). The average thermal conductivity of conventional concrete is between 0.62 W/(mK) and 3.3 W/(mK) (Cuthbertson et al. 2019). On the addition of a higher mixing ratio of biochar into a cement-based material, a thermal conductivity of 0.138–0.155 W/(mK) was achieved. This was 49.68–67.21% lesser than the conventional cement biocomposite (Lee et al. 2019) It was achievable because the pores in the additional biochar disrupt the thermal bridge in the cementitious materials to enhance the thermal insulation in the various applications. As a result, it is anticipated that energy expenses for heating and cooling structures will be reduced.

2.3 Flammability

Using biochar as a construction material, flammability is a critical determinant for fire safety. Biochar produced by slow pyrolysis shows no combustion front propagation (Zhao et al. 2014). However, fast pyrolysis produced biochar with a higher combustion front is by virtue of the presence of more reactive volatiles on the surface, such as alcohol and carboxylic acid groups, than slow pyrolysis produced biochar. Slow pyrolysis of biochar has a smaller surface area than fast pyrolysis and is more successful in reducing carbon-free radicals, which causes biochar to be less flammable. It was observed that besides the chemical stability, biochar are thermally stable materials and hinder fire propagation by slowing the passage of oxygen and fuel required for combustion in the presence of a carbonaceous wall. Thermal treatment of biomass produces free radicals that can react with oxygen, metals, and halogens in the environment (Amonette and Joseph 2009).

After production, the storage of biochar is reported to enhance the elimination of free radicals by reactivity with air and the rearranging of carbon planes, which reduces flammability. The majority of cement-based constructions are engineered with fire safety in mind. This is because engineered biochar, made by altering pristine biochar is prone to ignite when incorporated in buildings. As a result, extra caution must be taken to ensure that the substance is nonflammable (Table 1).

3 Effect of Engineered Biochar on the Characteristics of Building Materials

Engineered biochar has a tremendous influence on the physical, mechanical, and long-term durability of construction materials, in particular, cement and mortar (Fig. 1).

Table 1 Effect of pyrolysis conditions on properties of engineered biochar as construction material (Akinyemi and Adesina 2020)

S no	Raw material	Pyrolysis conditions	Changed properties of biochar	References
1	Peanut and Hazel nutshells	Pyrolysis at 850 °C for 1 h	- Increased toughness and flexural strength - 353% higher shielding efficiency - Reduced shrinkage	Khushnood et al. (2016)
2	Rubberwood sawdust	Pyrolysis at 450–850 °C	- Surface area of 220 m^2/g was recorded between 550 and 850 °C - Maximum C content in biochar at 750 °C - Maximum CO_2 adsorption capacity was recorded at 650 °C	Ghani et al. (2013)
3	Papermill sludge, rice husk, and poultry litter	Slow pyrolysis at 450 °C and gasification at 500 °C for 20 min	- 0.1% of pulp sludge and rice husk biochar enhanced mechanical strength - Poultry litter improved water absorption	Akhtar and Sarmah (2018)
4	Pine wood (Pinus taeda)	Pyrolysis at 600–1,000 °C	- With increase in pressure, char particles tend to become more spherical - Swelling increased with a decrease in externally applied pressure - Highest micropore area was recorded at 1,000 °C	Newalkar et al. (2014)
5	Wheat straw	Pyrolysis at 650 °C	- 0.5–1.5% biochar lead to 4.1–17.3% higher compressive strength	Ahmad et al. (2020)

Table 1 (continued)

S no	Raw material	Pyrolysis conditions	Changed properties of biochar	References
6	Bagasse, bamboo	Pyrolysis, hydrothermal carbonization at 200 °C	- Surface area of biochar made at 600 °C increased 30 times - Thermal stability of char made by dry pyrolysis was higher than those made by hydrothermal carbonization	Sun et al. (2014)
7	Wood chips	Pyrolysis between 200 and 500 °C then gasified at 900 °C	- Increased dosages resulted in a slight reduction in compressive strength	Sirico et al. (2020)
8	Cotton stalk	Polygeneration by pyrolysis at 250–950 °C	- Increased pyrolysis temperature increased the degree of carbonization of chars	Chen et al. (2012a, b)
9	Softwood	Pyrolysis at 680° for 12 min	- Production parameters and features influenced the formation of strong covalent carbon leading to improved flexural strength and fracture energy	Cosentino et al. (2019)
10	Safflower seed press cake	Pyrolysis at 400–600 °C	- With increase in temperature from 400 to 500 °C, micropore volume and total pore volume increased - Above 500 °C, micropore volume decreased, which may be due to pore expansion due to heating	Angın (2013)
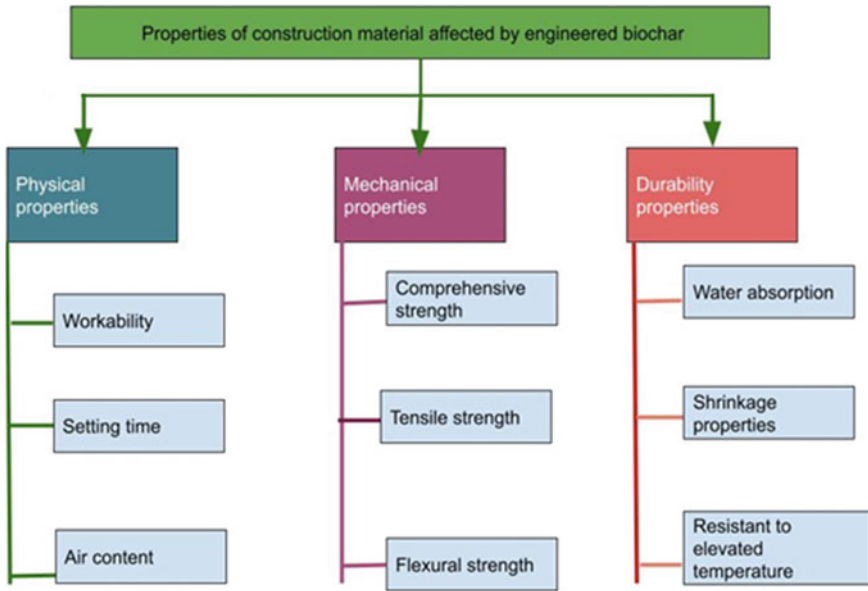
Fig. 1 Properties of construction material affected by engineered biochar

3.1 Physical Properties

Workability, setting times, and air content are some physical properties that can be affected by biochar. Since biochar has a lower specific gravity than Portland cement, it is expected to produce lower fresh and hardened densities in cementitious composites. The decreased specific gravity of the biochar, which results in a commensurate reduction in density, can be linked to the reduction in the dry and fresh densities of cementitious composites (Gupta et al. 2018a, b, c, d).

3.1.1 Workability

The workability of mortar mixtures containing food and wood waste engineered biochar was observed to be reduced. The addition of 3% biochar from wood and food waste reduced the flow of mortar mixtures by 13% and 10%, respectively. The increased water absorption of biochar as a substitute to Portland cement resulted in less water available for workability, resulting in reduced workability of mortar mixtures (Gupta et al. 2018a, b, c, d).

3.1.2 Setting Times

The use of biochar in mortar mixtures has been shown to lessen both the initial and final setting times of Portland cement (Gupta et al. 2018a, b, c, d). The reduction in set times was attributed to the reduction in free water and a filler effect of the biochar particles, resulting in higher cohesion of the mixture. The rapid hydration reaction caused by the incorporation of biochar into the mortar mixtures can also be responsible for the shorter setting time. Biochar particles operate as nucleation sites for cement hydration, resulting in the formation of extra hydration products when they are included in cement-based composites. There is a commensurate decrease in the time it takes for the composites to set on account of the faster production of these additional products (Bouasker et al. 2008; Poppe and Schutter 2005; Ltifi et al. 2011).

3.1.3 Air Content

The incorporation of biochar into mortar mixtures resulted in an optimization of the amount of air in the mixtures (Gupta et al. 2018a, b, c, d). The rise in air content of the mortar mixtures with the addition of biochar was attributed to the porous character of biochar, in addition to the increased amount of free water available in the matrix and the presence of more free water in fresh cementitious mixtures leads to a larger air content (Mindess et al. 2003).

3.2 Mechanical Properties

3.2.1 Compressive Strength

Biochar prepared from wood wastes was shown to boost the compressive strength of mortar mixtures by up to 1% when Portland cement was replaced with biochar. When biochar was applied in higher concentration, its compressive strength was reduced. The higher absorption capacity of biochar from wood and mortar waste, which results in a lower binder ratio and a corresponding densified microstructure, was linked to the upgrading in strength. The greater strength can also be linked to the biochar particles pore filling ability, which also leads to a commensurate refinement of the microstructure (Choi et al. 2012; Restuccia et al. 2017; Cyr et al. 2005). Furthermore, the compressive strength of all biochar-containing mortar mixtures grew with age, demonstrating that adding biochar had no negative impact on the development of hydration reaction. The use of various types of biochar as a substitute for Portland cement in concrete resulted in a reduction in compressive strength. As the size of the biochar particles grows larger, the compressive strength decreases even more (Odimegwu et al. 2018).

3.2.2 Flexural Strength

The diluting influence on the cement, along with the accumulation of biochar particles, can be blamed for the decrease in flexural strength (Gupta et al. 2018a, b, c, d). The addition of higher biochar content has been shown to improve flexural strength. The pore-filling impact of the biochar, which provides a link between the components in the concrete and increases the flexibility of composite, was attributed to the improvement in flexural strength (Muthukrishnan et al. 2019). It has been observed that reducing the number of pores in concrete improves the flexural strength of construction material (Snoeck et al. 2014; Awoyera et al. 2019; Adesina and Awoyera 2019).

3.3 Durability Properties

3.3.1 Water Absorption

The use of biochar at a concentration of 2% resulted in a decrease in water absorption in connection with the depth of water penetration of the mortar mixtures (Gupta et al. 2018a, b, c, d). The decrease in absorption caused by the incorporation of biochar is attributable to a decrease in the porosity of the mixtures, which makes water infiltration more difficult (Akhtar and Sarmah 2018).

3.3.2 Shrinkage Properties

The shrinkage attributes of cementitious composites with biochar have received little attention. Nonetheless, it was shown that replacing cement with biochar resulted in early drying shrinkage (Gupta et al. 2018a, b, c, d). Later on, it was found that incorporating 1% biochar into mortar reduced drying shrinkage; however, the drying shrinkage of mortar containing 2% was greater than the control. Biochar can be employed as an internal curing agent to reduce shrinkage in cementitious composites due to its stable porous structure (Cosentino et al. 2019; Gupta et al. 2018a, b, c, d; Batista et al. 2018). In a study, it was observed that to prevent self-shrinkage in cement pastes, biochar can be used as an internal curing agent alongside magnesium oxide. The integration of biochar under the pretense of a 2% replacement for cement resulted in a 16% reduction in self-shrinkage. The progresses were credited with a considerable reduction (Mo et al. 2019).

3.3.3 Resistance to Elevated Temperature

Concrete mixtures including up to 2% wood waste biochar as a Portland cement replacement have been shown to ameliorate the durability of concrete at high temperatures (Gupta et al. 2020). At 550 °C of pyrolysis temperature, concrete compositions containing biochar lost nearly 4% of their mass, while concrete combinations containing simply Portland cement lost around 6% of respective mass. The higher pores in concrete integrating biochar, that prevented the accumulation of pressure within the composites, were attributed to the increased temperature resistance with the inclusion of biochar. In comparison to those prepared with solely Portland cement as a binder, biochar-infused concrete has been stated to have no serious cracking (Gupta et al. 2020).

4 Applications of Engineered Biochar for Geoengineering

Soil additives to promote water absorption, plaster to absorb humidity, and energy alternatives to supersede fossil fuels are all examples of current use of biochar (Joseph et al. 2007). Biochar has also been used in construction materials. In addition to abundance of properties of engineered biochar such as increased surface area, porosity, functional groups, and mineral content, biochar-based building materials provide the possibility of carbon-negative construction. The Ithaka Institute in Switzerland constructed the first building utilizing this material in 2013, and it is currently undergoing comprehensive performance testing. However, the structure already has proven to be extremely insulated and has excellent humidity control. There are also significant chances to employ the char-clay material to upgrade old buildings that have poor insulation, humidity issues, or contaminations like lead paint (Schmidt 2014).

4.1 Insulation Material

Due to the sheer ability of the pores of biochar to store water, biochar is an extremely efficient medium for storing moisture. The pores also trap significant amounts of nearly immobile air, making biochar one of the well-known insulating materials currently available. Low heat conductivity and potential to absorb water up to five times its weight are two of the characteristics of biochar. Due to these characteristics; biochar is an excellent substance for insulating buildings and for controlling humidity (Schmidh 2014).

4.2   Biochar-Based Clay and Lime Plasters

Biochar can be used as an additive for plaster at a ratio of up to 80% in combination with clay, lime and cement mortar. Biochar-based clay and lime plasters have been developed by Ithaka Institute, with black carbon accounting for up to 80% of the material. This high percentage is feasible because biochar may completely replace sand and the ensuing plaster is five times lighter in compared to the ordinary version because of its high porosity. Along with carbon storage, the biochar-clay plaster provides good insulation, humidity control, and electromagnetic radiation mitigation. This mixing produces inside walls with proper insulation and breathing capabilities, allowing for humidity levels in a space to be maintained at 45–70% in both summer and winter. This keeps the air within the rooms from becoming too dry, which can cause respiratory difficulties and allergies. It also keeps condensation from accumulating around thermal bridges and on the outer walls, thus preventing mold growth (Schmidth 2014). The interior climate of building is influenced by insulation, humidity, and electromagnetic radiation qualities. If a building is demolished, the biochar-based plaster can be recycled into the soil as a compost supplement, increasing the soil's carbon-trapping potential (Schmidt 2014).

4.3   Building Bricks, Tiles, and Concrete

Building materials including bricks and tiles can also be made from biochar. Earlier, biochar brick prototypes contained a binder substance such as cement or lime and had a tensile strength of 20 N/mm^2, whereas typical brick has a minimum tensile strength of about 3.5 N/mm^2. The research reveals that bricks built with 50% biochar and 50% high-density polyethylene had the maximum compressive strength and the biochar–cement brick outperformed in the context of insulating value, hardness, and water absorption (Barton et al. 2020). When using cement and lime, biochar can totally replace sand, lowering the weight of materials by a factor of five (Schmidth 2014). If used globally, the biochar–cement bricks would result in 6% reduction in CO_2 emissions from cement manufacture (Brownell 2021).

4.4   Biochar Roof Tiles

Biochar roof tiles were created in a similar way by a student team at Rochester Institute of Technology. Due to the expensive cost and the noise generated by the traditional roof tiles during rain, the students sought an alternative to the traditional sheet-metal roof. They designed a roof tile made from 30% biochar mixed with cement, sand, water, and reinforcing plastic from shredded waste soda bottles, resulting in a

product that sequesters carbon and reduces overall embodied energy (Barton et al. 2020).

