Engineered Biochar Production and Its Potential Benefits in a Closed-Loop Water-Reuse Agriculture System

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Received: 17 September 2020; Accepted: 12 October 2020; Published: 13 October 2020

Abstract: Biochar’s potential to remove various contaminants from aqueous solutions has been widely discussed. The rapid development of engineered biochar produced using different feedstock materials via various methods for wastewater treatment in recent years urges an up-to-date review on this topic. This article centers on summarizing state-of-the-art methods for engineered biochar production and discussing the multidimensional benefits of applying biochar for water reuse and soil amendment in a closed-loop agriculture system. Based on numerous recent articles (<5 years) published in journals indexed in the Web of Science, engineered biochar’s production methods, modification techniques, physicochemical properties, and performance in removing inorganic, organic, and emerging contaminants from wastewater are reviewed in this study. It is concluded that biochar-based technologies have great potential to be used for treating both point-source and diffuse-source wastewater in agricultural systems, thus decreasing water demand while improving crop yields. As biochar can be produced using crop residues and other biomass wastes, its on-farm production and subsequent applications in a closed-loop agriculture system will not only eliminate expensive transportation costs, but also create a circular flow of materials and energy that promotes additional environmental and economic benefits.

Keywords: engineered biochar; circular economy; crop residue; soil amendment; sustainable agriculture; water resilience; water reuse

1. Introduction

Water is essential for agriculture. Nevertheless, as a result of the continually soaring global human population and intensifying urbanization, the shortage of water supply to agriculture is inevitably exacerbating the sustainability of food supply, especially in arid and semi-arid areas [1]. A recent study shows that 76% of global croplands are scarce in green water (i.e., root-zone soil moisture available for uptake by plants) for at least one month a year and about 42% are troubled for five months a year [2]. Water scarcity can be quantity-based, quality-based, or based on the combined effect of the two [3]. In arid and semi-arid areas, groundwater is usually the single most important source of irrigation water [4]; however, with the prevalent overuse of synthetic fertilizers, groundwater is oftentimes very vulnerable to contamination due to the leaching of unutilized nutrients (e.g., nitrate (NO$_3^-$) and nitrite (NO$_2^-$)) [5] and the flushing of dissolved elements of toxicological concern (e.g., As(III)) [6]. It is,
therefore, critical to highlight the importance of conserving water quality while introducing extra sources of freshwater to increase water quantity in agricultural practices.

Biochar, a stable charcoal-like porous material, has been widely investigated as a soil amendment for improving water holding capacity of soil in recent years [7]; whereas, it has also been explored as a potent sorbent for removing various contaminants from wastewater [8]. In agricultural fields, the most commonly used method of irrigation in many developing regions is surface irrigation, which may lead to low water use efficiency (WUE) due to a significant loss of water mainly through evapotranspiration (especially during dry seasons) and/or through infiltration (especially in porous soils) [9]. Considering the fact that more than 70% of freshwater withdrawn is used for irrigation globally [10], innovative solutions for treating/reusing the large portion of water unutilized by crops are of particular exigency. In many studies, biochar also exhibited remarkable capacity to adsorb different nitrogen species [11] and a variety of dissolved elements of toxicological concern [12]. In view of the large specific surface area, abundant surface functional groups, and other favorable properties of biochar [13], its real-world applications have been extended to the treatments of various types of wastewater, including industrial wastewater, municipal wastewater, agricultural wastewater, and stormwater [8].

Biochar can be produced using lignocellulosic crop residues, which has the great potential to turn the huge quantities of biomass waste (in a traditional point of view) into value-added resources [14]. As another advantage, the production of biochar occurs under oxygen-limiting (if not oxygen-absent) conditions, during which the emissions of suspended particulate matter, smoke and/or greenhouse gases (GHGs) are significantly less compared with burning or passive composting of crop residues [15,16]. At the same time, the large portion of recalcitrant carbon preserved in biochar is considerably more unsusceptible to thermal and microbial degradation [13], thus slowing down the emissions of carbon dioxide (CO₂) and/or methane (CH₄) into the atmosphere [17]. Therefore, on-farm production and application of biochar may provide multidimensional benefits that promote sustainable agronomy and circular economy [18].

The applications of biochar as a soil amendment in agricultural fields have been widely investigated and reviewed over the last decade [19]. Popular topics include biochar’s physicochemical characteristics [20], sorption for different soil contaminants [21], influences on soil productivity [19], effects on soil GHG emissions [22], and interaction with soil microorganisms [17]. Yet insufficient attention has been paid to the effectiveness of biochar-based technology in treating diffuse sources of wastewater, especially in the agriculture sector. Most current applications of biochar in agricultural fields focus on enhancing water and nutrient retention, thus improving the WUE and nutrient use efficiency and minimizing the negative impacts of runoff and infiltration on nearby water bodies or underneath aquifers (i.e., indirect reuse) [7,21]; but there is an emerging trend of using biochar for treating various types of wastewater [8]. If both point-source and diffuse-source agricultural wastewater could be efficiently treated and reused for irrigation (i.e., direct reuse), water demand for croplands from external sources would be appreciably cut down. To discuss biochar’s potential in agricultural wastewater treatment, it is important to review its various properties relevant to its role as a potent adsorbent for different contaminants and to be updated about state-of-the-art techniques for modifying these properties.

The main objectives of this work are (1) to review up-to-date advances in the production methods, modification techniques, and physicochemical properties of engineered biochar and (2) to articulate the potential benefits of using biochar in a closed-loop agriculture system for sustainable development. In the following sections, current biochar production methods, performance-oriented biochar engineering techniques, and diverse advantages and pitfalls of biochar applications in an integrated circular agriculture system are reviewed.