Results like these are relatively new, but intriguing. Rather than burying carbon with carbon capture and storage technology (CCS), we may utilize stored carbon in the construction of buildings to make a visible and functional contribution. Moreover, carbon-rich envelope materials can also be utilized to construct green walls and roofs, and they could play a new role once a building's useful life has passed.

5   Limitations of Engineered Biochar for Geoengineering

Biochar as a geoengineering material has only been studied in the lab. According to the existing research, biochar has yet to be deployed for a wide range of applications. Considering geoengineering applications, specifically for insulating materials, roof tiles, building bricks, tiles, and concrete, research is needed to establish these building materials on a large scale and its applicability in the field.

As discussed in this chapter, the engineered biochar can be accustomed into cementitious composites as a sustainable additive to enhance certain properties. Furthermore, the effect of biochar on the efficiency of composites varies greatly depending on the source, potential mechanism, and concentration of biochar used. As a result, certain considerations must be taken before biochar is applied to cementitious composites (Wani et al. 2021). There is an immediate need for a comprehensive study to be carried out to validate the research.

6   Conclusions and Future Prospects

Engineered biochar has made significant progress in recent years in terms of modification technologies along with environmental, agricultural, and energy storage purposes. Growing concern in the beneficial application of engineered biochar has spawned a slew of new scientific and engineering fields, particularly in the realms of environmental science and engineering. Along with its vast usage in the atmospheric, water, and soil systems, it plays an important role in promoting environmental sustainability. The methods of manufacture and modification, chemical and physical properties, and adsorption mechanisms have all been widely investigated up to this point. Biochar application as a construction material has a great potential. Carbon sequestration would be possible if biochar is used as construction materials. By doing so, the impact of construction material production on climate change will be reduced, as greenhouse emissions will be considerably decreased. As biochar bricks, plaster and concrete are generally inexpensive, environmental friendly, and easy to make, they are a safe alternative to cementitious materials and concrete. As a result, it is critical that such materials should be used to minimize the harmful levels

of CO_2 in the atmosphere, to which the construction and building industry contribute significantly.

Given the focus on sustainable construction and recent advances in biochar research, more widespread utilization of biochar as a material used for construction, not only as a waste management method but also for carbon capture and storage technology (CCS), may be a realistic expectation. However, the identified technological and technical difficulties must first be addressed so that this could be achieved. To produce engineered biochar with physical properties suitable for CO_2 adsorption, effective raw material preparation and control of pyrolysis process parameters such as pyrolysis temperature, pressure as well as heating rate are critical. Tests on the endurance and structural qualities of biochar-concrete along with the associated economical, environmental, and social benefits of these new materials should also be studied. This will be particularly important to investigate how incorporating biochar into buildings and structures can result in broader sustainability benefits than just climate change mitigation. However, the effects of biochar dosage on the biochar long-term performance of cement require additional examination in future investigations.

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Engineered Biochar as Feed Supplement and Other Husbandry Applications

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Abstract Biochar is a carbonaceous material produced by pyrolysis of biomass, and its physiochemical properties are determined mostly by raw material used and conditions of pyrolysis process. Biochar when used as feed supplement in production animals offers several benefits on digestibility, immunity, feed efficiency, as well as the quality of the products received from these animals. It has also been reported to mitigate the notorious greenhouse gas emissions by production animals, particularly ruminants. Biochar as feed supplements is being used both in a wide range of production animals from cattle to pigs, poultry, and fish. Due to its positive impact, research is being conducted around its use as feed supplements as well as other animal farm-related areas like animal beddings and poultry litter. Thus, when combined with other good farmer practices, biochar has the potential to improve the overall sustainability of animal husbandry.

1 Introduction

Biochar is a carbonaceous material produced by pyrolysis of biomass; a process carried out under limited oxygen conditions. This thermo-chemical treatment, combined with the characteristics of biomass used in the process, yields a charcoal-like material with a unique physical structure and chemical makeup (Ramola et al. 2014). Biochar offers an incredibly vast surface area, which can capture and hold minute particles, lending strong adsorbing properties to biochar, as well as provides an excellent habitat for microbial growth. While these characteristics and the origin of biochar have led to its explosive growth in towards soil amendment, researchers are beginning to discover that these same capabilities can offer more to agriculture than just soil replenishment. Biochar for animal feed supplementation is produced from a wide range of biomass like wheat straw, crop residues, corn cobs, and wood waste. After pyrolysis, chemical or physical activation, biochar can be applied as a

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feed supplement. The physiochemical properties of biochar are determined mostly by raw material and pyrolysis temperature. Raw material with high lignin content usually produces higher biochar, whereas some, contain specific components, which can enhance the growth and taste of livestock products.

2   Biochar in Animal Farming

Livestock farming is offering a new and growing area of unforeseen uses for biochar. Animals from earthworms to chickens, cattle, and pigs show promising results, when it is added to their food. Farmers and scientists around the globe are exploring the use of biochar in livestock production. In the European Union, biochar is meticulously defined and approved for use in agriculture, with most fed to livestock or spread on farmland with manure. Biochar is increasingly being adopted as a feed supplement in livestock and has the potential to improve the health of farm animals. Apart from feed supplement, biochar is also being used for other animal husbandry applications such as a bedding material. There is scientific evidence that these practices have many benefits to livestock and soil health, pasture production and the financial bottom line of farmers.

   The applications of biochar as feed supplement of farm animals are based on the ability of activated charcoal in treating digestive disorders in animals. Broadly, the use of biochar as a feed supplement can benefit the animal rearing industry, agriculture, as well as our ecosystem. Biochar as feed supplement for livestock has shown promising results, with improved animal growth (nutrient intake, feed conversion ratio and weight gain) of cattle, goats, pigs, poultry, and fish. Biochar derived from rice husk when added in animal feed has been shown to increase weight gain of cattle, pigs as well as chicken. Biochar is reported to reduce enteric methane production in ruminants by offering favourable microhabitat for methanogenic–methanotrophic microbial interactions in the gut and enhancing anaerobic methane oxidation (Liu et al. 2012). With properties like activated charcoal, having a porous structure and extensive surface area, biochar possesses a high sorption capacity, which can help remove toxic substances from animals' body, as well as from the farming environment. Biochar incorporated into feeds has been reported to improve blood profiles of poultry and reduces pathogen uptake through adsorption, which may help reduce the usage of antibiotics. Including biochar in animal diets is gaining popularity and due to increasing biochar applications, guidelines have been provided by FAO, WHO, International Biochar Initiative (IBI) and European Biochar Foundation (EBF) for classifying and certifying standard biochar as a feed supplement, as well as a soil amendment. This will certainly help regulate future utilization of biochar in animal feeds and possible development of biochar for human usage (Man et al. 2021).

3 Preparing Biochar for Animal Use

Preparation of biochar feed additives involves thermochemical treatment of organic matter at temperatures from 350 to 1100 °C, with a heating rate of 7 to 40 °C/min and a holding time from 3 min to 12 h. As per EU regulations for making biochar as animal feed, the pyrolysis temperature should not vary by more than 20% during the process. Major variables that determine the functionality of biochar products for feed supplementation are temperature, heating rate, and residence time. Both animal and plant origin organic materials are used to produce biochar. Biochar used as a feed additive is mostly made from biomass such as rice husks, woody husks, woody green waste, pinewood chips and jarrah wood (Schmidt et al. 2019).
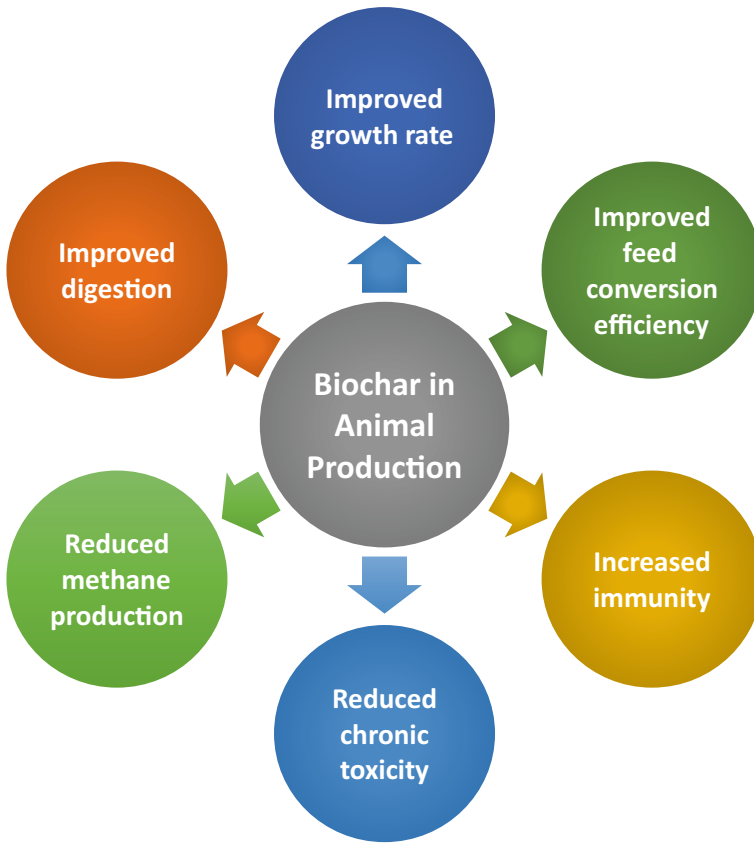
4 Role of Biochar in Farm Animal Production

4.1 Biochar as Adsorbent in Livestock Farming

High adsorption properties of biochar can be used in improving farm hygiene and animal well-being by binding toxic substances and controlling pathogens, limiting the spread of diseases as well as removing ammonia, hydrogen sulphide, odours, and toxins (Toth and Dou 2016). The sorption capability of biochar for toxicants depends on the preparation treatment of biochar and its physiochemical properties. Biochar produced from higher temperature usually has higher adsorption capacity. The increased pyrolysis temperature also results in smaller biochar particles, which can improve forage digestibility and rumen fermentation kinetics. Farmers are becoming aware of multiple benefits of using biochar in animal farming. Spreading biochar on top of animal manure can significantly mitigate the odour from the emission of ammonia from livestock excreta (Maurer et al. 2017). Similarly applying biochar to poultry farm litter can control moisture level of farm litter, reduce ammonia, and improve the odour problems of chicken farms (Gerlach and Schmidt 2012).

Addition of biochar to animal bedding can also limit the growth of pathogenic bacteria and coccidiosis and help limit the spread of infection within animal houses (Steiner et al. 2010). Low thermal conductivity of biochar allows good insulation and warmth when used as animal bedding. Other organic beddings such as sawdust can contain pathogens, and non-organic beddings such as sand can be difficult to handle. Biochar bedding solves both problems by being easy to handle and pathogen-free. Additionally, the biochar makes a great soil amendment after being used as bedding, as it holds nutrients in the carbon for slow release to plants.

There is growing evidence that biochar helps improve gut digestion, which, in turn, increases feed conversion efficiency, weight gain and reduces methane production in ruminants. Biochar has an adsorbing effect in the digestive tract of animals by helping bind nutrients and toxins very efficiently, which can improve the immunity of animals and help reduce the ill effects of chronic toxicity, respectively. This helps improve

Fig. 1 Benefits of using biochar in farm animal production

health, activity, and well-being of the animals. In addition, the risk of infection for pathogenic microorganisms is reduced and the immune system of the animals is stabilized.

Animal feed sourced from plants usually contains a variety of toxins, which mostly comes from either fungal contamination or from the plant feed itself. When animals consume the toxin laden feed for an extended period, they can suffer from numerous health-related complications and diseases. These toxins may have terato-genic, immunosuppressive, carcinogenic, mutagenic effects as well as gastrointestinal activity impairments and an overall reduction in production. Mycotoxins are mainly derived from mould fungi, whose growth on fresh and stored animal feed is difficult to prevent, especially in humid climates. Mycotoxin-contaminated feed can result in serious diseases of farm animals. The use of adsorbents such as biochar, activated carbon and other non-charcoal adsorbents like zeolites and alumino-silicates have shown promising results in reducing assimilation of these toxic compounds into the animal bloodstream. The adsorption capacity of biochar and activated charcoal

is mainly influenced by its surface area and pore size distribution and surface acidity, and binding the toxins reduces bioavailability of myco- and plant toxins, which helps improve animal productivity. To protect the animals, adsorbents are usually added to the feed to bind the mycotoxins before ingestion. In addition to the frequently used aluminosilicates, activated carbon and special polymers are increasingly being used.

4.2 Biochar as an Immune Booster

As an adsorbent, biochar has been shown to lock up toxins in the digestive tract. This maintains the balance of microbial activity and avoids subsequent damage to the animal's digestive system. A study on pigs indicated that supplementation of bamboo charcoal led to decrease in cortisol levels, which could protect fattening pigs from stress and diseases (Chu et al. 2013). Same study reported increased concentrations of immunoglobulin G (IgG) and immunoglobulin A (IgA) in serum of pigs supplemented with bamboo charcoal.

4.3 Control of Pathogenic Activity

Biochar has been reported to reduce the activity of harmful bacteria such as *Escherichia coli* and *Salmonella* sp. within the gut of the animals. Although different theories have been put forward to explain a possible mechanism of action of biochar against these bacteria, particularly adsorption of these pathogens to biochar and increased activity of beneficial microbe species such as *Bifidobacterium*, *Enterococcus* and *Lactobacillus* in the gastrointestinal tract. There is not sufficient evidence to support the mechanism of action of activated charcoal against these hazardous microbes.

4.4 Reduced Methane Production

Biochar being highly porous with a large internal surface area (Thies and Rillig 2012) adsorbs gasses and carbon, detoxifies them via binding, and provides habitat biofilms for desirable proliferation of microbiota (Jeffery et al. 2016; Leng 2017). Biochar also has electron-mediating properties in biological redox reactions, which provides a benefit of higher feed-conversion efficiency in ruminants and reduced greenhouse gas emissions (Kammann et al. 2017). Therefore, biochar is looked upon as a promising additive for methane mitigation in livestock production.

Bamboo charcoal has been reported to decrease the emission of ammonia, methane, amine and hydrogen sulphide from fattening pigs. Wood charcoal can effectively neutralize anti-nutrients from feed, negative effects of gases, toxins and

other products of digestion and fermentation in the gastrointestinal tract. Bamboo charcoal is considered to have a high adsorption capacity because of the special structure of micro-pores found in bamboo stems (Chungpin et al. 2004). Asada et al. (2002) described that bamboo charcoal can decrease odours of ammonia because of pore volume at the micro-pore range, and these micro-pores of bamboo charcoal could suppress noxious gas emissions from faeces of fattening pigs.

5 Use of Biochar in Production Animal Farming

5.1 Ruminants

Ruminants are unable to digest their food directly and obtain nutrients from plant-based food by fermenting it in a specialized forestomach prior to digestion, principally through microbial actions. These animals are not particularly efficient at digesting and absorbing nutrients when compared to monogastric animals and produce huge quantities of methane, wasting a lot of energy that would otherwise go towards the animal. Poor gut health in these animals can further compromise the feed efficiency, with animals requiring more feed to meet their nutrient requirements. The use of biochar as feed additive has been reported to increase feed efficiency and improve weight gain of these animals by various ways. Biochar has been shown to increase the surface area in the gastrointestinal tract on which beneficial microbes attach to digest and cycle nutrients, which are later absorbed by the animal. Biochar also adsorbs toxins in the gut that can impact the health of animals, and the quality of the products they produce (Joseph et al. 2015; Leng et al. 2012).