2. Methods for Producing Biochar

Biochar is produced as a solid residue via the thermal decomposition of biomass at elevated temperatures in an environment with limited or no oxygen, a process known as pyrolysis. The same
process also produces crude oil (a.k.a., bio-oil), which has a high energy density of approximately 26,800 MJ/m$^3$ and can be further processed to produce biofuel and other value-added products [23].

2.1. Pyrolysis Reactors

Traditionally, fire pits, earth kilns, cinder block kilns, and brick kilns have been widely used for small-scale biochar production; these methods still remain popular in some low-income developing countries [24]. However, these traditional methods require high energy consumptions and extensively long process times; in addition, the biochar produced using these methods also lacks adequate homogeneity and effectiveness as a soil amendment [25]. Custom-designed kiln-based technology is preferred by the modern biochar industry, which is attributed to the reactor’s unique multi-zone combustion, airflow negative pressure, and recipe-driven control system that ensures the stability and quality of biochar [26,27]. The temperature and residence time can be programmed and precisely controlled with the use of thermal sensors [28].

The various designs of pyrolysis reactors by different manufacturers are stemmed from two basic designs in terms of their reactor positions, i.e., horizontal and vertical reactors (Figure 1). The reactor position plays an important role in the feedstock loading and unit operation. With horizontal reactors, the loading of feedstock and the discharge of biochar can be performed manually (very labor intensive) or mechanically (using conveyer belts, bucket elevators, or tractor scoops) [24]. Vertical reactors use gravitational forces to move biomass and/or biochar during pyrolysis, but the loading of feedstock can be difficult; in addition, temperature gradients can be present and affect the consistency in biochar quality [29]. To reduce the overall energy cost, a portion of the syngas generated during pyrolysis can be recycled and flared to recover heat energy for drying and pyrolyzing feedstock, to provide mechanical energy for irrigation pumps via a heat exchanger and modern steam engine, and/or to generate electricity [25,27].

Pyrolysis reactors can be operated in batch, semi-batch, or continuous mode [24]. Batch mode typically involves a heating period (for biochar production) followed by a cooling period (for discharging produced biochar and beginning the next batch). While batch reactors are popular for small-scale biochar production, the energy cost to heat and reheat the reactor can be prohibitive [25]. A semi-batch system uses a series of portable batch reactors (i.e., mobile units) to improve the efficiency of oven heat; its capacity is a function of the number of batch runs that can be accomplished within a period of time [24]. Continuous reactors are operated continually except for occasional maintenance. The typical biochar production in a continuous system is >2.75 t/h, with a remarkable unit attainment of 90-95% [24]. Hence, continuous reactors are often more economically feasible for large-scale biochar production [30,31].
Some recent studies investigated the use of microwave heating for the production of biochar [8]. In these studies, the electromagnetic energy of ultrasound and/or microwave was transferred into thermal energy via dipolar and interfacial polarization effects [32]. The heating of biomass to desired temperatures was found to be faster (i.e., require less time) than conventional heating methods [32]. The pretreatment of raw material (e.g., drying) is not necessary for microwave pyrolysis, which can significantly reduce energy use and increase product value [33]. The cavity of produced biochar can be enhanced by ultrasound waves that exfoliate and break apart the regular shape of graphitic oxide layers of biochar, thus increasing the porosity and permeability of the final product [26]. The ultrasound activation can be accomplished under room temperature within a short duration [26].

2.2. Slow and Fast Pyrolysis

Pyrolysis is a versatile process, as its yields of biochar (solid), bio-oil (liquid), and syngas (gas) can be optimized by varying the process conditions and residence times [25,30]. Depending on the rate of temperature ramping, stabilized pyrolysis temperature, and different residence times, pyrolysis is categorized into two broadly different regimes: slow pyrolysis and fast pyrolysis [25].

Slow pyrolysis is usually operated at low to moderate temperatures (e.g., 300–700 °C with a relatively slow heating rate (e.g., 5–10 °C/min and long residence times (i.e., from hours to days) [24,34]. Since most organic components in biomass (especially lignin) have very limited thermal degradability at these temperatures, a large portion (e.g., 40–70% by weight) of the carbon in raw biomass is preserved as biochar, resulting in a higher yield of biochar and less bio-oil and syngas generation compared to fast pyrolysis [25]. The physicochemical properties of biochar gradually evolve throughout the whole process [11,20,28]. Diverse surface functional groups containing oxygen and hydrogen are retained during slow pyrolysis [13]; as a result, the participation of slow-pyrolysis biochar in soil microbiochemical systems can be maximized [19,20].

Fast pyrolysis is popular in biofuel industry for its high yields of highly energy-intensive bio-oil (typically ~65% by weight). characterized by high temperatures (e.g., 300–1000 °C), fast heating rates (usually >300 °C), and short residence times (<2 s) [24,34]. The yield of bio-oil is sensitive to the temperature set for pyrolysis. For example, the maximum bio-oil yield (60–75% by weight) from woody feedstock typically occurs around 500 °C and further temperature increase will decrease bio-oil yield because of rapid quenching of vapors [24]. As a large portion of the biomass undergoes extensive thermal reactions to produce bio-oil, the yield of biochar via fast pyrolysis is generally low (15–30% by weight) [35]. The produced biochar is often powdered because small particles of biomass are typically used during fast pyrolysis [36]. Recent research revealed that an organic coating could be formed on the surface of high-temperature biochar that is produced from nutrient-rich biomass; this organic coating would greatly contribute to soil fertility, thus making the biochar a preferable soil amendment [37].

As shown in Table 1, slow pyrolysis and fast pyrolysis generally produce biochars with contrasting properties. It should also be noted that the resulting biochar may also have different properties depending on the feedstock used for the production, thus making some more successful as soil amendments than others. The factors affecting the physicochemical properties of biochar are further discussed in Section 3.

Table 1. Physicochemical properties (pH, surface area, and pore volume) of biochar produced at different types of feedstock at various temperatures.

| Feedstock         | Pyrolysis Method (Residence Time) | Temperature (°C) | PH   | Surface Area (m²/g) | Pore Volume (cm³/g) | Ref. |
|-------------------|-----------------------------------|------------------|------|---------------------|---------------------|-----|
| Soybean stover    | Slow pyrolysis (3 h)              | 300              | 7.27 | 5.61                | -                   | [38]|
| Peanut shell      | Slow pyrolysis (3 h)              | 300              | 7.76 | 3.14                | -                   | [38]|
| Pine wood         | Slow pyrolysis (0.5 h)            | 400              | 8.5  | 140                 | 0.06                | [39]|
| Paper mill sludge | Slow pyrolysis (2 h)              | 400              | 8.23 | 33.56               | 0.051               | [40]|
| Herb residue      | Slow pyrolysis (3 h)              | 400              | 10.2 | 49.2                | 0.042               | [41]|
Table 1. Cont.

| Feedstock            | Pyrolysis Method (Residence Time) | Temperature (°C) | PH  | Surface Area (m²/g) | Pore Volume (cm³/g) | Ref. |
|----------------------|----------------------------------|------------------|-----|---------------------|---------------------|------|
| Pine wood            | Slow pyrolysis (0.5 h)           | 500              | 8.7 | 380                 | 0.15                | [39] |
| Wood bark            | Slow pyrolysis (0.5 h)           | 500              | 9.8 | 350                 | 0.14                | [39] |
| Wood bark            | Slow pyrolysis (2 h)             | 500              | 10.9| 67.5                | 0.054               | [42] |
| Rice husk            | Slow pyrolysis (2 h)             | 500              | 7.99| 230.91              | -                   | [43] |
| Paper mill sludge    | Slow pyrolysis (2 h)             | 500              | 8.78| 47.42               | 0.063               | [40] |
| Dairy manure         | Slow pyrolysis (4 h)             | 500              | 10.5| 13.0                | -                   | [44] |
| Paper mill sludge    | Slow pyrolysis (2 h)             | 600              | 9.17| 50.44               | 0.074               | [40] |
| Rice straw           | Slow pyrolysis (3 h)             | 600              | 9.7 | 156.2               | 0.084               | [45] |
| Wheat straw          | Slow pyrolysis (3 h)             | 600              | 9.1 | 183.3               | 0.091               | [45] |
| Herb residue         | Slow pyrolysis (3 h)             | 600              | 10.1| 51.3                | 0.051               | [41] |
| Soybean stover       | Slow pyrolysis (3 h)             | 700              | 11.32| 420.3               | 0.19                | [38] |
| Peanut shell          | Slow pyrolysis (3 h)             | 700              | 10.57| 448.2               | 0.20                | [38] |
| Pine wood            | Fast pyrolysis (2 s)             | 400              | -   | 4.8                 | -                   | [46] |
| Pine sawdust         | Fast pyrolysis (3 s)             | 400              | 4.2 | 6.2                 | 0.011               | [47] |
| Sawdust              | Fast pyrolysis (3 s)             | 400              | 6.35| 83.90               | 0.012               | [48] |
| Pine wood            | Fast pyrolysis (2 s)             | 425              | -   | 1.35                | -                   | [49] |
| Switchgrass          | Fast pyrolysis (30 s)            | 450              | 9.1 | 1.4                 | 0.012               | [50] |
| Pine wood            | Fast pyrolysis (2 s)             | 500              | -   | 175.4               | -                   | [46] |
| Sawdust              | Fast pyrolysis (3 s)             | 500              | 6.42| 36.60               | 0.015               | [48] |
| Rice husk            | Fast pyrolysis (acid)            | 500              | -   | 46.8                | 0.033               | [51] |
| Sawdust              | Fast pyrolysis (3 s)             | 600              | 7.00| 30.20               | 0.010               | [48] |
| Switchgrass          | Fast pyrolysis (30 s)            | 600              | 10.6| 2.1                 | 0.023               | [50] |
| Rice husk            | Fast pyrolysis (alkali)          | 500              | -   | 117.8               | 0.073               | [51] |
| Sawdust              | Fast pyrolysis (3 s)             | 700              | 9.08| 65.20               | 0.016               | [48] |
| Sawdust              | Fast pyrolysis (3 s)             | 800              | 9.31| 330.00              | 0.048               | [48] |
| Switchgrass          | Fast pyrolysis (30 s)            | 800              | 11.2| 17.2                | 0.032               | [50] |
| Straw pellet         | Microwave (-)                    | 200              | -   | 1.14                | 0.37                | [52] |
| Willow chips         | Microwave (-)                    | 170              | -   | 3.87                | 2.07                | [52] |
| Corn stover          | Microwave (15 min)               | 650              | 10.5| 43.4                | -                   | [53] |
| Pine wood            | Microwave (15 min)               | 650              | 7.85| 52.1                | -                   | [53] |
| Switchgrass          | Microwave (15 min)               | 650              | 9.73| 48.0                | -                   | [53] |
| Sludge               | Microwave (10 min)               | 700              | -   | 110.80              | 0.07                | [54] |
| Peanut shell          | Microwave (-)                    | 200              | 6.40| 4.93                | 0.018               | [55] |
| Peanut shell          | Microwave (-)                    | 400              | 6.76| 20.8                | 0.034               | [55] |
| Peanut shell          | Microwave (-)                    | 600              | 7.78| 587                 | 0.289               | [55] |

2.3. Major Challenges for Biochar Production Technologies

Despite the increased biochar yields with the use of existing technologies, the emissions of excessive air pollutants during the pyrolysis of biomass (and as a result of incomplete fuel combustion) has not been effectively resolved. The contaminants in the syngas of biochar typically include but are not limited to ammonia (NH₃), hydrogen sulfide (H₂S), particulate matter (PM), alkalis, and tars [56]. The emission levels often do not comply with current environmental regulations in many states, including some large agricultural states like California [57,58]. Although the United States is one of the largest producers of biochar in the world, most of the biochar used in the country is imported from elsewhere [25]. Considering the continually increasing market demand of biochar in the decades to come, more investment is urged to enhance the environmental performance of pyrolysis units and add more production options in the United States as well as in other countries.