Studies have been done where ruminants were fed on different forages and fodders supplemented with biochar. Majority of these studies indicate an increase in dietary protein digestion, dry matter intake and related increase in growth rate of these animals. However, there are some inconsistent results, where there was no positive association between biochar inclusion, live weight gain and carcass quality, as well as the performance of the biochar fed animals was not significantly different from the animals not receiving biochar in their feed (Phongpanith et al. 2013; Kim and Kim 2005).

There are studies indicating that using biochar as a feed additive not only improves feed efficiency in cattle but can also increase nutrient availability of the manure, and this manure when added to soil improves soil fertility, can protect ground, and surface water, and improve carbon sequestration in the soil (McHenry 2010). Thus, biochar supplementation not only improves animal performance and welfare but also helps enrich ecosystem (Joseph et al. 2015; Schmidt and Shackley 2016; Kammann et al. 2017). In addition to the improvement of the fertilizing properties of biochar-amended manure, the addition of biochar to manure either through animal feed or bedding is supposed to reduce manure related greenhouse gas emissions (Kammann et al. 2017).

From last one decade, farmers in Germany and Switzerland are using biochar in the production of feed silage. Addition of biochar to the silage helps stabilize lactic acid fermentation, prevent fermentation failure, and reduce risks of fungal infestation and formation of mycotoxins (O'Toole et al. 2016). Lower levels of acetic acid and especially butyric acid are supposed to curtail the risk of Clostridia infestation. The high-water retention capacity of biochar seems to buffer the water content of the silage, reducing the formation of excess fermentation liquids.

5.2 Pigs

Biochar feed supplementation has been reported to benefit pigs in terms of health and performance. There are reports of improved performance in terms of feed conversion rates, carcass characteristics, live weight gain and immune response with biochar supplementation (Choi et al. 2012; Chu et al. 2013). However, the response does depend on the rate of biochar supplementation, the primary source of biochar, the length/duration of the supplementation (Chu et al. 2013). Besides, reports of improvement in pig health and production with biochar supplementation, there are several studies reporting some contrasting findings. Some feeding experiments involving piglets supplemented with biochar (Mekbungwan et al. 2004) reported that increased weight gain and feed utilization efficiency were not different compared to piglets receiving no biochar.

5.3 Chicken

Majority of the studies on production performance and biochar supplementation have been conducted on poultry, the reason being that working with birds during a scientific trial is much easier and economical when compared to ruminants or pigs (Schmidt et al. 2019). Feeding experiments on broiler chicks fed biochar demonstrated that the chicks receiving diets supplemented with biochar had improved feed conversion rates and higher weight gains (Majewska et al. 2011). The mechanisms behind these benefits are postulated to be due to detoxification potential of biochar in the feed along with the reduced surface tension of the digesta within animals' gastrointestinal tract. Another mechanism postulated by some researchers is the ability of biochar to bind the antinutritional factors in the feed (Kutlu 1998). Apart from broilers, studies on biochar inclusion on layers feed have been reported to improve the quality and quantity of eggs and egg components. Inclusion of biochar in the hens has been reported to significantly reduce the number of cracked eggs compared to hens not receiving any biochar (Kutlu et al. 2001). Moreover, biochar supplementation has shown to augment the membrane collagen of eggs (Yamauchi et al. 2010) as well as increase the egg production (Kim 2006; Yamauchi et al. 2013).

Biochar is reported to improve digestion, energy absorption, and as such feed efficiency in chicken. Toxins like dioxin, glyphosate, mycotoxins, and pesticides are efficiently bound by biochar, helping prevent adverse effects of these toxins on digestive system and the intestinal flora. The health of the birds improves, and immune system is stabilized, reducing the risk of infection from pathogenic microorganisms.

The enormous economic impact of diarrhoeal diseases in poultry is well recognized. The cause of these diseases is often infection of bacterial pathogens like *E. coli*, *Clostridia*, coccidia and mycobacteria. Chicken also carry *Salmonella* and *Campylobacter* bacteria, which although rarely cause disease in poultry, are infectious to humans. Non-infectious causes of disease are mostly poor feed quality and biocide contamination of feed, resulting in increased susceptibility to disease, growth depression and digestive disorders. There are several factors which help improve and stabilize the intestinal milieu. The major factors are stabilization of the intestinal barrier and the functionality of the liver. Several beneficial bacterial species such as lactobacilli and enterococci, and non-pathogenic yeasts play an indispensable role in maintaining a healthy gut. Feeding biochar has been reported to stimulate the activity of these desired microorganisms in the digestive system and also bind the toxins helping healthy liver functions. Charging of biochar with specific lactobacilli to direct the symbiosis in the gastro-intestinal tract of chicken has been reported to further potentiate the benefits of biochar (Kana et al. 2011).

5.4   Fish

Biochar supplemented fish feed (at 0.5% of basal diet) was shown to significantly increase weight gain of fish by almost 20% and led to improvement in fishpond water with a significant decrease in pond water nitrate levels (Thu et al. 2010). Another study reported that at 1% of feed supplementation, biochar increased growth rates by 44% and improved fishpond water quality with marked reductions in nitrite, phosphate, ammonia, and chemical oxygen demand (Lan et al. 2016).

5.5   Biochar and Wild Animals

Apart from production animals, wild animals tend to eat charcoal residues from wildfires that remain in nature. Deer and elk were found to eat it from charred trees in Yellowstone National Park. Charcoal consumption in small monkeys, Zanzibar red colobus, is believed to be a self-learned behaviour to increase the digestibility of their usual leaf diet. Charcoal with its high adsorption properties helps these small monkeys in digesting young Indian almond and mango leaves that contain toxic phenolic compounds (Cooney and Struhsaker 1997). Further, as there is no report

of negative long-term effect of charcoal consumption, population density of this monkey species has increased worldwide.

6 Limitations

Despite the fact that use of biochar has shown promise in both agriculture and animal nutrition globally, there is still a knowledge gap for farmers, the end-users of biochar. There is disparity on practical applications of biochar as well as its acceptance among farmers and stakeholders like environmental managers and policymakers. Further research on biochar, best-use biochar application protocols and programs in educating farmers through extension and field officers will assist the farmers and decision-makers in adopting and supporting the use of biochar through regulations and safety standards.

7 Conclusion and Future Prospects

The use of biochar as a feed additive has been shown to improve animal health, feed efficiency and livestock productivity. It is also reported to reduce nutrient losses and greenhouse gas emissions and help enhance manure quality and thus soil fertility. When combined with other good farmer practices, establishment of best-use biochar application protocols and programs educating farmers, biochar has the potential to improve the overall sustainability of animal husbandry.

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Application of Engineered Biochars for Soil Amelioration

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Abstract Application of engineered biochar for soil amelioration is an emerging research area. Co-pyrolysis of biomass-chemical and different biomass combinations are commonly explored methods for engineered biochar production. Other methods include polymer coating, chemical treatment, nanoparticles integration, electrochemical treatment, and nutrients sorption on biochar. The biochars are engineered to obtain desired characteristics such as high aromatic carbon, nutrient content, bioavailable nutrients fractions with slow-release kinetics, along with lesser bioavailable fractions of toxic contaminants (e.g., heavy metals). Lab-based studies on the application of engineered biochar exhibit several positive results in terms of improving soil properties like water holding capacity, cation exchange capacity, bioavailable nutrients, and immobilization of heavy metals. Furthermore, engineered biochars are also reported to improve the development and growth of plants. However, research focussing on engineered biochar for soil application is still in preliminary stage and, therefore, more detailed practical studies are required to explore full potential and effectiveness of engineered biochar for soil amelioration.

Keywords Engineered biochars · Co-pyrolysis · Slow-release fertilizer · Heavy metal immobilization · Soil amelioration

1 Introduction

Application of biochar has been extensively studied worldwide for soil amelioration. However, contrasting performance results of biochar are reported (Lehmann and Joseph 2015; Kookana et al. 2011). The positive performance of biochar is mostly observed in acidic and sandy soils. This is due to biochar mediated improvement in the soil physico-chemical properties such as texture, density, structure, particle size distribution and porosity. Furthermore, biochar application also causes liming effect and improved the electrical conductivity, water-holding capacity (WHC), cation

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exchange capacity (CEC), and nutrient availability (Laird et al. 2009; Jeffrey et al. 2011; Song et al. 2014a; Hien et al. 2021). Oxidation of aromatic carbon structures and formation of negatively charged functional groups in biochar contributes towards increasing the CEC and retention of nutrients in soils (Liang et al. 2016; Sohi et al. 2010). The better soil pH and CEC also further enhanced the bioavailability of nutrients specifically phosphorus and potassium in soils (Atkinson et al. 2010; Nguyen et al. 2020). Biochar has porous structure and surface area that provides shelter to bacteria, mycorrhizae and other soil microorganisms, which are beneficial for improving soil health and productivity. This indirectly helps in cycling and supply of nutrients to plants through microbial action (Cheng et al. 2008; Joseph et al. 2010; Hammer et al. 2014).

In some cases, biochar application in alkaline and calcareous soils has highlighted no or negative effects on soil characteristics and plant growth (Lentz and Ippolito 2012). This can be because of biochar alkaline pH, which if applied in alkaline soil further increases the pH of soil (above recommended pH) that limits the plant growth by decreasing the nutrient bioavailability. Negative results could be attributed to decrease in nutrients phyto-availability due to their precipitation like calcium phosphate, and competition with soil microorganisms (Woods et al. 2006; Xu et al. 2013). Soil quality and plant growth further improved when additional fertilizer and compost have been applied along with biochar. In addition, biochar application in soil considerably reduces the recommended dose of synthetic fertilizers. Biochar can provide direct nutrient value and/or increases nutrient availability for plants by decreasing leaching and enhancing nutrient retention for long time in soils (Woods et al. 2006; Xu et al. 2013; Mohan et al. 2018).

The biochar amendment was also reported for exhibiting contrasting efficacy for remediation of toxic contaminants (e.g., heavy metals, antibiotics) in soils (Ramola et al. 2020a). The efficacy of biochar-based soil remediation varies according to biochar characteristics, application rate, soil properties and chemical nature of contaminants. Application of biochar minimizes the bioavailable fractions and immobilizes heavy metals (mostly positively charged Cu, Ni, Cd, Zn, and Pb) in soils. This is due to biochar mediated sorption, surface complexation, and chemical precipitation in stabilized form (e.g., metal phosphates) facilitated by alkaline pH. Biochar amendment in soils caused higher mobility and bioavailability of negatively charged toxic elements like chromate and arsenate. Amelioration of soils contaminated with toxic organic compounds by biochar application are probably facilitated by increased microbial action, which helps in the mineralization of organic contaminants (Paz-Ferreiro et al. 2014; Mendez et al. 2014; Askeland et al. 2020; Liang et al. 2016; Netherway et al. 2019; Paz-Ferreiro et al. 2017; Guo et al., 2020).

The effectiveness of biochar for soil amelioration depends on several factors such as biochar characteristics, application rate, soil characteristics, plant growth and environmental conditions (Jeffrey et al. 2011; Liu et al. 2013). Among these factors, diverse characteristics of biochar were found to be one of the major reasons for the effectiveness of biochar towards soil quality improvement (Karim et al. 2019a, b; El-Naggar et al. 2019; Mohapatra et al. 2020). Characteristics of biochar depend on the composition of raw material and production conditions, specifically temperature,

heating rate and reaction condition. Major properties of biochar that change due to aforesaid factors are pH, elemental constituents, porosity, surface area, aromaticity, polar functional groups, nutrients bioavailable fractions, presence of toxic contaminants like heavy metals and polyaromatic hydrocarbon (PAH) (Laird et al. 2009; Lehmann and Joseph 2015). Several research studies have recently focused on production of biochar with desired controlled characteristics for soil application, this will obviate the drawbacks of general pristine biochar having unfavourable characteristics. These biochar are termed as engineered biochar or designer biochar or modified biochar. For example, biochar pH can be reduced/neutralized for application in alkaline soils. Enhancement of potassium and calcium content could be useful for saline and sodic soils reclamation. Phosphorus nutrient forms in biochar could be controlled to prepare slow-release fertilizer source with high nutrient use efficiency. Heavy metals in biochar can be transformed into stable immobilized form thus reducing its toxicity potential and environmental risks.

This chapter discussed about the application of engineered biochar produced through different methods for soil amelioration. The engineered biochar efficacy towards the improvement of soil physico-chemical properties and remediation are described. Limitations related to engineered biochar application for soil amelioration are also outlined. The chapter ends with the concluding remarks and future prospects to highlight the crucial information regarding advancement of engineered biochar research.

2 Engineered Biochar Efficacy for Soil Amelioration

Limited research studies (presented in Tables 1 and 2) are undertaken on investigating engineered biochar efficacy for soil amelioration. These are mainly lab-scale experiments, focused on improving soil properties, and for remediation of contaminated soils. Major benefits of soil application of engineered biochar produced through different methods (Karim et al. 2021) are depicted in Fig. 1.