Another major challenge for biochar production technologies is linked to the economic feasibility of biochar and agriculture coproduction. According to a stochastic analysis conducted on a slow-pyrolysis biochar production budget, the fixed and variable costs were about 505.14 USD/t and 499.13 USD/t, respectively [59]. The application of biochar to a beet field (Labrador, Canada) increased the beet
yield from 2.9 t/ha to 11.4 t/ha and resulted in an average annualized net return of 4953 USD/ha and an maximum annualized net return of 11,288 USD/ha (both over variable costs of biochar) [59], demonstrating that biochar as a soil amendment has great potential to improve food security; however, the same experiment in a potato field led to a minimum annualized net return of –318.82 USD/ha over variable costs of biochar [59], indicating that biochar application would not be a panacea for all crops. To further improve the economic feasibility of biochar and agricultural coproduction, pyrolysis units should be installed and operated for biochar production near feedstock sources, thus reducing the high cost of long-distance transportation of low-energy-density biomass [60]. The crude oil generated during pyrolysis can be transported to nearby refineries (economically feasible if <500 km) to further increase biochar’s commercial values (i.e., marketability) for its applications in agriculture [24,61].

3. Physicochemical Properties of Pristine and Engineered Biochar

Biochar’s physicochemical properties, especially its pH, specific surface area, and pore volume, are decisive for its applications and effectiveness [21,62]. These physicochemical properties of pristine biochar are largely determined by many factors during its production, including but not limited to its pyrolysis method and pyrolysis temperature, as well as the feedstock type [20,28]. In recent years, a variety of engineering methods have been developed and used to expand biochar’s application and enhance its performance [63]. In this section, the discussion is focused on properties closely pertinent to the use of biochar for water and wastewater treatment.

3.1. Properties of Pristine Biochar and Major Impacting Factors

As shown in Table 1, the feedstock type is crucial to the physicochemical properties of biochar. Even when the pyrolysis conditions are set to be identical, the biochar produced from different raw materials is not likely to be the same because of their compositional and structural differences [62]. For example, both after a slow pyrolysis process for 3 h at 300 °C, the soybean stover biochar had a specific surface area of 5.61 m²/g, while the peanut shell biochar had a specific surface area of 3.14 m²/g [38]. A more pronounced difference between two different feedstocks often leads to more significant dissimilarities between the produced biochar. For instance, the biochar produced from rice straw at 600 °C via slow pyrolysis for 3 h had a pH of 9.7, a specific surface area of 156.2 m²/g, and a total pore volume of 0.084 cm³/g [45]; however, the same pyrolysis process using herb residue as the feedstock resulted in a very different biochar that had a pH of 10.1, a specific surface area of 51.3 m²/g, and a total pore volume of 0.051 cm³/g [41].

The influences of pyrolysis method and residence time are also decisive. In a previous study, the biochar derived after pyrolyzing pine wood at 400 °C for 30 min had a specific surface area of 140 m²/g [39]; in another study, the pine wood biochar produced via fast pyrolysis for a residence time of 2 s only had a specific surface are of 4.8 m²/g [46]. A longer residence time allowed more heat energy to transfer through the feedstock, alternating the compositions and structures of the carbonaceous material via thermal degradation [55]. Therefore, given the same pyrolysis temperature, slow pyrolysis is typically more favorable for increasing the specific surface area and porosity of the resulting biochar, as more energy can contribute to the intensive carbonization [7]. Microwave pyrolysis, as a novel method, is effective in preserving more carbonaceous matter and diverse functional groups [55]. The microwave-mediated pine wood biochar had a specific surface area of 52.1 m²/g, which was significantly higher than that produced via fast pyrolysis of similar conditions due to its high abundance of micropores [53].

As reported by many previous studies, pyrolysis temperature is probably the most important factor deciding the physicochemical properties of biochar [42,43,62]. For the same feedstock and pyrolysis methods, increased pyrolysis temperatures typically resulted in higher pH values, larger specific surface areas, and greater pore volumes of the produced biochar (Table 1). In addition to these property changes, biochar produced at a higher pyrolysis temperature is also more stable and more resistant to
biodegradation when applied to the environment, which can greatly contribute to carbon sequestration and carbon emission mitigation [27].

3.2. Biochar Engineering Methods

Considering the versatility of biochar, different physical, chemical, and biological techniques could be used to tailor its physicochemical properties in hope of optimizing its performance in any specific application. The engineering of biochar could be accomplished during its production (by designing specific pyrolysis conditions) and/or after its production (by modifying/improving the original properties of pristine biochar [63].

3.2.1. Physical Methods

Biochar’s physicochemical properties, including porosity, permeability, and functional group diversity and abundance, could be enhanced at relatively low costs and with minimum environmental risks with the use of physical biochar engineering techniques such as ball milling modification, gas/steam activation, magnetization, and microwave irradiation (Figure 2).

Ball milling (Figure 2A) is a grinding method that can significantly reduce the size of pristine biochar and produce nano-scale fine biochar powders. As the hollow cylindrical shell rotates, the stainless steel balls (typically 12–125 mm), which occupies approximately 30–50% of the inside volume, are lifted up on the rising side and cascade down from near the top of the shell; at the same time, biochar is ground in between colliding balls and reduced in size [64]. For any given ball mill, the fineness of ball-milled biochar increases as the rotating speed of the shell increases until an intrinsic limit is reached. In a recent study, the ball-milled biochar produced from sugarcane bagasse, bamboo, and hickory wood chips exhibited remarkably higher specific surface area and total pore volume compared to the pristine biochar [65]. For example, the Brunauer-Emmett-Teller surface area and Barrett-Joyner-Halenda pore volume of the pristine biochar derived from bamboo at 450 °C were 4.7 m²/g and 0.003 cm³/g, which drastically increased to 299 m²/g and 0.083 cm³/g, respectively [65]. The same study also revealed that, in addition to the increased external and internal surface areas, ball milling of biochar also increased the number of acidic surface functional groups that are favorable to electrostatic interaction and surface complexation with environmental contaminants (e.g., heavy metals) [65]. Many other studies also demonstrated similar improvements [64–66], making ball milling technique an economic method of biochar engineering for environmental applications. However, the nano-scale ball-milled biochar particles may easily disperse in water and be carried by surface runoffs into nearby water bodies [63].

Gas/steam activation (Figure 2B) is a widely used biochar engineering technique for inducing the formation of porosity, increasing specific surface area, enhancing surface reactivity, and removing trapped residues generated due to incomplete combustion during pyrolysis [63,67]. When water vapor is applied for steam activation, the surface of biochar may be activated by the H₂ and CO₂ generated via surface oxidation reactions illustrated by Equations (1), (2), and (3):

\[
\begin{align*}
C + H₂O & \rightarrow CO + H₂ \quad (1) \\
2C + H₂ & \rightarrow 2CH \quad (2) \\
CO + H₂O & \rightarrow CO₂ + H₂ \quad (3)
\end{align*}
\]

Alternatively, gases such as CO₂ and air can be directly used for the activation of biochar [68]. Recent studies showed that steam-activated biochar had enhanced sorption capacities compared with pristine biochar produced via slow pyrolysis [67]. When applied in agricultural soils, it was found that steam-activated wood biochar could mitigate emissions of CH₄ and N₂O by 14–70% and 10–41%, respectively [69]. In practice, gas/steam activation may be integrated with other surface modification techniques for the production of more specifically engineered biochar.
Magnetic biochar (Figure 2C) is often used for its water and wastewater treatment applications to improve the timeliness and efficiency of separating saturated biochar from treated water [70]. With the incorporation of an appropriate magnetic medium (e.g., zero-valent iron, CoFe₂O₄, gamma-Fe₂O₃, and Fe₃O₄), engineered biochar could be effectively separated from aqueous phase by use of magnetic forces [71]. In addition, magnetic biochar is also ideal for removing certain heavy metals and organic contaminants from different types of wastewater [72–74]. Recent studies also revealed that magnetic biochar was able to considerably boost catalytic activity by introducing reactive oxygen species via the activation of persulfate, peroxydisulfate, or hydrogen peroxide; as a result, the degradation of organic compounds in wastewater could be enhanced [75–77]. Magnetic biochar can be synthesized using a variety of techniques, including but not limited to:

- Impregnation pyrolysis, i.e., pyrolyzing the dried residue of a metal solution impregnated with feedstock under an inert atmosphere with limited or no oxygen [78].
• Co-precipitation, i.e., drying the residue of a biochar-metal solution after removing the supernatant, during which the transition metals are precipitated by NaOH or NH$_4$OH [79,80].
• Reductive co-deposition, i.e., similar to co-precipitation except that transition metals are reduced by reducing agents such as sodium borohydride or potassium borohydride [71].
• Hydrothermal carbonization, i.e., heating the homogeneous mixture of the feedstock and a metal solution at a temperature lower than that of pyrolysis (<300 °C) [81].
• Ball milling, i.e., enforcing the incorporation of feedstock and iron oxides using a ball mill [82].
• Cross-linking of biochar and iron oxides [83].

Based on the search results from the Web of Science, the popularity of existing magnetic biochar production techniques was discussed in a recent review, indicating that 39.29% of the magnetic biochar was synthesized via impregnation pyrolysis, 30.36% via co-precipitation, 1.78% via reductive co-deposition, 3.57% via hydrothermal carbonization, and 25% via other methods (e.g., ball milling and cross-linking of biochar and iron oxides) [71]. The synthesis of magnetic biochar requires a certain level of operation training, as inappropriate handling may cause partial blockage of pores and loss of biochar surface area.

Microwave pyrolysis (Figure 2D) is an emerging biochar engineering technique. Unlike conventional pyrolysis, the heating of feedstock is based on microwave irradiation (0.03–300 GHz), raising the thermal reaction temperature to 200–300 °C within a short duration of 10–30 min and resulting in high-performance engineered biochar with a high yield (>60% by weight), large specific surface area up to 800 m$^2$/g, and many hydrophilic surface functional groups [32]. Microwave-induced biochar are of particular interest to various environmental applications regarding its greatly improved water holding capacity and cation exchange capacity [52]. In addition, microwave pyrolysis is compatible with other biochar engineering methods; its integration with other methods (e.g., steam activation or impregnation) has significantly improved the physicochemical properties of the produced biochar [54,78,84]. Once fully developed, with precise and stable control of power and temperature, this method may be more cost-effective compared with the other methods since feedstock pretreatment steps such as shredding and drying can be omitted [32].

### 3.2.2. Chemical Methods

Pristine biochar can be activated using a variety of chemicals through mainly two categories of reactions, including (1) oxidation of biochar with strong acids, bases, and other oxidizing agents, and (2) synthesis of biochar-based composites with amino groups, chitosan, metal oxides, or carbon nanotubes, etc. The chemical reactions are designed to improve biochar’s physicochemical properties and enhance its performance in any specific application.