2.1 Improving Soil Physico-Chemical Properties

Soil is a physically, chemically, and biologically diverse natural system with non-uniform geographical distribution in world. Consequently, soils exhibit different fertility and productivity, based on its composition, properties, and environmental conditions. Sandy soil has loose structure, macroporous, low organic matter, and very poor water retention capacity. These properties also accelerate nutrient leaching and decrease fertility. Engineered biochar (derived by microwave pyrolysis of mixed raw material-biomass + 10 wt.% K_3PO_4 and 10 wt.% clinoptilolite) application showed an increase in WHC, CEC and nutrient contents of sandy loam soil (Mohamed et al. 2016). Main mechanisms for improved WHC by biochar application were

Table 1 Important research studies on engineered biochar towards improving soil fertility/productivity

Engineered biochar	Raw material	Production methods	Biochar characteristics	Soil experiments	Impact on soil fertility/productivity	References
Acidic biochar	Switchgrass biomass	Biomass pyrolysis at 350 °C in N_2 gas presence, then steam activation at 800 °C	pH-5.8, Ash-5.86%, surface area-219 m²/g, C-88.0%, N-0.68%; P-700 mg/kg	Soil type—Eroded calcareous soil; Soil pH: 7.8–8.2; Biochar application rate up to 10% in soil; Experiment: Lab-scale study up to 6 months	Biochar application not significantly influence soil pH, initial increased micronutrient availability, and improved the gravimetric soil water content, reductions in soil NO_3–N	Ippolito et al. (2016)
Acidic biochar	Poultry manure	Pyrolysis at 300 °C for 2 h for biochar production, Biochar modification phosphoric acid and nitric acid after pyrolysis	pH-4.10, nutrients (g/Kg): N-55.20, P-44.13, K-39.0, Ca-91.30, Mg-9.06	Soil type—Clay loam; Soil characteristics: pH-7.93; Biochar application rate -0.5% (w/w) to pot soil; Experiment: ammonium nitrate and potassium dihydrogen phosphate added to soil, growth of maize studied for 2 months	Acid treatment (HNO_3 + HPO_4) increased the water-soluble fractions of nutrients; dry weights and nutrients contents (NPK) of maize plants were improved by biochar use	Sahin et al. (2017)
Designer biochar	Poultry litter mixed with pine chips (1:1 wt/wt)	350 °C for 2 h	pH- 7.25, K-4.1%, P-1.4%	Soil type: Norfolk soil (pH-6.0); Application rate: 10 g/Kg of biochar applied to the soil Experiment: lab incubation study for 78 days	Designer biochar application increased soil organic carbon, pH, and P and K bioavailable fractions	Novak et al. (2014)

(continued)

Table 1 (continued)

Engineered biochar	Raw material	Production methods	Biochar characteristics	Soil experiments	Impact on soil fertility/productivity	References
MgO-enriched biochar	Rice husk mixed with $MgCO_3$ (mass ratio: 1:1)	Co-pyrolysis at 600 °C with a 20 °C/min heating rate, 2 h residence time	C-22.13%, H-0.17%, N-0.20%, Specific surface area- 216 m²/g	Water retention experiment-mixing powdered biochar treated soil in watch glass, water added every 10 min till constant weight; relation curve of water loss rate and time was obtained. Nutrient retention conducted using leaching study of biochar soaked with K_3PO_4 solution	$MgCO_3$-treated biochar showed maximum water retention capacity and higher adsorption capacity of the soil nutrient (K^+ and PO_4^{3-})	Shen et al. (2020)
MgO-biochar	Peanut shell treated with $MgCl_2$	Co-pyrolysis at 600 °C, 4 h, 10 °C/min, N_2 atmosphere	pH-8.85; C-60.83%; Mg-6.81%; Si-0.64%; P-0.27%; Ca-0.59%	Soil type—Saline-alkaline soil (Sandy-loam texture), pH-8.10; Biochar application rate- 4.5 Mg/ha; Experiment: Biochar field trial in soil, chemical fertilizers (N, K, Zn) added for other nutrients except phosphorus; Growth of rice plant studied	MgO-Biochar increased P adsorption and available fractions in soil, improved the rice plant biomass and P content in root but not shoot	Wu et al. (2019)

Table 1 (continued)

Engineered biochar	Raw material	Production methods	Biochar characteristics	Soil experiments	Impact on soil fertility/productivity	References
Si-rich biochar	Rice straw treated with KOH (KOH: Biomass ratios 10:100)	Pyrolysis at 550 °C, 60 min residence time in N_2 presence	pH-10.51, C-34.21%, N-1%, P-1.75 g/kg, K-138.46 g/kg, Ca-4.39 g/kg, Mg-3.09 g/kg, Al-0.46%, Fe-0.31%, Soluble Si at 4.67%	Soil type—acidic soil; Soil characteristics—pH 5.2, fine-silty; Experiment: rye grass (*Lolium perenne*) 20 g/m² in each pot for 5 weeks	Si rich biochar application significantly increases available Si for 1% application rate, It also enhanced Si content by 35.56% in ryegrass plant, compared to control	Wang et al. (2018)
Biochar modified with clinoptilolite and K_3PO_4	Switchgrass biomass mixed with 10% clinoptilolite and 10% K_3PO_4	Microwave-assisted catalytic pyrolysis at 400 °C, 750 W (single mode 2.45 GHz microwave oven)	C-34.16%, H-0.21%, N-0.31%, Ash—51.23%, K_2O-248.21 g/kg, P_2O_5-182.76 g/kg, MgO-10.29 g/kg; CaO-37.20 g/kg	Soil type: Loamy sand soil; Soil characteristics: sand-76.8%, silt-18.4% and 4.8% clay; Experiment: Biochars mixed at 2 (w%); Experiment: 6 weeks incubation	Modified biochar application increase WHC of the soil by 22.9%, also improved CEC, surface area, pore volume of soil	Mohamed et al. (2016)

Table 2 Major research studies about engineered biochar application for soil remediation

Engineered biochar	Raw material	Production methods	Engineered biochar characteristics	Soil experimental conditions	Soil remediation findings	References
Phosphorus modified biochar	Rape straw biomass and orthophosphate (KH_2PO_4) mixture	Co-pyrolysis at 500 °C for 2 h under oxygen limited condition	pH-8.78; Ash-41.9%, C-42.3%; H-2.24%; N-0.63%; S-0.45%	Soil Type: Agricultural soil nearby lead–zinc mine; Soil Characteristics: 52% Silt, 17% clay; pH-5.1; Biochar application rate- 3% w/w; Experiment: Lab incubation, 90 days duration,	Immobilization of Pb, Cd, Cu in biochar amended by 81.7, 23.7, and 31.0%	Gao et al. (2020)
Biochar modified with clinoptilolite and K_3PO_4	Switchgrass biomass mixed with Clinoptilolite and K_3PO_4	Microwave-assisted catalytic pyrolysis at 400 °C and single mode (750 W) microwave oven	Not mentioned	Soil Type: loamy sandy soil; Soil Characteristics: 76.8% sand, 18.4% silt, 4.8% clay, pH- 5.73; Biochar application rate- 1 or 2% in soil spiked with heavy metals; Experiment: PVC columns incubated for 6 weeks, five days wheat germination study	Biochar improved CEC, pH and nutrients content, and reduced bioavailable fractions of Co, Pb, and Ni in soils Biochar improved germination and shoot length, along with decreased uptake of heavy metals in wheat plants	Mohamed et al. (2017)

Table 2 (continued)

Engineered biochar	Raw material	Production methods	Engineered biochar characteristics	Soil experimental conditions	Soil remediation findings	References
Chitosan-clay-biochar nano-biocomposites	Residual bark chips, obtained from Wood and Paper Industry)	Pyrolysis: 600 °C, heating rate- 10 °C/min, residence time- 2 h, nitrogen presence; Biochar treated with Montmorillonite nanoclay, chitosan suspension	Base biochar: C-77.74; H-1.92; N-0.66; S-0.55; O-11.15; P-0.34; Biochar composite surface area: 272.49 m^2/g	Soil type: Copper Mine simulated silty sand soil; Soil Characteristics: sand-50%, silt- 35%, and 15% kaolinite, contaminated with Cu, Pb, and Zn; Biochar application rate: 10%(w/w) biochar treatment of soil Experiment: biochar-soil suspension shaked for 24 h in an end-over-end shaker	Biochar reduces the leaching of metals from soil medium (by 100% for Cu^{2+}, 100% for Zn^{2+}, and 52.29% for Pb^{2+}	Arabyarmohammadi et al. (2018)
Calcium-rich magnetic biochar	Mixture of rice straw, $CaCO_3$, and Iron oxide	Co-pyrolysis at 400 °C for 2 h, limited oxygen	pH-8.51, CEC-32.4 cmol kg^{-1};	Soil Type: Cd and As contaminated Paddy soil; Soil characteristics: 12.05% clay, 28.32% silt and 59.63% sand particles, pH −4.65, CEC −7.1 cmol kg^{-1}, 12 g kg^{-1} organic matter; Biochar Application rate- 1 to 3%; Experiment- lab incubation study for 160 days	Biochar reduced the As and Cd bioavailable fractions in soil	Wu et al. (2020)

Table 2 (continued)

| Engineered biochar	Raw material	Production methods	Engineered biochar characteristics	Soil experimental conditions	Soil remediation findings	References
Nano-hydroxyapatite-supported biochar	Bagasse	Pyrolysis at 600 °C, heating rate-10 °C/min, 2 h residence time. Freshly produced bagasse biochar treated with suspension of nanohydroxyapatite particles	Not mentioned	Soil type—Soil of Guangzhou, China spiked with Pb ($NO_3)_2$ solution; Biochar application rate- 8% (w/w) in soil; Experiment: Incubation study for 28 days to study heavy metals immobilization, Pot experiments using Cabbage mustard seeds for 6 weeks	Immobilization rate of Pb in the biochar treated soil was 74.8% cabbage mustard stem length in biochar treated soil improved by 17.1%	Yang et al. (2016)
KOH-activated biochar	Rice straw	Pyrolysis at 550 °C for 60 min under N_2 flow rate of 200 mL/min; Biochar treated with KOH solution for activation	Not mentioned	Soil type: Briley soil and commerce soil; Biochar application Rate- 1% and 3% (w/w) in soil; Experiment: Incubation study for 8 days. Pot study done using Ryegrass plant in temperature and light controlled growth chamber	Biochar increased the pH and available Si in soil, results vary based on application rate	Wang et al. (2018)

(continued)

Table 2 (continued)

Engineered biochar	Raw material	Production methods	Engineered biochar characteristics	Soil experimental conditions	Soil remediation findings	References
Sulphur-modified biochar	Rice husk	Pyrolysis at 550 °C, heating rate—15 °C/min and residence time of 2 h in N_2 atmosphere for rice husk biochar produced. This rice husk biochar mixed with elemental S in 1:1 ratio (Dry wt/wt) and pyrolyzed at 550 °C for 2 h in N_2 atmosphere for sulphur modified biochar production	S-13%	Soil type: local field soil sample spiked with Hg^{2+} solution (1000 mg/kg Hg); Biochar Application rate: 1, 2 and 5% (w/w) in soil Experiment: Toxicity Characteristic Leaching Procedure (TCLP) tests were used for evaluating Hg leachability	In biochar treated soils, amount of dissolved Hg in the leachate (TCLP) was reduced below 1.2 mg/l, Removal Efficiencies were more than 94%	O'Connor et al. (2018)
KOH-enhanced biochar	Rice husk	Pyrolysis at 300 °C, 5 °C/min heating rate, 1 h residence time for rice husk biochar. Thereafter powdered biochar treated with KOH solution (1:20 solid to liquid ratio)	Not Mentioned	Biochar application rate-5% (w/w) in soil; Experiment: Incubation study for 21 days under constant moisture of 50%	Biochar application increases the soil pH. KOH concentration (1 M) favoured Cd and Pb Immobilization in soil	Wan et al. (2020)
$ZnCl_2$-treated biochar/attapulgite composite	Attapulgite and $ZnCl_2$ pre-treated rice straw biomass	Co-pyrolysis at 450 °C for 1 h in N_2 atmosphere	Not mentioned	Sample—river sediment biochar application rate—2% added to 50 g of sediment samples. Experiment: Incubation in artificial climate chamber under dark conditions at 20 °C for 60 days	Biochar composite reduced the bioavailable fraction of As (Up to 43%) and Cd (up to 11%) in the sediment effectively, compared to pristine biochar	Wang et al. (2019)

Table 2 (continued)

Engineered biochar	Raw material	Production methods	Engineered biochar characteristics	Soil experimental conditions	Soil remediation findings	References
Acid-activated biochar	Burcucumber (*Sicyos angulatus L.*)	Biomass pyrolysis at 700 °C at a rate of 7 °C/min and 2 h holding time. Biochar undergoes acid activation of using 30% sulphuric and oxalic acids	pH—5.04, C—65.65%, O—22.56%, H—2.73%, N—4.40%, BET surface area—571 m²/g	Soil type: Loamy sand soil- Sand—84.1%, Silt—6.2%, Clay—9.7%, pH—5.95. Sorption experiment: 2% acid-treated biochar -soil mixture shaken in an incubator shaker at 100 rpm for 24 h	Acid treatment enhanced the sorption of sulfamethazine antibiotic from soil	Vithanage et al. (2015)
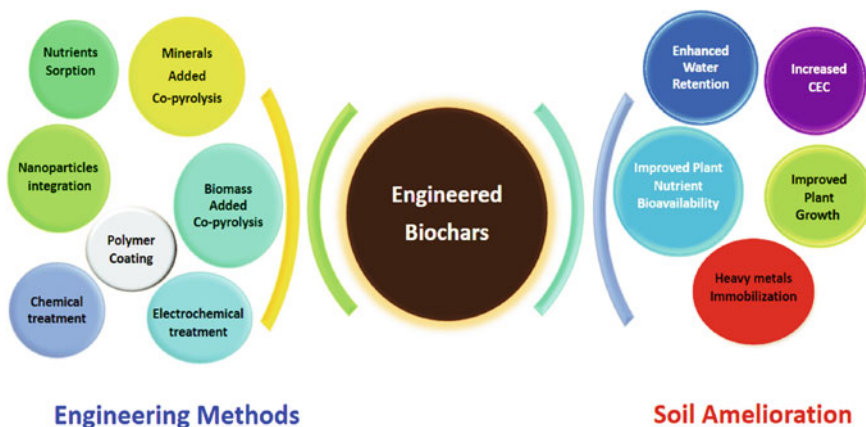
Fig. 1 Different methods of engineered biochar production and soil amelioration effects

sorption of H_2O molecules, formation of H bonds between H_2O molecules and carboxyl/hydroxyl groups, covalent bonding between cations of engineered biochar and lone pairs of oxygen in H_2O molecules. Moreover, the engineered biochar enhanced the microporosity, surface area, and adhesion between soil particles (Major 2009). Formation of ionizable functional groups like carboxylate due to oxidation of biochar surfaces improves the soil CEC (Liang et al. 2006).

Saline soils have high alkaline pH, and low organic matter content (Song et al. 2017). In addition, they are high in sulphate and carbonate concentrations, which acts as competitor and limits the bioavailability/uptake of nutrients (specifically phosphate) by plants (Sun et al. 2012). This severely restricts the plant growth and productivity. Application of MgO-biochar composite in a coastal saline-alkaline soils increased the bio-available fractions of phosphorus, which resulted in improved yields of rice plants (Wu et al. 2019). MgO-biochar adsorbed 20% more phosphate than pristine biochar due to the strong interaction between MgO and phosphate ions. Adsorption was optimal at pH value of 6, higher alkaline pH negatively impacted phosphate adsorption due to the de-protonation of functional groups and repulsion between negatively charged biochar surface and phosphate ions. MgO-biochar application in saline soil reduced the leaching of phosphate ions even in the presence of sulphate and carbonate ions and resulted in higher rice plants biomass (Wu et al. 2019).

Calcareous soils are highly alkaline with low organic carbon, water and nutrient retention capacity. Due to high pH, the nutrients' uptake by plants was also limited. Few studies explored the potential of acidic biochar for improvement of calcareous soil. Ippolito et al. (2016) evaluated the influence of acidic biochar (produced by steam activation of low-temperature switch grass biochar) amendment in calcareous soil. Biochar improved the soil water, and organic C content, but not showed any significant change in pH of soil that could be strong buffering by free carbonates of soil. This study also highlighted that higher application rate (10% by weight) reduced

the NO_3–N in soil. In another study, application of acidic poultry manure biochar (acid treatment with $HNO_3 + H_3PO_4$) was evaluated for availability of nutrient and growth of maize plant in alkaline calcareous soil. This research demonstrated that acidic biochar enhances the water-soluble fractions of nutrients (P, K, Ca, Mg, Fe, Zn, Cu, and Mn). As a result, the phyto-availability of nutrients and plant biomass increases in calcareous soil after acidic biochar application (Sahin et al. 2017). Acidification of biochar surface causes the transformation of alkaline nutrients into more soluble and labile forms, i.e., nitrate/phosphate salts. However, the above study not reported about the influence on pH of calcareous soil after acidic biochar treatment.