The oxidation of biochar can be conducted either before pyrolysis (to modify the properties of raw materials) and/or after pyrolysis (to improve the properties of pristine biochar) [85–87]. In previous studies, biochar could be engineered (1) with different acids (e.g., HCl, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, and H$_2$O$_2$) to increase the availability of surface carboxyl groups and other oxygen-containing functional groups; (2) with different alkali (e.g., NaOH and KOH) to form more aromatic groups and other carbon-containing functional groups and to optimize surface electrostatic attraction, π stacking, surface precipitation, and/or surface complexation; and (3) with different other oxidizing agents (e.g., Fe(III) and KMnO$_4$) to improve the surface area and pore size distribution [88]. In recent years, novel techniques such as oxygen plasma activation were developed to engineer pristine or chemical-activated biochar at relatively low costs [89]. The process is conducted using a dielectric barrier discharge in a plasma chamber under a discharge pressure of ~2 Torr (Figure 3). When the reactive gas (O$_2$) flows through the chamber, the electron-gas interactions (i.e., ionization, excitation, and elastic scattering) generated a great many of reactive species (i.e., excited atoms (O*) and oxygen ions (O$^+$)) and electrons [89]. With oxygen plasma for biochar activation for 5 min, the capacitance of engineered biochar was improved by 72.3% and 183.8% compared with conventional chemical-activated biochar and untreated
biochar, respectively [89]. Once fully developed, environmentally-friendly and cost-effective chemical methods have great potential for high-performance engineered biochar production.

As shown in Figure 4, a great diversity of biochar-based composites could be synthesized as either nano-metal oxide/hydroxide biochar composites, magnetic biochar composites, or nanoparticle-/clay-coated biochar [21,63,87,90]. For the production of nano-metal oxide/hydroxide biochar, one technique is to pyrolyze the biomass impregnated with metal ions (after being immersed in a solution of metal salts). Common metal salts include but are not limited to FeCl₃, AlCl₃, MgCl₂, CaCl₂, ZnCl₂, and CoCl₂, which would be transformed into nano-metal oxides like Fe₂O₃, Al₂O₃, MgO, CaO, ZnO, and CoO, respectively [82,91–93]. Because of these nano-metal oxides, the surface area of biochar can be significantly improved, as well as the reactivity of its surface for the adsorption of organic/inorganic compounds and heavy metals [93]. Target elements (e.g., Fe, Al, Mg, Ca, and Mn) can also be enriched in the biomass (i.e., plants) through bioaccumulation. When the biomass is pyrolyzed, the accumulated biomass could be transformed into nano-metal oxides or hydroxides [94]. Alternatively, nano-metal oxides and/or hydroxides can be inserted to pristine biochar via heat treatment, hydrolysis, and impregnation and other methods [95,96]. Similarly, for the synthesis of functional nanoparticles-coated biochar, the treatment can be conducted before the pyrolysis by immersing pristine biochar in suspensions of homogenized nanoparticles, carbon nanotubes, or clays; otherwise, the coating materials could be impregnated after the pyrolysis [97,98].
3.2.3. Biological Methods

Microorganisms can colonize in the porous structures of biochar and develop a biofilm on the inside and outside surfaces (Figure 5), which enhances biochar’s ability to adsorb and degrade specific organic contaminants [21]. For example, in a recent study, biochar’s removal of naphthenic acids from oil sand process water was increased from ~30% to ~87% due to the introduction of biofilms [99]. Another recent study concluded that biochar with an active biofilm would be a promising medium for the removal of pharmaceuticals in onsite sewage systems [100]. Biologically modified biochar is also recognized for its improved immobilization and biotransformation of dissolved elements of toxicological concern. It was reported that microorganism-colonized biochar was able to effectively remove up to 74.8% of the dissolved Mn(II) in solutions and could oxidize it into less toxic particulate Mn(III) and/or Mn(IV) [101], indicating that biologically modified biochar could be used as a high-performance biofiltration medium for wastewater treatment.

![Figure 5](image-url)

**Figure 5.** Focused Ion Bean Scanning Electron Microscope (FIB-SEM) images of (A) wood-derived pristine biochar; (B) biologically modified biochar with colonized microorganisms; (C) and (D) *Streptomyces violarus* strain SBP1 (GenBank: MK212369) on biochar [101]. Reprinted from Youngwilai et al., 2020, Copyright ©2020, with permission from Elsevier, License No. 4920570708956.

4. Multidimensional Benefits of Biochar in Circular Agriculture

4.1. Water Treatment and Reuse

Previous studies indicated that pristine biochar and engineered biochar were capable of effectively removing various contaminants (e.g., heavy metals, mineral nutrients, pathogens, and emerging organics) from contaminated aqueous phase (Table 2). Generally, engineered biochar exhibited improved performance for wastewater treatment. For example, a remarkable adsorption capacity for Cu$^{2+}$ of 69.37 mg/g by a magnetic microalgae biochar was recently reported [102], which was...
considerably higher than the Cu$^{2+}$ adsorption of 11.65 mg/g by pristine biochar produced using anaerobic wastewater sludge [103]. The large number of small mesopores (2–20 nm) and micropores (<2 nm) of biochar significantly increased its surface area (compared with untreated biomass), and consequently improved its uptake and retention of dissolved and/or suspended contaminants [8]. In addition to the rapid pore filling process, the diffusion and partitioning of these contaminants into the porous structure simultaneously occur, along with the influences of hydrophobic interaction, aromatic–π interaction, cation–π interaction, electrostatic interaction, and hydrogen bonding, each to different degrees [104]. The adsorption-desorption processes are reversible, indicating that biochar could be reactivated for renewable use after its saturation [105].