In alkaline-calcareous soil, fixation of phosphorus is a critical problem that affects the plant growth. Qayyum et al. (2021) explored the potential of acidified biochar (HCl treated rice husk biochar) for improving phosphorus availability and growth of maize plant in calcareous soil. Pot experiment exhibited significant increase of 80.5% and 110.7% in root dry-matter of maize plants applied with pristine and acidified biochar, respectively. Results obtained from this study suggest that acidified biochar amendments can help in improving agronomic benefits of P but may be inconsistent sometimes. It also demonstrated that acidified biochar can contribute to amelioration of alkaline soils in terms of P availability. Efficacy of biochar (derived from pine chips mixed with poultry litter) for improving fertility of soil (fine-loamy, thermic, kaolinitic, Typic Kandiudult) was evaluated by Novak et al. (2014). Major results from pot experiment include reduction in soil pH, extractable soil P and K concentrations, in comparison to pristine poultry litter biochar.

Silicon deficiency in soils negatively affects the plants' capability to maintain its mechanical strength, resistance against pathogens, disease, toxicity and extreme environmental conditions like drought and salinity (Epstein 2009; Keller et al. 2015). Plants take up the silicon in form of monosilicic acid (H_4SiO_4) and retained as phytoliths (SiO_2–nH_2O) (Epstein 2009). Phytoliths in plant biomass are highly water soluble and constitutes an important source of Si (Fraysse et al. 2006; Song et al. 2014b). However, removal of crop residues after harvesting restricts the recycling and causes deficiency of bio-available Si in soils (Datnoff et al. 2001; Vandevenne et al. 2012). A modified biochar with increased phyto-available fractions of Si was produced by pyrolysis of biomass (rice straw, sugarcane residue switchgrass, and miscanthus) pre-treated with KOH. The KOH pre-treatment of rice straw increased the water-soluble Si up to 4.67%. Application of biochar showed an increase in Si bioavailability in acidic soil (5.2 pH) with less impact on soil pH. Application of rice straw-based biochar exhibited the highest release of Si in soils and enhanced the Si uptake by 31% in perennial ryegrass (Si accumulator plant- Nanayakkara et al., 2008). Biomass pyrolysis with KOH changed the morphology and structure of phytoliths, increasing its soluble fractions in biochar and a reason behind an increase in bioavailable Si (Wang et al. 2018).

Mixture of bentonite, cotton straw and K_3PO_4 was used for the production of biochar-based slow-release fertilizer. During co-pyrolysis process, the bentonite presence leads to improvement in porous structure that eventually positively influence the slow-release behaviour of K from biochar. Bentonite also substantially

improved P slow release by supporting the formation of stable P-related chemical bonds in biochar. Pot experiments showed better pepper seedlings growth in bentonite containing biochar (An et al. 2020). Application of coating technology on biochar produced from cotton straw-bentonite-$Mg_3(PO_4)_2$ further improved the degradability, P slow release and peeper seedlings growth. Better slow-release performance of P could be because coating materials block the nutrients/fertilizer diffusion (An et al. 2021).

Adsorption of H_2S gas (released from anaerobic digestion process) on biochar was used for enriching it with more sulphur content (up to 36.5%). Application of this biochar significantly enhanced the corn plant biomass yields up to 49% and soybean biomass up to 14% (Zhang et al. 2017). Biochar treated with anaerobically digested slurry to enrich it with nutrients and application as slow-release fertilizer. The modified biochar improved the water retention capacity of soil and could act as slow-release potassium fertilizer (Oh et al. 2014). Controlled release of nutrients (P) from biochar to soil is highly desirable and crucial for improving nutrient use efficiency. Application of waterborne polyacrylate membrane coated biochar in waterlogged paddy soil for 1 year showed lesser biodegradation of biochar particles, which indicates slow controlled release of nutrients from it. Also, it does not have any substantial negative impact on bacterial community of soil, thus could be practically applied (Zhou et al. 2015). Bacterial (*Pseudomonas Sp.*) loaded biochar was also developed for improving the enzymatic activity and heavy metals (Cd, Cu) immobilization in soil (Tu et al. 2020).

2.2 Remediation of Contaminated Soils

Heavy metal contamination of soils leads to toxicity in plants, which restricts its growth and bioaccumulation poses serious health risks. However, chemical speciation of heavy metals governs its leachability, mobility, bioavailability and toxicity risks (Bolan et al. 2014). Therefore, research studies on remediation of contaminated soil focus on immobilization of heavy metals by transforming it into a stable less bioavailable chemical form (like metal phosphates) through adsorption, complexation, and bonding (Beesley et al. 2011). Modified biochar produced from rape straw and orthophosphate (KH_2PO_4) co-pyrolysis was investigated in an incubation study for the remediation of agricultural soil contaminated with Cu, Pb, and Cd. Research findings exhibited that the modified biochar immobilized the heavy metals, as indicated by a decrease in toxicity characteristic leaching procedure (TCLP) leachable fractions (up to 81.7%). This was due to transformation of heavy metals into stable forms caused by the precipitation of heavy metals with phosphate and hydroxyl groups of modified biochar, along with the complex formation with its carboxyl groups in contaminated soils. An increase in pH value and bioavailable phosphate in soils after modified biochar application also facilitated the heavy metal immobilization, which was found highest for Pb followed by Cu and Cd (Gao et al. 2020). Engineered biochar (EB) derived from microwave pyrolysis of biomass, K_3PO_4

and clinoptilolite were researched for remediation of Pb, Ni, and Co contaminated sandy soil. This biochar application decreases the bioavailable fractions of heavy metals and increases the growth rate of wheat plant by 145%. Several dominant mechanisms responsible were sorption (EB surface area—405 m^2/g), ion exchange with Ca, Mg, Fe, and formation of insoluble forms of heavy metals after chemical bonding with phosphate groups of biochar (Mohamed et al. 2017). Biochar-based bio-nanocomposite was prepared using nano-clay coating on biochar with chitosan polymer. Its application (10% w/w) in mine-affected acid soil showed high sorption capacity for Cu (25.42 mg/g), Pb (76.68 mg/g), and Zn (24.96 mg/g). The nano-clay and chitosan polymer increased the surface area, and active functional groups of biochar, which immobilized heavy metals through complexation with -NH$_2$ groups (Arabyarmohammadi et al. 2018).

Calcium-rich magnetic biochar prepared (co-pyrolysis method) from a mixture of rice straw biomass, CaCO$_3$ and Fe$_2$O$_3$. Amendment of this biochar in soil increased the dissolved organic carbon, pH value and immobilized the Cd and As. Stabilization of Cd was mostly facilitated by elevated pH, and high CEC; whereas bi-dentate chelate and complex formation on iron oxide surface supported the As stabilization. The high metal adsorption capacity of biochar on its porous surface also contributed for soil remediation (Wu et al. 2020). Biochar-based nanohydroxyapatite composite application also demonstrated higher immobilization rate (74.8% based on column experiment) of Pb in soil. Pot experiments showed nano-hydroxyapatite-biochar reduced the translocation and uptake in cabbage mustard aerial part (Yang et al. 2016). Hydroxyapatite could have helped by increasing the surface area and sorption capacity of modified biochar (Li et al. 2018).

Amendment of sulphuric acid-activated biochar derived from burcucumber sorbed and retained more sulfamethazine antibiotic than pristine biochar from loamy sand soil. Enhancement in intraparticle diffusion, and bonding with protonated functional groups proposed to be major mechanism for sulfamethazine sorption (Vithanage et al. 2015). The application of alkaline (KOH) activated rice husk biochar showed enhanced stabilization of toxic metals (Cd and Pb) in soils. The main mechanism for stabilizations was found to be complexation of toxic metals with oxygen-containing functional groups on biochar surface. However, alkaline activation damaged the biochar structures, so moderate alkali concentration should be used for its modification (Wang et al. 2018).

Elemental sulphur modified biochar (derived from rice husk) application decreases the free availability of Hg in contaminated soil. This could be due to Hg adsorption by biochar (adsorptive capacity—67.11 mg/g) and formation of less soluble HgS (O'Connor et al. 2018). Magnetic biochar adsorbents derived from cedar sawdust containing Fe$_3$O$_4$ sorbed up to 30% As, Cd and Pb from contaminated soil slurry (Wan et al. 2020). Engineered biochar produced from rice straw biomass pre-treated with attapulgite and zinc chloride possessed higher cation exchange capacity, pore volume, surface area and oxygen-bearing functional groups. Its application decreased bioavailability and improved the immobilization of As and Cd in river sediment (Wang et al. 2019). An overall proposed mechanism for engineered biochar mediated remediation of contaminated soil is presented in Fig. 2.
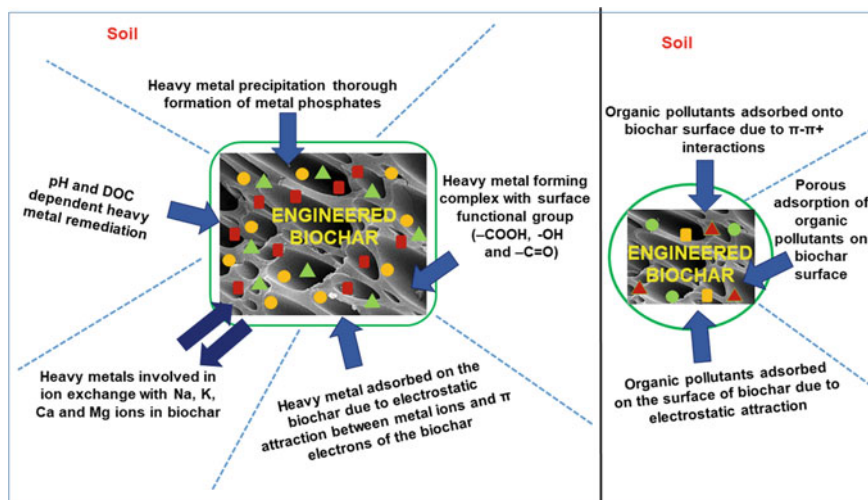
Fig. 2 Mechanism of engineered biochar mediated heavy metals and organic pollutant remediation in contaminated soil

Overall, research studies highlighted that development of engineered biochar for soil amelioration must be done based on the specific properties and problem of a particular soil-environment system. In this context, the selection of appropriate raw material, additives and adapted modification methods are predominant factors for the production of engineered biochar with characteristics beneficial for amelioration of the targeted soil system.

3 Limitations

The major focus of engineered biochar research has been done primarily as adsorbent for wastewater treatment (Yao et al. 2013; Mohan et al. 2015; Karim et al. 2017; Wang et al. 2017; Karunanayake et al. 2018, 2019; Boguta et al. 2019; Jang et al. 2019; Han et al. 2019; Vimal et al. 2019; Panahi et al. 2020; Ramola et al. 2020a, 2021, b; Xiang et al. 2020; Ibrahim et al. 2021; Imam et al. 2021; Singh et al. 2021), and few studies reported about soil amelioration. In most of the research work, lab-scale engineered biochars are produced and their experimental results are unable to assert the scope of its bulk application as soil ameliorants. Also, the engineered biochar produced through chemical modification needs associated environmental toxicity-safety studies. Heavy metal remediation in soil through engineered biochar is extensively explored (Wang et al. 2020), but studies on remediation of pesticides, emerging organic contaminants etc. need special attention. Earlier studies mainly documented about the influence of engineered biochar on physico-chemical properties of soil; however, information on soil biota is unexplored. Due to diverse

characteristics of engineered biochar and its complex influence on edaphic conditions, the use of statistical analysis, machine learning techniques like random forest data mining (Zhu et al. 2019) are having great potential to delineate tailor-made engineered biochar for specific soil conditions.

4 Conclusions and Future Prospects

Mineral/biomass-based co-pyrolysis method is mostly explored for the production of engineered biochar for soil application. Other methods like nanocomposite integration, polymer coating, chemical salt (e.g., KOH, H_3PO_4) treatment, gaseous (H_2S) treatment, and electrochemical system are scarcely studied. In general, engineered biochars have the potential to be better soil ameliorants, as they possess more favourable characteristics such as desirable pH, and high-water holding capacity, cation exchange capacity, bioavailable nutrients fractions, controlled slow release of nutrients, stabilization of toxic constituents, etc. Lab-scale studies undertaken on application of engineered biochar primarily in acidic, sandy and heavy metal contaminated soil exhibited positive results specifically regarding immobilization of heavy metals. Currently, research on engineered biochar production and application for soil amelioration is at preliminary stage, and promising methods need to be studied in detail. Future research studies should be more focussed and extensively done on tailoring of engineered biochar characteristics on the basis of specific soil–plant system requirement, lab and field trials in different soil–plant-environment conditions, upscaling of known methods, inventing suitable methods for bulk production of engineered biochar, life cycle and socio-techno economic assessment. In addition, robust computational analyses are needed to extract more knowledge regarding engineered biochar efficacy with a better understanding about underlying mechanisms as soil ameliorants.

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Engineered Biochar as Adsorbent for the Removal of Contaminants from Aqueous Medium

Stuart Cairns, Gabriel Sigmund, Iain Robertson, and Richard Haine

Abstract Biochar is a relatively low cost, sustainable product which can be utilized in the removal of both inorganic and organic contaminants from aqueous media. This chapter outlines the mechanisms of immobilization for both inorganic and organic contaminants and summarizes the key properties that underpin these processes. Immobilization as a result of cation exchange, complexation, electrostatic interactions, cation–π bonding, precipitation and reduction is discussed for inorganic contaminants and immobilization due to H-bonding and charge-assisted H-bonding (CAHB), π–π Electron Donor–Acceptor (EDA) interaction, electrostatic interaction, and steric effect are discussed for organic contaminants. The properties examined include the role of functional groups, cation exchange capacity, specific surface area and pH for inorganic contaminants, and specific surface area, aromaticity, and polarity for organic contaminants. The effect of raw materials and pyrolysis conditions on these properties is also reviewed. Future research needs to bridge the knowledge gained from laboratory work and fieldwork to support the effective use of biochar in real-world environments.

Keywords Biochar · Contaminated water · Mechanisms · Properties · Heavy metal · Inorganic contaminants · Organic contaminants · Immobilization · Sorption

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1   Introduction

Biochar is defined as a porous, carbonaceous material that is produced by biomass pyrolysis at temperatures ranging from 350 to 1000 °C under limited oxygen conditions (European Biochar Foundation 2016). During pyrolysis highly aromatic clusters are formed which are responsible for several key features of biochar, specifically it's high chemical stability and high porosity. Biochar is reported to have several functions such as the ability to sequester carbon, enhance soil fertility and remediate environmental contaminants including the removal of contaminants from aqueous media (Inyang et al. 2016; Kätterer et al. 2019). The use of biochar in the remediation of inorganic and organic pollutants has been highlighted for various aqueous media such as road runoff (Cairns et al. 2020), mine waters (Bandara et al. 2020), stormwater (Boehm et al. 2020) drinking water (Hu et al. 2019) and biologically treated wastewater (Hagemann et al. 2020). Its attractiveness is further enhanced due to its relatively low cost, simple production process, and versatility in utilizing renewable raw material, including biomass waste materials (Ahmad et al. 2014; Zhang et al. 2015; European Biochar Foundation 2016; Wang et al. 2018; Xiao et al. 2018).