### Table 2. Removal of various contaminants from different types of wastewater using biochar.

| Contaminants          | Feedstock                  | Pyrolysis Temperature (Time) | Maximum Adsorption Capacity | Ref.   |
|-----------------------|----------------------------|------------------------------|-----------------------------|--------|
| **Heavy metals**      |                            |                              |                             |        |
| Cu$^{2+}$             | anaerobic digestion sludge | 400 °C (0.5 h)               | 11.65 mg/g                  | [103]  |
| Pb$^{2+}$             | anaerobic digestion sludge | 600 °C (2 h)                 | 51.20 mg/g                  | [106]  |
| Cr$^{6+}$             | anaerobic digestion sludge | 300 °C (2 h)                 | 208 mg/g                    | [107]  |
| Cr$^{3+}$             | rice straw, chitosan       | 600 °C (2 h)                 | 312.50 mg/g                 | [102]  |
| Ti$^{4+}$             | watermelon rinds           | 500 °C (1 h)                 | 178.4 mg/g                  | [108]  |
| Cu$^{2+}$             | kelp, FeCl$_3$·6H$_2$O     | 500 °C (2 h)                 | 69.37 mg/g                  | [109]  |

| **Plant nutrients**   |                            |                              |                             |        |
| Total P               | hickory wood chips, AlCl$_3$·6H$_2$O | 600 °C (1 h) | 8346 mg/g                  | [110]  |
| Total P               | banana straw, MgCl$_2$      | 430 °C (4 h)                 | 31.15 mg/g                  | [111]  |
| Total N               | corn straw                  | 500 °C (15 h)                | 86.4 ± 0.5% removal         | [112]  |
| NH$_4^+$-N            | corn straw                  | 500 °C (15 h)                | 96.2 ± 0.6% removal         | [112]  |
| NH$_4^+$-N            | cassava straw, MgCl$_2$     | 430 °C (4 h)                 | 24.04 mg/g                  | [111]  |

| **Pesticides & herbicides** |                            |                              |                             |        |
| Catechol              | oak wood chips              | 400 °C (3 h)                 | 20 mg/g                     | [113]  |
| Carbofuran            | rice husk                   | 700 °C (3 h)                 | 25.2 mg/g                   | [114]  |
| Triazine              | corn straw (P doped biochar)| 300 °C (2 h)                | 79.6 mg/g                   | [115]  |
| 2,4-D                 | switchgrass                 | 425 °C (60 s)                | 134 mg/g                    | [116]  |

| **Plasticizers**      |                            |                              |                             |        |
| Diethyl phthalate     | bamboo                      | 650 °C (3 h)                 | 31.43 mg/g                  | [117]  |
| Oxytetracycline       | corn stalk, MnSO$_4$·6H$_2$O| 600 °C (2 h)                | 40.33 mg/g                  | [109]  |

| **Dyes**              |                            |                              |                             |        |
| Congo red             | residual algae              | 450 °C (2 h)                 | 82.6% removal               | [118]  |
| Methylene blue        | anaerobic digestion sludge | 400 °C (0.5 h)               | 99.5% removal               | [119]  |
| Malachite green       | residual algae              | 800 °C (1.5 h)               | 99.9% removal               | [120]  |

| **Pharmaceutical and personal care products** |                            |                              |                             |        |
| Carbamazepine         | coconut shells (bail milled)| 500 °C (1.5 h)-microwave    | 135.1 mg/g                  | [121]  |
| Triclosan             | biosolids                   | 400 °C (4 h)                 | 277 mg/g                    | [122]  |
| Ibuprofen             | biosolids                   | 400 °C (4 h)                 | 10.7 mg/g                   | [122]  |
| salicylic acid        | walnut shell, FeCl$_3$·6H$_2$O| 600 °C (2 h)-microwave   | 683 mg/g                    | [123]  |

| **Pathogens**         |                            |                              |                             |        |
| *Escherichia coli*    | forestry wood waste        | 700 °C (15 h)                | 98% removal                  | [124]  |

Compared with existing technologies for water/wastewater treatment (e.g., chlorination, sand filtration, solar disinfection, etc.), biochar is more sustainable as its feedstock can be any carbonaceous material, especially biomass that use to be considered as waste (e.g., crop residues, anaerobic digestion sludge and residual algae) [62]. The use of residual and/or low-cost materials for biochar production makes biochar-based technologies ideal for water/wastewater treatment in low-income communities. Unlike most existing technologies that mainly focus on the removal of biodegradable organic contaminants and pathogens, biochar-based technologies are capable of simultaneously removing various contaminants, including many contaminants of emerging concern (CECs) that are typically resistant to chemical and biological degradation during conventional treatment processes [67,121]. With the increasing amounts of various species of CECs detected in wastewater in recent years [125,126], the advantage of biochar-based wastewater treatment is becoming more
pronounced than ever. Moreover, organoleptic properties of water can be well preserved using biochar-based technologies [127], while existing technologies may generate by-products that adversely affect human health (e.g., chlorination) or aggravate hazards as contaminants are concentrated (e.g., boiling) [128].

4.2. Soil Fertility Enhancement

In addition to the benefits for treating water/wastewater, biochar can also be used as a soil amendment to improve soil fertility and crop production [7]. In a recent field study, the application of biochar derived from waste willow wood (Salix spp.) significantly enhanced various soil physicochemical properties, including soil organic carbon, soil moisture, holding capacity for different N and P species, and cation/anion exchange capacity [129]. As a result, the maize grain yield was increased by up to 29% [129]. The crop yield benefits are found to be particularly more pronounced in areas with highly weathered soils, and yield response increases over time since initial application [130]. In a 4-year field study, maize grain yield was found to be 28, 30, and 140% higher compared with the control for the second, third, and fourth year, respectively [131]. Soil cation exchange capacity and organic carbon are strong predictors of yield response, indicating the potent ability of biochar to improve these properties [130]. However, the improvements might decline after longer than four years, possibly due to leaching of biochar-associated alkalinity, thus resulting in the fading effectiveness of biochar in maintaining positive effects on yield [132]. Therefore, reapplication of biochar after 3 to 5 seasons is recommended [132].