Biochar itself is a reasonably broad term which covers production from a vast number of different biomass raw materials produced at different pyrolytic temperatures yielding biochar with different characteristics. Essentially raw material, pyrolysis, and modification such as the addition of minerals, activation or magnetization alter the efficacy, and the mechanisms of the biochar to remediate contaminants in aqueous media. Comparative studies primarily review either raw material, pyrolysis temperature, or modified vs unmodified biochar to review sorption capacity or mechanisms (Table 1).

2   Immobilization of Inorganic Contaminants

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation–π bonding, reduction and subsequent sorption, and precipitation (Fig. 1). It is worth noting that these mechanisms do not work in isolation and often several mechanisms are relevant at the same time (Ramola et al. 2020a).

3   Cation Exchange

Cation exchange occurs most notably at early stage adsorption (Mohan et al. 2007; Uchimiya et al. 2010; Ifthikar et al. 2017; Shen et al. 2017). During cation exchange, the biochar releases exchangeable cations such as alkali and alkaline earths, typically

Table 1 Immobilization mechanisms of inorganic contaminants by biochar produced from different raw materials

Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
Plant biomass	Oak bark	400 and 450	-	As, Cd, Pb	Ion exchange	Mohan et al. (2007)
	Pine bark		-	As, Cd, Pb		
	Oak wood		-	As, Cd, Pb		
	Pine wood		-	As, Cd, Pb		
	lucerne shoot	550	-	Cd, Cu	Precipitation, complexation and electrostatic interaction	Bandara et al. (2020)
	Norway spruce	450–500	-	Cd, Cu, Pb, Zn	Electrostatic attraction	Cairns et al. (2020)
	Norway spruce amended with wood ash	450–500	-	Cd, Cu, Pb, Zn	Electrostatic attraction and precipiation	
	Norway spruce amended with basalt rock dust	450–500	-	Cd, Cu, Pb, Zn	Electrostatic attraction and precipiation	
	Tobacco stem	300–700	-	Cd	Cation-p interaction, precipitation	Zhou et al. (2018)
			-	Cu	Complexation	
			-	Pb	Precipitation	
	Canna indica	500	125.8	Cd	Precipitates, cation exchange, binding to oxygen-containing groups	Cui et al. (2016)

Table 1 (continued)

Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
	Pennisetum purpureum Schum	500	119.3	Cd	Precipitates, cation exchange and binding to oxygen-containing groups	Wang et al. (2015)
	$KMnO_4$ modified hickory wood	600	28.1	Cd	Surface adsorption	
			34.2	Cu	Surface adsorption	
			153.1	Pb	surface adsorption	
	Miscanthus	300	11.4	Cd	Surface sorption, precipitation	Kim et al. (2013)
		400	11.99	Cd	Surface sorption, precipitation	
		500	13.24	Cd	Surface sorption, precipitation	
		600	12.96	Cd	Surface sorption, precipitation	
	Honey mesquite	200, 300, 350, 550, 650	-	Cd, K	Ion exchange, cation-pi bond	Harvey et al. (2011)
	Cord-grass	200, 300, 350, 550	-	Cd, K	Ion exchange, cation-pi bond	
	Koblolly pine	200, 300, 350, 550	-	Cd, K	Ion exchange, cation-pi bond	

(continued)

Table 1 (continued)

| Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
	Anaerobically digested sugarcane bagasse	600	-	Cd, Cu, Pb, Ni	Precipitation and surface adsorption	Inyang et al. (2011)
	Sugarcane bagasse	600	-	Cd, Cu, Pb, Ni	Surface adsorption	
	Hardwood mix	450	12.52	Cu	H bonding	Chen et al. (2011)
			11	Zn	H bonding	
	Straw	600	6.79	Cu	H bonding	
			4.54	Zn	H bonding	
	Celery	500 and 350	288–304	Pb	Precipitation, cation exchange and surface complexation	Zhang et al. (2017a, b, c)
	Wheat straw pellets	550	-	Ni	Cation exchange, electro- static adsorption and surface precipitation	Shen et al. (2017)
	Acacia wood chip	550	4.02	Zn	Precipitation, chelation (complexation)	Van Hien et al. (2020)
Sewage/Manure	Dairy manure	350	7.28–15.68	Cd	Complexation, precipitation	Xu et al. (2013b)
			4.16–8.96	Cu	Complexation, precipitation	
			13.45–28.98	Pb	Complexation, precipitation	

Table 1 (continued)

Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
			4.23–9.1	Zn	Complexation, precipitation	
	Broiler litter	350 and 700	-	Cd, Cu, Ni, Pb	Coordination by π electrons (CdC) of carbon and precipitation	Uchimiya et al. (2010)
	Magnetised Sewage sludge	400	249	Pb	Electrostatic attraction, ion exchange, complexation, precipitation	Ifthikar et al. (2017)
	Sewage sludge	550	30.88	Pb	Coordination with organic hydroxyl and carboxyl functional groups, coprecipitation and complexation	Lu et al. (2012)
	Dairy manure	500	140.76	Pb	Precipitation	Cao et al. (2009)
Food waste	Nut shells	600		Cd, Pb	Ion exchange	Trakal et al. (2014a, b)
	Plum stones			Cd, Pb	Ion exchange	
	Wheat straws			Cd, Pb	Ion exchange	
	Grape stalks			Cd, Pb	Ion exchange	
	Grape husks			Cd, Pb	Ion exchange	
	Rice husk	350	>54.432	Cd	Complexation, precipitation	Xu et al. (2013b)

Table 1 (continued)

Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
			>31.104	Cu	Complexation, precipitation	
			>100.602	Pb	Complexation, precipitation	
			>31.59	Zn	Complexation, precipitation	
	Peanut	400	-	Cr (III)	Complexation	Pan et al. (2013)
	Soybean	400	-	Cr (III)		
	Canola	400	-	Cr (III)		
	Rice straw	400	-	Cr (III)		
	Sugar beet tailing	300	123	Cr (VI)	Electrostatic attraction, reduction and complexation	Dong et al. (2011)
Other	Sediment	400 and 500	-	Cd, Cu, Pb	Cation–pi bond	Dong et al. (2014)
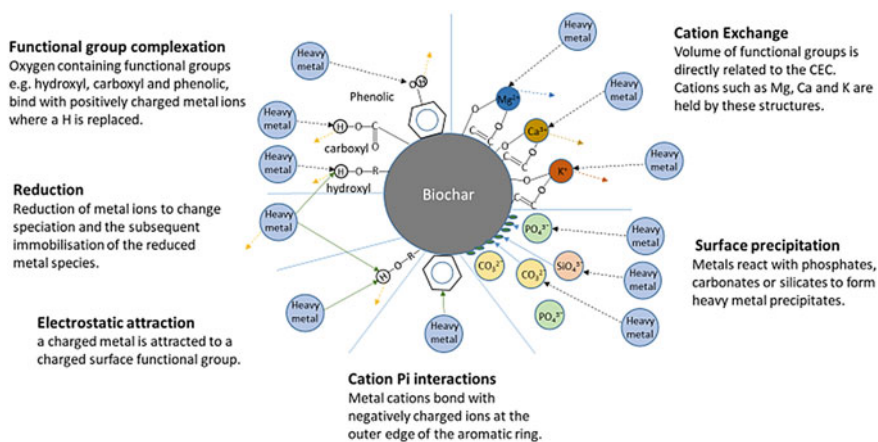
Fig. 1 The six major mechanisms of heavy metal immobilization by biochar

Mg, Na, K, and Ca (Kumar et al. 2016). These cations are effectively replaced by heavier metal cations found in the aqueous media which bind to the biochar in their stead. Immobilization mechanisms often do not work in isolation but rather work simultaneously or are intrinsically linked. Studies, such as Mohan et al. (2007), cite several other mechanisms working alongside cation exchange in the remediation of inorganic contaminants, i.e., precipitation and physical adsorption. Similarly, cation exchange capacity (CEC) is recognized as being controlled by surface oxygen related functional groups (Trakal et al. 2014a; Ding et al. 2016), these functional groups also being of great importance in the remediation of inorganic contaminants through complexation.

4 Complexation

Several authors cite functional group complexation as a major mechanism of immobilization specifically of transition metals such as Cr, Cu, and Cd and post-transition metals such as Pb (Lu et al. 2012; Pan et al. 2013; Cui et al. 2016; Peng et al. 2017). Complexation occurs when a H ion is replaced in functional groups such as phenolic, carboxy, or hydroxyl (Fig. 1) (Xu et al. 2013b; Dong et al. 2014). Complexation is cited in studies with a variety of raw materials including sewage/manure (Zhang et al. 2020a), food waste such as millet bran (Qiu et al. 2019), and plant biomass (Wang et al. 2018) (Table 1). Again, complexation is often described as working in conjunction with other mechanisms. Lv et al. (2018) reported complexation working alongside electrostatic interaction to remove Pb and Cu from an aqueous solution.

5 Electrostatic Interactions

Electrostatic interaction occurs between positively charged metals, such as Pb^{2+}, and the negatively charged surface of the biochar, particularly with a proliferation of oxygenated functional groups such as –COOH or –OH (Cui et al. 2015; Lv et al. 2018). Electrostatic attraction is a weaker process than precipitation or complexation and as a result, metals immobilized via this mechanism are more susceptible to desorption (Bandara et al. 2020). During their study, Bandara et al. (2020) described the major mechanisms of Cd and Cu removal as electrostatic interaction with O-containing functional groups, surface complexation, and precipitation. Ifthikar et al. (2017) also saw electrostatic attraction as being involved in the immobilization of Pb alongside ion exchange, complexation, and precipitation; electrostatic attraction was linked specifically to carboxyl groups. Cui et al. (2016) proposed that electrostatic interactions are likely the primary driving force for Cd sorption on wetland plant-derived biochar, however, even here it is indicated that electrostatic interaction is not the sole mechanism of Cd sorption with complexation playing a role. Ramola et al. (2020b) found electrostatic interaction to be one of the important mechanisms between Pb ions and mineral groups, i.e., bentonite and calcite present in biochar–bentonite composite and biochar–calcite composite, respectively prepared at 700 °C.

6 Cation–π Bonding

Cation–π bonding is a stabilizing electrostatic interaction of a cation with the polarizable π electron cloud of an aromatic ring. During the pyrolysis of biochar, graphene sheets are formed with aromatic structures (Wang et al. 2020). Within these aromatic structures are electron-rich domains on the edge of the aromatic structure which attract inorganic contaminants such as Cd (Harvey et al. 2011). Uchimiya et al. (2010) recognized the sorptive interactions between d-electrons of metals and aromatic π-electrons of the biochar as one of the primary mechanisms for the retention of Ni and Cd by broiler litter biochar. Xu et al. (2013b) also found interactions between d-electrons of metals and aromatic π-electrons when using dairy manure-derived biochar, however, their study reported that this was important for Zn and Cd remediation but less so for Cu. Kim et al. (2013), Yuan et al. (2020), and Qiu et al. (2019) also recognized the positive impact of aromaticity on adsorption of Cd.

7 Precipitation

In dependence of pH, metals can react with anions including CO_3^{2-}, PO_4^{3-}, and SiO_4^{3-} to form solid precipitates (Šráček and Zeman 2004). Again raw material is critical to this process being the main driver of the availability of these mineral

components (Lu et al. 2012; Xu et al. 2013b). Ifthikar et al. (2017) found silica coprecipitation to be of importance in the remediation of Pb by sewage sludge biochar due to the abundance of silica in the sewage sludge raw material. Precipitation was also significant in the study by Zhang et al. (2017a, b, c) of celery-derived biochar, however, due to the characteristics of the raw material carbonate rather than silica coprecipitation was evident. The importance of raw material is further highlighted by Arán et al. (2017) who reiterated that the formation of metal carbonates and phosphate precipitates is favored in biochar from mineral-rich raw material. Several studies assert that precipitation is the primary mechanism for immobilization (Cao and Harris 2010; Inyang et al. 2012; Lu et al. 2012; Xu et al. 2013b). These studies typically use a raw material of sewage sludge/manure or an amended raw material which provides a high pH and high levels of phosphate and carbonate to be released to precipitate with metals (Inyang et al. 2012). However, precipitation is usually not the sole immobilization mechanism even when such mineral-rich raw materials are used. Xu et al. (2013a) studied P-rich dairy manure as a raw material where electrostatic attraction and precipitation were both seen to be the governing mechanisms for the removal of Pb, Cu, Zn, and Cd. Similarly, Van Hien et al.'s study (2020) illustrated the importance of precipitation alongside complexation in the immobilization of Zn.

8 Reduction

Metals can be reduced by biochar enabling the reduced metal species to be immobilized. Dong et al. (2011) reported that due to its high redox potential, Cr(VI) is easily reduced to Cr(III) under acidic conditions in the presence of organic matter. The immobilization of Cr occurred by electrostatic attraction of the negatively charged Cr(VI) to positively charged surface sections of a sugar beet biochar and reduction of Cr(VI) to Cr(III) facilitating complexation with functional groups. Cr(VI) reduction to Cr(III) was also reported by Mohan et al. (2011) in their study of oak biochar; by-products of lignin pyrolysis such as catechol were seen to act as reducing agents as well as being important constituents of units that chelate Cr allowing the biochar to both reduce and bind Cr cations. Klüpfel et al. (2014) also highlight the importance of the pyrolysis process by demonstrating that new redox-active moieties can be formed in the charring process. Bogusz et al. (2015) assert that this reduction can happen in metals with a positive normal potential such as Cu but not with metals such as Cd and Zn that have a negative normal potential.

9 Key Material Properties for Inorganic Contaminant Immobilization

9.1 Functional Groups

Surface functional groups of biochar are essential to several immobilization mechanisms including cation exchange, electrostatic attraction, and complexation. Ding et al. (2016) discuss the increase in cation exchange of the modified biochar as being resultant from the increase of oxygenated functional groups most notably carboxyl and hydroxyl groups. Other studies, such as Kharel et al. (2019) and Huff et al. (2018) acknowledge the role of functional groups in cation exchange and have specifically tried to increase carbonyl, carboxyl, and hydroxyl groups to increase CEC. Functional groups such as carboxyl and phenolic groups also underpin electrostatic interactions as a charged surface to interact with a given contaminant (Cui et al. 2015). Hydroxyl, carboxyl, and phenolic groups also enable complexation to take place when a H^+ ion is replaced by a metal (Trakal et al. 2014b; Wang et al. 2018). The formation of these functional groups depends on raw material properties and pyrolysis temperature.

Trakal et al. (2014a, b) suggest that differences in the relevance placed on functional groups can be explained by differences in pyrolysis temperature with studies around 350 °C giving greater importance to functional groups and studies around 550–600 °C attributing less significance to functional groups as the levels of O reduce. Oxygenated functional groups, such as carboxyl, carbonyl, and hydroxyl, start to form at ~120 °C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350 °C (Fig. 2) beyond which the O/C ratio is lowered (Lehmann and Joseph 2009). Studies done by Gray et al. (2014) and Zhang et al. (2020b) have recorded a decrease in these oxygenated functional groups as pyrolysis temperatures rose, with Gray recording a decrease from 370 to 500 °C and a further decrease to elimination from 500 to 620 °C. Similarly in a comparative study, Chen
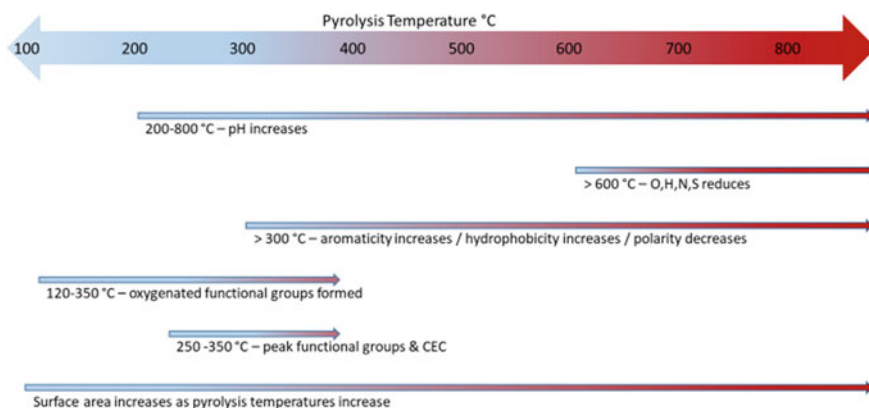

Fig. 2 Biochar property changes as a result of pyrolysis temperature

et al. (2011) saw that pyrolysis of hardwood at 450 °C resulted in a larger number of functional groups and a higher O/C ratio than straw pyrolyzed at 600 °C. Although temperatures below 450 °C appear to be the best conditions for oxygenated functional groups, at pyrolysis temperatures as high as 600 °C the adsorption by hickory wood biochar was still seen to be primarily driven by functional groups (Wang et al. 2015). While raw material and pyrolysis temperature are the primary drivers of the abundance of functional groups they can also increase as a result of oxidation; such oxidation can be a due to natural aging or by chemical oxidation such as with HNO_3–H_2SO_4 or NaOH–H_2O_2 (Fan et al. 2018).

9.2   Cation Exchange Capacity

CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are key drivers of CEC (Trakal et al. 2014a, b). Studies show peak CEC to occur at pyrolysis temperatures of 250–350 °C where functional groups are most abundant, and a diminishing of CEC as pyrolysis temperatures rise past this level (Fig. 2) (Harvey et al. 2011). Mohanty et al. (2018) concur with the paradigm that low pyrolysis temperature (250–350 °C) leads to high CEC and suggests that this is a result of the considerable volatile organic matter remaining on biochar rather than it being lost at higher temperatures. If a raw material has high levels of alkali and/or alkaline earths, it has the potential for these elements to be available in the biochar for cation exchange. Ifthikar et al. (2017) used sewage sludge as a biochar raw material which contained high levels of Ca and Mg, as a result, the exchange of these alkaline earth metals was shown to be involved in the early stage adsorption of Pb. Similarly, the use of celery biomass as a raw material, which is rich in alkali and alkaline earth metals, resulted in cation exchange playing a significant role in adsorption (Zhang et al. 2017c). Conversely, in studies such as Mantonanaki et al. (2016) or Van Hien et al. (2020) where the raw material, such as coffee grounds or bamboo, have low levels of Ca, K, or Mg, cation exchange is either not highlighted or is described as neither a driver nor a good predictor of adsorption.

9.3   Specific Surface Area

Specific surface area (SSA) is a property of biochar that is very often cited by authors due to its importance in the immobilization of contaminants in aqueous media; the higher the SSA the more sites are available for sorption to occur. Ifthikar et al. (2017) in their study of magnetic sewage sludge biochar, described surface area as critical in the adsorption of Pb. When they compared magnetized and unmagnetized sewage sludge biochar, an increase in the surface area allowed access to a large number of active sites for remediation to take place increasing removal rates. In their study of oak bark and pinewood biochar, Mohan et al. (2007) also suggest that higher

adsorption levels were at least partially due to the higher surface area of the oak bark biochar. It is worth noting that a higher surface area does not always result in higher rates of immobilization particularly if chemisorption rather than physisorption is the driving factor. In studies where precipitation is the major immobilization mechanism such as Cao and Harris (2010) and Xu et al. (2013b), surface area is not a major factor. Xu et al.'s study (2013b) demonstrated that dairy manure biochar had lower surface areas than rice husk biochar ($5.61 m^2 g^{-1}$ vs. $27.8 m^2 g^{-1}$) but higher sorption (486 mmol kg^{-1} vs. 65.5–140 mmol kg^{-1}) as a result of precipitation being the driving mechanism.

As with functional groups, the surface area is primarily driven by raw material and pyrolysis temperature (Fig. 2). Zhang et al. (2020b) described a surface area increase as a result of temperature increase with rice straw biochar pyrolyzed at 400 °C having a surface area $0.367 m^2 g^{-1}$ which increased to $51.105 m^2 g^{-1}$ at 700 °C. The largest surface area increase occurred between 600 to 700 °C with an increase from 8.598 $m^2 g^{-1}$ to $51.105 m^2 g^{-1}$. Ramola et al. (2020b) reported increased surface area of porous biochar–bentonite composite with increase in temperature from $44.68 m^2 g^{-1}$ at 300 °C to $53.08 m^2 g^{-1}$ at 500 °C. However on further increasing the temperature to 700 °C, a decrease in surface rea i.e. $51.12 m^2 g^{-1}$ was observed. Ahmad et al. (2012) report a surface area increase from $6 m^2 g^{-1}$ to $448 m^2 g^{-1}$ when temperatures increased from 300 to 700 °C. Chen et al. (2018) demonstrate an increase from 1.26 $m^2 g^{-1}$ to $351 m^2 g^{-1}$ with an increase in temperature from 300 to 900 °C. As explained by Kercher and Nagle (2003) SSA increases due to the condensation of biomass to graphene like carbon structures forming pyrogenic micro and mesopores. Hale et al. (2016) describe the increase in SSA at high temperatures as a result of amorphous components arranged into turboclastic chrystallites. Chen et al. (2011) and Ippolito et al. (2020) assert that it is raw material rather than pyrolysis temperatures that play major role in the SSA of biochar.

9.4   pH

The pH of biochar is usually alkaline (Lehmann and Joseph 2015) and as a result, it increases and buffers its environment pH. These increases are dependent on raw material and pyrolysis temperatures (Fig. 2) (Fidel et al. 2017). Studies have shown that the solution pH which effects the metal speciation can be influenced by the pH of the biochar (Cairns et al. 2020), the increase in aqueous media pH can induce changes in metal speciation that are favorable for cationic metals such as Pb or Cd and unfavorable for anionic metalloids such as As. The pH of the aqueous solution is cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent (Kilic et al. 2013). pH is a key determinant of metal solubility and bioavailability; the more bioavailable a metal is, the more toxic it is to the surrounding ecosystem (Charters et al. 2016). Metals such as Pb and Cd are more mobile at low pH whereas metalloids such as As are more mobile at high pH and as a result, the maximum sorption of these metals is

seen at different pH (Mohan et al. 2007). Metals that are more mobile at low pH such as Cd, Co, Ni, Pb, and Zn are removed best at pH of ~5–6, above pH levels where the metals are mobile (Chen et al. 2011; Lu et al. 2012; Kilic et al. 2013; Trakal et al. (2014b). In contrast, the removal of metalloids that are more mobile at higher pH, such as As, fall when pH is above 8 and the metalloid is more mobile (Navarathna et al. 2019). In terms of cationic heavy metals Lu et al. (2012) cited surface charge as being the primary mechanism for Pb sorption and that higher surface charge was driven by increasing pH from 2 to 5. Increasing adsorption was attributed to deprotonation as pH increased. Chen et al. (2011) also saw an increase in adsorption until a pH of 5 due to competition between protons and metal cations for sorption sites, with a decrease over pH 5 due to the formation of hydroxide complexes. Despite pH 5 being suggested as the pH of maximum sorption by Lu et al. (2012) and Chen et al. (2011), most studies cite a pH of 6 as being ideal. In their study of activated maple wood biochar, Wang et al. (2018) saw that with an increasing pH there was an increasing surface charge due to the deprotonation of functional groups up to a pH of 6, above which soluble hydroxyl complexes or surface precipitation formed. Kilic et al. (2013) reported similar findings in their study where they saw an increase in electrostatic charge from pH 2 to 6, improving Ni and Co interaction with binding sites. At above pH 6, formation of hydroxylated complexes which compete for active sites were again found. Tran et al. (2017) were also in agreement in their study where they investigated the effect of solution pH on the adsorption process of Cu(II) in solutions with pH values from 2.0 to 6.0. They found that up to pH 6 the negative charge of carboxyl groups increased improving adsorption of Cu. Studies also show pH to have an impact on co-precipitation with pH influencing the speciation of metals (Kilic et al. 2013). Inyang et al. (2011) suggest that the coprecipitation of Pb and CO_3^{2-} forming hydrocerrusite and cerrusite was as a result of high pH. Similarly, Cao and Harris (2010) note that high pH (~pH 10) allows Pb coprecipitation with both phosphate and carbonate. Biochar pH is effected by pyrolysis temperatures with increases of pH demonstrated from 370 to 600 °C (Gray et al. 2014), 350 to 750 °C (Domingues et al. 2020), and 300 to 700 °C (Yuan, Xu and Zhang 2011; Ahmad et al. 2012). Ramola et al. (2020b) found a significant increase in adsorption capacity of biochar–calcite composite prepared at 700 °C, with increase in pH from 3 to 9. This may be because calcite form stronger bond with Pb under alkaline conditions.

9.5 Modification

A number of papers study the effect of modifying biochar to enhance adsorption mechanisms of inorganic contaminants in aqueous media. These modifications generally take the form of activation (creating activated carbon/activated biochar), addition of minerals, or magnetization.

Several studies look to activate the pristine biochar, increasing sorption through an increase in specific surface area (SSA) and modifying the surface chemistry, creating activated carbon from biomass sometimes referred to as activated biochar.
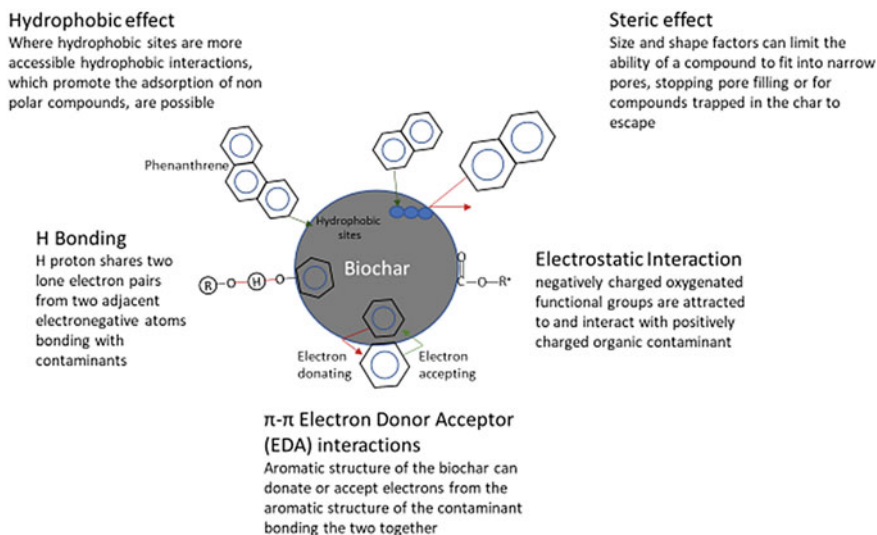
Methods to chemically activate biochar include the addition of chemicals such as hydrogen peroxide (Wang et al. 2018), sodium hydroxide (Ding et al. 2016), or zinc chloride (Ifthikar et al. 2017). Each of these studies demonstrated an increase in functional groups and surface area leading to an increase in sorption capacity. However, these methods do increase production costs and produce contaminated effluents during production (Hagemann et al. 2020). Physical rather than chemical methods using steam, oxygen, or carbon dioxide are also used to increase SSA and remove contaminants (Uchimiya et al. 2010; Grycová et al. 2016; Hagemann et al. 2020).

The addition of minerals to modify biochar commonly takes place pre pyrolysis such as in Wang et al.'s (2015) study where potassium permanganate ($KMnO_4$) was added to increase oxygen functional groups. Under high temperature, $KMnO_4$ was converted to MnO_x particles onto the surface of the biochar which resulted in an increase in hydroxyl and carboxyl functional groups due to oxidizing effect of $KMnO_4$. These modifications increased the sorption capacities of biochar by 2.1 times for Pb, 2.8 times for Cu, and 5.9 times for Cd. Gan et al. (2015) used ZnO modification to adsorb Cr (VI) ions. Again, the raw material was pre-treated with ZnO prior to pyrolysis. The sorption of the modified biochar was 1.2–2 times greater than the sorption of the pristine biochar.

Magnetizing biochar is a further direction investigated by Yuan et al. (2020), Mohan et al. (2014) and Chang et al. (2006), who introduced Fe^{3+} and/or Fe^{2+} to the pristine biochar to increase the sorption of metals. Magnetization was carried out with a variety of raw materials including sewage sludge (Ifthikar et al. 2017), oak wood and bark (Mohan et al. 2014) and chitosan (Chang et al. 2006). Each of these studies introduces Fe via a solution that is mixed with the biochar and then oven-dried to bind the Fe to the surface of the biochar. SSA has been reported to increase with magnetization in some studies (Chang et al. 2006; Mohan et al. 2014; Ifthikar et al. 2017), however, in Mohan et al.'s study (2014), this was dependant on raw material with oak bark SSA decreasing with magnetization but SSA increasing with oak wood magnetization. Biochar loaded with Fe^{3+} increased the oxygen-containing functional groups and enhanced the ability of complexing Cd (Yuan et al. 2020). Ramola et al. (2014) observed that iron impregnated tyre biochar (FeTy) was able to remove Pb better than its pristine biochar. The maximum removal of Pb by FeTy was 95% that followed Temkin adsorption isotherm.

9.6 Immobilization of Organic Contaminants

As with inorganic contaminants in aqueous media several mechanisms have been documented in the removal of organic contaminants primarily H-bonding and charge-assisted H-bonding (CAHB), π–π Electron Donor–Acceptor (EDA) interaction, electrostatic interaction, and steric effect. These are driven by the structure and properties of the biochar, in particular specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio and polarity which can be approximated

Hydrophobic effect
Where hydrophobic sites are more accessible hydrophobic interactions, which promote the adsorption of non polar compounds, are possible

Steric effect
Size and shape factors can limit the ability of a compound to fit into narrow pores, stopping pore filling or for compounds trapped in the char to escape

Phenanthrene

Hydrophobic sites

Biochar

H Bonding
H proton shares two lone electron pairs from two adjacent electronegative atoms bonding with contaminants

$R-O-H \cdots O$

$C-O-R^*$

Electrostatic Interaction
negatively charged oxygenated functional groups are attracted to and interact with positively charged organic contaminant

Electron donating

Electron accepting

π-π Electron Donor Acceptor (EDA) interactions
Aromatic structure of the biochar can donate or accept electrons from the aromatic structure of the contaminant bonding the two together

Fig. 3 The major mechanisms of organic contaminant immobilization by biochar

by the molar O/C ratio. Sorption behavior differs strongly between aromatic and aliphatic compounds, as well as neutral, polar, anionic, cationic, and zwitterionic compounds (Hale et al. 2016; Sigmund et al. 2020). The types of organic contaminants found in aqueous media that have attracted the most concern and attention include pesticides, herbicides, polycyclic aromatic hydrocarbons, dyes, and antibiotics which are structurally diverse (Qiu et al. 2009; Beesley et al. 2010; Zheng et al. 2010; Teixidó et al. 2011) (Fig. 3).