4.3. Greenhouse Gas Emission Mitigation

Many studies demonstrated that the emissions of GHGs (e.g., CO₂, CH₄, and N₂O) could be significantly reduced with the applications of biochar [22,62]. For example, Wu et al., 2018 reported that the N₂O emission was decreased by 26.9% in acidic sandy soil amended by corn biochar and by 68.4% when olive biochar was applied [133]. A recent review revealed that biochar amendment might initially accentuate the flux of CO₂, but GHG emissions could be suppressed over time, which could be attributed to the phase complexation with the progressive interaction between biochar, soil, and soil microorganisms [134]. However, in some circumstances the results (especially N₂O emission) could be the opposite [62,135]. In a soil column experiment, the soil amended by the biochar derived from anaerobically digested pig manure had a higher N₂O emission than the control over 28 days of observation, which might be attributed to the higher water filled pore space and organic carbon content favoring denitrification [135]. A recent meta-analysis supported this observation that biochar derived from animal waste and biosolids could be more likely to induce N₂O emission instead of inhibiting it when applied to agricultural fields [62]. Similarly, pyrolysis methods and conditions may also influence biochar’s effectiveness in mitigating/increasing GHG emissions [62]. Therefore, using biochar as a GHG emission inhibitor requires the use of carefully selected feedstock and specifically designed pyrolysis for biochar production.

4.4. Multidimensional Benefits in Circular Agriculture

Following a properly designed circular material (and energy) flow by integrating biochar into existing units and processes, future farms in remote areas can be operated in such a way to minimize water demand and reduce waste generation, which promotes circular economy and has great potential to create additional economic and environmental profits (Figure 6). According to the proposed circular plan of agricultural waste utilization, plant residues, animal manures, and food wastes are recycled to produce engineered biochar are specifically designed for treating the wastewater generated from agricultural and domestic sources. At the same time, biochar can be applied to agricultural fields as a soil amendment to improve WUE [136], remediate diffuse-source contamination [137], and/or improve crop yields [48]; it can also be used as a clean fuel for energy supply (heating value >23 MJ/kg) [138,139]. It has been reported that the addition of biochar to soil could often enhance the plant available water
(PAW) and WUE, although the soil type played an important role on the influence [140]. Due to the improved PAW and WUE (as well as many other soil properties), biochar exhibited a positive effect on plant productivity [19]. By compiling 57 independent studies, a recent meta-analysis found that biochar amendment in ~70% of those studies resulted in higher yields regardless of its application rate [136]. Recent economic analysis studies imply that biochar production for agricultural/forestry production may lead to a potential annual income of at least 179 USD/ha [141–143]. Besides, Roberts et al., 2010 reported that the reduced 864 and 885 kg CO\textsubscript{2} equivalent (CO\textsubscript{2}e) emissions with the application of stover and yard waste biochar have a high potential for economic profitability (+69 USD/t dry feedstock when CO\textsubscript{2}e emission reductions are valued at 80 USD/t CO\textsubscript{2}e) [60]. Economic parity could be achieved at carbon prices as low as 80 USD/t CO\textsubscript{2}e [144]. Higher economic profitability could be realized by developing novel technologies to produce biochar at a lower cost to reduce its market price and with a booming carbon offset market as climate change looms [145].

![Figure 6. A biochar-based closed-loop water-reuse agriculture system.](image)

Despite the benefits posed by biochar applications, it should also be noted that unintended risks to the ecosystem may occur if the circular system is not cautiously designed or well managed. Potential pitfalls related to biochar in soil include: (1) excess increase in soil pH and salinity, (2) overaccumulation and oversupply of plant nutrients, (3) deactivation of agrochemicals such as herbicides and fungicides, (4) alternations in soil microbial community composition and structure, (5) decreased bioavailability and increased persistency of toxicants such as insecticides, and (6) release of toxicant such as heavy metals, polynuclear aromatic hydrocarbons, and CECs [90,146,147]. The organo-mineral interactions and microbiological interactions of biochar over time need to be fully understood for developing production protocols that optimize biochar’s eco-friendliness. In addition, due to the aging of biochar in soil, its particle size may diminish, and its sorption capacity may be masked. As a result, the mobility of these small-size biochar particles in the aqueous environment will increase [148], and the nearby water bodies may be contaminated if any toxicants are carried by these small particles. The same issue is also associated with the use of biochar for water/wastewater treatment, as small-size particles of biochar (if not immobilized) may suspend in the treated effluent and pose ecotoxicological risks.

5. Conclusions

In this study, biochar’s production methods, physicochemical properties, and performance as a powerful absorbent in wastewater treatment has been discussed based on up-to-date literature reviews
and current research. It is promising for biochar-based technologies to be both environmentally and economically profitable with a well-designed circular material and energy flow on future farms. When agricultural residues are converted into biochar at low costs, engineered for enhanced performance, and applied for water/wastewater treatment and soil quality improvement, the circular system’s waste generation and water/energy demand can be minimized while its crop yields can be optimized. However, there remains a lack of design information on biochar-based wastewater treatment technologies, as well as their potential environmental and public health uncertainties. Besides extending the research on the production and characterization of novel engineered biochar, future work needs to focus on developing scaled-up biochar-based water treatment and reuse systems, testing their robustness and stability, and analyzing their techno-economic viability.

Author Contributions: Conceptualization, S.L. and H.T.; methodology, S.L. and C.Y.C.; validation, M.S. and S.D.; writing—original draft preparation, S.L. and C.Y.C.; writing—review and editing, C.Y.C. and M.S.; visualization, S.L.; supervision, S.L.; project administration, H.T. and M.S.; funding acquisition, S.L., H.T. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by grant no. 2020-38422-32253 from the USDA National Institute of Food and Agriculture and by grant no. R20AC00007 from the United States Department of Interior.

Acknowledgments: The authors would like to thank the anonymous reviewers for helping improve the quality of this article.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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