9.7 π–π *Electron Donor–Acceptor Interactions*

π–π Electron Donor–Acceptor (EDA) has been highlighted as one of the most important interactions in the adsorption of aromatic organic compounds to biochar in aqueous media. π–π EDA can occur between π–electron-accepting moieties in the center of the aromatic cluster within the biochar structure and π–electron-donating compounds such as phenols or polyaromatic hydrocarbons (PAHs) (Zhu and Pignatello 2005). The π–π EDA mechanism has been reported as the major mechanism in organic contaminant removal for contaminants including PAHs such as phenanthrene, dibutyl phthalate, sulphides (sulfamethoxazole and sulfapyridine), carbaryl, and atrazine (Zhang et al. 2013; Jin et al. 2014; Xie et al. 2014). A study by Ahmed et al. (2018) also determined that functionalized biochar can act both as π–electron-donor (sorbing phenanthrene) and π–electron-acceptors (sorbing dinitrobenzene). Therein the π-electron donating sites are located at the outer edges of the grapheme-like structures within the biochar. For polar contaminants, π–π EDA

is often reported in conjunction with H-bonding such as in the adsorption of tetracycline, estrone, 17β-estradiol, estriol, 17α-ethynylestradiol, bisphenol A and acetate (Saquing et al. 2016; Zhou et al. 2017; Ahmed et al. 2018). The strength of π bonds is in the realm of weak interactions comparable to H-bonds (Pignatello et al. 2017).

9.8 H-Bonding

H-bonding occurs between a single proton covalently bound to more electronegative atoms and another electronegative atom bearing a lone pair of electrons. Such electronegative atoms can be found on the biochar surface (e.g., O-containing functional groups) (Gilli and Gilli 2010). Studies have highlighted the importance of H-bonding in the removal of several polar organic contaminants such as tetracycline (Jing et al. 2014; Tang et al. 2018), norflurazon, and fluridone (Sun et al. 2011) and florfenicol (Zhao and Lang 2018). Charge-assisted H-bonding (CAHB) is a special type of H-bonding that occurs when the dissociation constant of the H donor and H acceptor groups are very similar (Δ pKa approaches 0) creating an exceptionally strong H-bond (Li et al. 2013). The formation of negative charge-assisted H-bonds has also been reported by Ahmed et al. (2017) in the sorption of negative species (sulfonamide antibiotics) form aqueous media. Similarly at a pH of ~8 where deprotonation of the amino group and sulfamido were enhanced, sulfadimine (an antibiotic contaminant) converted to an anion state enabling a strong negative CAHB between sulfadimine and the carboxylate or phenolate functional groups on the biochar (Wan et al. 2020).

9.9 Electrostatic Interactions

Electrostatic interactions refer to the attraction of oppositely charged groups. For example, negatively charged oxygenated functional groups can bind positively charged organic contaminants, such as methyl violet or methyl blue (Xu et al. 2011; Dawood et al. 2017). The charge of the biochar is heavily pH dependant, at pH below the point of zero charge (PZC) the surface charge is positive causing electrostatic repulsion of positively charged contaminants such as sulfadimidine (SMT^+) (Wan et al. 2020; Ramola et al. 2020a); as the pH of the biochar increases the ionization shifts depending on the functional group and compound dissociation constants and the effect of the electrostatic repulsion declines.

9.10   Steric Effects

Steric effects can influence sorption behavior of organic compounds. Size and conformational factors may limit the ability of a molecule to fit into narrow pores (pore exclusion), or limit a molecule's approach to sorption sites on the surface (Pignatello et al. 2017). Removal of organic contaminants from aqueous media by biochar must be considered in conjunction with the pore size of the biochar, the size of the organic contaminant, and the shape of the organic contaminant.

Size exclusion was reported by Yang et al. (2018) in their study of wood chips, rice straw, bamboo chips, cellulose, lignin, and chitin biochar. Organic molecules were seen to be restricted and could not access biochar pores smaller than the molecule diameter. Tang et al. (2018) also reported size exclusion in their study of the removal of tetracycline by sewage sludge biochar suggesting that adsorbent shows its best adsorption property when pore diameter is 1.7–3 times larger than that of the adsorbate molecule. Schreiter et al. (2018) attributed the higher max sorption capacity for trichloroethylene (TCE) over tetrachloroethylene (PCE) to size exclusion with the smaller TCE molecules able to access a bigger portion of the pore volume of the biochar. Zhang et al. (2013) also conducted a bisolute study about the removal of carbaryl and atrazine by pig manure biochar. In a similar manner to Schreiter et al. (2018) the higher removal of atrazine was attributed to the smaller molecular size of atrazine compared to carbaryl (0.61 nm vs. 0.71 nm). Kah et al. (2016) also highlighted size exclusion as a phenomenon in their study of a diverse series of sorbents pyrolyzed at different temperatures. Size exclusion was significant for plant-derived materials but not so for biochar derived from sewage sludge or pig manure raw materials. These raw materials did not have a microporous structure and as a result, did not develop the porosity associated with size exclusion when pyrolyzed. For small molecules, pore filling can occur which is dependent on pore geometry, pore volume, and pore size distribution. When these factors are favorable for contaminant condensation in these pores, pore filling can play a dominant role in the immobilization of organic contaminants (Nguyen et al. 2007; Zhu et al. 2014; Zhao and Lang 2018). Wang and Xing (2007) studied the sorption of the hydrophobic compounds phenanthrene and naphthalene and noted that at low solute concentrations, sorption of phenanthrene and naphthalene by biopolymer biochar was dominated by the micropore-filling mechanism; however, with an increase in the solute concentration, immobilization of these two compounds shifted to a surface-sorption-dominant process.

10   Key Material Properties for Inorganic Immobilization

10.1   *Specific Surface Area*

Specific surface area (SSA) is a property of biochar that, as with inorganic immobilization, is often cited as important for the sorption of organic contaminants as a larger SSA means access to more sorption sites. The larger the SSA, the more opportunity the contaminant has to be removed by the biochar from aqueous media (Prévoteau et al. 2016). SSA is cited as being a primary property in the removal of organic contaminants in aqueous media by many papers (Zhang et al. 2013; Lattao et al. 2014; Wang et al. 2016; Zhao and Lang 2018). SSA is driven by pyrolysis temperature and raw material (Fig. 2). The role of raw material is discussed by Kah et al. (2016) who demonstrate that plant-based raw materials can develop micropores, increasing SSA and pore-filling potential, but animal waste or sewage-based raw materials do not show evidence of such micropore structures. Similarly Wang et al. (2016) highlight that the SSA of plant-based biochar was significantly higher than animal-based biochar with the result that there were positive correlations between SSA and removal of organic contaminants by wood dust biochar but no such correlations were apparent for swine manure biochar. In their meta data analysis review, Ippolito et al. (2020) assert that although pyrolysis temperature is important in determining SSA, raw material has the largest influence on SSA with SSA being greatest in wood-based biochar. Nonetheless, pyrolysis temperatures are still an important tool to control SSA: at higher pyrolysis temperatures amorphous carbons condense to crystalline structures, more pores are formed and volatiles are removed causing a higher SSA (Chen et al. 2012; Zhang et al. 2013; Wang et al. 2016).

10.2   *Aromaticity*

The molar H/C ratio is widely recognized as an index for the degree of aromaticity/carbonization of biochar which is essential for π–π EDA and hydrophobic interactions. As pyrolysis temperatures increase and aromaticity increases stacks of graphene grow enabling the π–π mechanism to dominate in the removal of contaminants from aqueous media (Jin et al. 2014). Hydrophobic interactions which promote the immobilization of non-polar/hydrophobic compounds, such as phenanthrene, are also possible where aromatic groups are more accessible (Sun et al. 2013). The hydrophobicity of a contaminant is generally described by the octanol–water partition coefficient (K_{ow}). The aromaticity of biochar is affected by pyrolysis temperature, above ~300 °C an increase in pyrolysis temperature leads to greater carbonization and an increase in aromatic compounds (Fig. 2) (Uchimiya et al. 2010; Mukherjee, Zimmerman and Harris 2011; Lehmann and Joseph 2015; Lou et al. 2016). However**,** the degree of carbonization in the biochar is also relevant to partitioning with the partitioning of organic contaminants occurring in the

uncarbonized fraction of the biochar (Chen et al. 2018; Schreiter et al. 2018). At lower temperature pyrolysis (<400 °C) removal of organic pollutants by biochar is dominated by partitioning due to the amorphous structure of the biochar making them effective media for the partitioning of more polar organic compounds (Chen et al. 2008; Sun et al. 2012).

10.3   Polarity

The O/C ratio is commonly accepted as an index for polarity and is intrinsically linked to the abundance of oxygenated functional groups. The higher the polarity, and therefore the higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations/polar contaminants via H-bonding and electrostatic attraction (Xu et al. 2011; Qiao et al. 2018; Schreiter et al. 2018; Zhao and Lang 2018). However, a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups repulsing nonpolar/hydrophobic contaminants, further demonstrating the importance of the relationship between contaminant structure and properties with the biochar structure and properties (Zhu et al. 2005; Rajapaksha et al. 2015; Chen and Ni 2017; Schreiter et al. 2018). Zhang et al. (2017a, b, c) also discussed the link between partitioning and the polarity of the contaminant with acetone, cyclohexane, and toluene partition rates relating directly to polarity; hydrophilic/polar contaminants were adsorbed more easily by biochar that was less polar as the low pyrolysis temperatures lent themselves to the presence of noncarbonized organic matter where partitioning takes place. Polarity, indexed by the O/C ratio, is determined in the main by pyrolysis temperatures; at lower temperatures, O is more abundant, and as such the biochar is more polar (Fig. 2) (Chen and Chen 2009; Zhang et al. 2017c).

11   Limitations

While there is extensive literature on biochar and the removal of organic and inorganic pollutants more research should be conducted to bridge the gap between laboratory results and fieldwork. The majority of research continues to revolve around laboratory findings rather than the use of biochar in the field or in simulated field conditions. Maximum sorption capacity is an important metric, however, it represents sorption in perfect conditions such as ideal temperatures, pH, contaminant concentrations, and flow. Single contaminant environments are often studied in laboratory batch experiments, yet these conditions are unlikely to be seen in the field where multiple contaminants exist together with dissolved organic matter affecting contaminant mobility, bioavailability, and toxicity. The impact of changes in temperature, pH, and contaminant concentrations have been studied providing useful insights but very

rarely use the parameters as seen in aqueous media where biochar could potentially be deployed such as rivers, runoff, or mine waters. Such laboratory findings are not fully transferrable to field conditions which limit their value when attempts are made to use these findings in practice. While the use of simulated field conditions such as stormwater, synthetic mine water, or even collected mine water has been used to undertake studies in a laboratory setting this approach is far from prevalent.

12 Conclusion and Future Prospects

This chapter highlights the successful use of biochar as an adsorbent for the removal of contaminants from aqueous media. Biochar is a relatively low-cost, sustainable product which has been demonstrated to be effective in the removal of both organic and inorganic contaminants. This has led to the study of biochar in relation to aqueous environments such as road runoff (Cairns et al. 2020), mine waters (Bandara et al. 2020), stormwater (Boehm et al. 2020) drinking water (Hu et al. 2019) and biologically treated wastewater (Hagemann et al. 2020). This chapter reviews the key immobilization mechanisms and underpinning material properties for both inorganic and organic contaminants.

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation–π bonding, reduction and subsequent sorption, and precipitation. These mechanisms do not work in isolation and it is common for several mechanisms to be relevant simultaneously.

Key material properties for inorganic contaminant immobilization include surface functional groups, cation exchange capacity, specific surface area, and pH. These material properties are primarily controlled by raw materials and/or pyrolysis temperatures. Surface functional groups of biochar are essential to cation exchange, electrostatic attraction, and complexation and are affected by both raw material and pyrolysis temperature. Functional groups start to form at ~120 °C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350 °C. CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are primary drivers of CEC with the lower pyrolysis temperatures allowing more functional groups and as such greater CEC. Specific surface area (SSA) is a further important property of biochar; the higher the SSA the more sites are available for sorption to occur. As opposed to functional groups and CEC, SSA is seen to increase as a result of an increase in pyrolysis temperature. Solution pH, which can be affected by the biochar, is also cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent.

Several mechanisms have been documented in the removal of organic contaminants from aqueous media, primarily: H-bonding and charge-assisted H-bonding (CAHB), π–π Electron Donor–Acceptor (EDA) interaction, electrostatic interaction and steric effect. These are driven by the structure and properties of the biochar,

in particular specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio, and polarity which can be approximated by the molar O/C ratio. Again, these material properties are primarily controlled by raw materials and/or pyrolysis temperatures. As with inorganic contaminants, specific surface area (SSA) is an important property of biochar in relation to the immobilization of organic contaminants. The molar H/C ratio is an index aromaticity/carbonization of biochar which is essential for $\pi-\pi$ EDA and hydrophobic interactions. Aromaticity increases with pyrolysis temperatures enabling the $\pi-\pi$ mechanism to dominate in the removal of contaminants from aqueous media. Hydrophobic interactions which promote the immobilization of nonpolar/hydrophobic compounds are also possible where aromatic groups are more accessible. The O/C ratio, which is commonly accepted as an index for polarity is intrinsically linked to the abundance of oxygenated functional groups. The higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations/polar contaminants via H-bonding and electrostatic attraction. However, a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups repulsing nonpolar/hydrophobic contaminants. This highlights the importance of the relationship between contaminant structure and properties with the biochar structure and properties.

Studies reviewing the removal of contaminants from aqueous media by biochar in the field are scarce and as a result, biochar onsite use in aqueous media necessitates further studies to systematically investigate the interplay of different environmental factors such as pH, dissolved organic matter (DOM), and the mix of contaminants seen in various real-world sites. Fouling as a result of these environmental factors could lead to "caking" and the subsequent blocking of biochar surface and pores; such fouling is discussed in the activated carbon community but less so by biochar researchers. A transfer of knowledge between these research communities would help drive meaningful further developments in the field. Furthermore, key material properties of biochar relevant to field conditions are often not reported, including the previously discussed point of zero charge. Understanding the impact of the environmental pH on the charge of the biochar underpins a number of key immobilization mechanisms and as such arguably should become standard to report bringing laboratory work and field study closer together.

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