

Review

# Agricultural Waste Valorization via Biochar-Based Supermaterials: Linking Process Design to Sustainability

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## Abstract

Agricultural waste management is a strategic priority for reducing greenhouse gas emissions and transitioning to a circular bioeconomy. The thermochemical conversion of residual biomass into biochar offers a dual solution: waste recovery and the production of high-value functional materials. This narrative review summarizes the relationships among the composition of agricultural biomass, the conversion process parameters, and the structural properties of biochar, highlighting advanced modification strategies: controlled pyrolysis, physical and chemical activation, surface functionalization, and hybrid composite formation. Fundamental adsorption mechanisms, redox processes, and photocatalytic behavior are discussed, with a focus on applications in water treatment (heavy metals, dyes, emerging contaminants). The article proposes an integrative structure–property–performance framework and explores emerging concepts such as sequential use and post-use valorization of saturated biochar. Challenges related to reproducibility, industrial scaling, life cycle assessment, and carbon accounting are analyzed. Finally, a SWOT analysis is presented that highlights the potential of modified biochar as a strategic material in the circular economy.

**Keywords:** biochar; agricultural residues; multifunctional composites; adsorption; photocatalysis; wastewater treatment; circular economy; life cycle assessment

## 1. Introduction

### 1.1. Agricultural Waste Management in the Context of Climate Change

The increase in global agricultural production, driven by demographic dynamics and the intensification of agri-food systems, generates considerable amounts of lignocellulosic residues and organic waste every year. Global primary crop production is associated with agricultural residues, such as straw, stalks, and chaff [1]. The percentage of total harvested biomass varies by species, weather conditions, and cropping system [2]. Managing these material flows is a major challenge from both environmental protection and resource efficiency perspectives. Natural lignocellulosic biomass derivatives could be considered valuable components of future design composites, fuels [3,4], adsorbents [5], or plastics [6], thereby reducing pressure on natural resources and limiting the use of chemically synthesized products. Ufitikirezi et al. highlight the potential to use the mentioned wastes in energy production as raw materials [7]. Liang mentioned the promising benefits of biofuels derived from agricultural waste and non-edible parts [8]. The study also emphasizes the current limitations of the first-generation production sources. Future large-scale implemen-



Academic Editors: Marija Simić,  
Jelena T Petrović and  
Marija Koprivica

Received: 27 February 2026

Revised: 24 March 2026

Accepted: 25 March 2026

Published: 27 March 2026

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tation of such a procedure must overcome various challenges, including increased costs, technological efficiency, standardization of methodologies, and product quality assurance.

Traditional disposal practices such as field burning or abandonment for natural decomposition are associated with significant greenhouse gas emissions, particularly CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Burning agricultural residues produces direct emissions of CO<sub>2</sub> and fine particulate matter, affecting air quality and public health. At the same time, anaerobic decomposition generates methane. Several studies underline the possible uses of agricultural waste or by-products. Shah et al. noted the benefits of incorporating agro-industrial by-products into the livestock cost-efficiency increase approach. The initiative demonstrated advantages in production quality and environmental protection [9].

In the context of the global objectives to limit average temperature increases, the sustainable use of agricultural waste is a strategic component of the transition to a low-carbon economy. Integrating these flows into circular economy models allows both for reducing climate impact and creating added value by converting residual biomass into functional products with industrial applicability [10].

Agricultural waste is not a uniform category and should be classified more carefully if it is to be used as a predictive basis for biochar design. From a resource perspective, these residues can be grouped into (i) field residues such as straw, stalks, leaves, and cobs; (ii) processing residues such as husks, shells, peels, pomace, seed coats, and fibrous press cakes; (iii) pruning and perennial-crop residues such as orchard trimmings, vine shoots, and woody cuttings; and (iv) manure- or digestate-associated agricultural by-products, which differ substantially from lignocellulosic residues because of their higher ash and nutrient contents. This classification is relevant because each class presents a distinct balance of cellulose, hemicellulose, lignin, extractives, ash, and inorganic elements, which directly affects pyrolysis behavior, carbon yield, mineral catalysis, contaminant burden, and the functionality of the resulting biochar [11]. Saleh et al. included comprehensive data on the potential of these resources as raw materials in their study [12]. The paper by Nair et al. integrates comprehensive information, from lignocellulosic wastes to possible product integration and their final use [13].

The broader valorization of agro-food residues is also gaining relevance beyond carbon materials, as recent work on oilseed cake-derived bio-modifiers in sustainable concrete has shown that food-industry by-products can be engineered into functional additives for construction applications [14–16], further supporting the view that waste biomass should be treated as a strategic materials resource rather than a disposal burden [17].

The recent 2026 literature continues to support the relevance of biochar in greenhouse gas mitigation while also showing that climate performance remains context-dependent; for example, recent syntheses indicate smaller average reductions in CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions in arid systems than in non-arid systems, emphasizing that site conditions mediate the climate response to biochar deployment [18–23].

### *1.2. Biochar as a Raw Material for Advanced Applications*

Biochar is a solid carbonaceous material obtained by the thermochemical conversion of biomass under limited or absent oxygen conditions, most commonly by pyrolysis. Unlike conventional activated carbon, biochar has a porous structure and surface chemistry that are highly dependent on the nature of the raw material and process parameters such as temperature, heating rate, and retention time. Pyrolysis temperatures between 300 and 700 °C result in significant variations in specific surface area, pore distribution, and the degree of aromatization of the carbon structure.

In the last decade, biochar has moved beyond its traditional role as a soil amendment [24] and has been extensively investigated as a precursor for advanced materials.

The properties include high chemical stability, surface functionalities (–OH and –COOH groups), tunable electrical conductivity, and the possibility of doping with heteroatoms (N, S, P). These make it a versatile platform for applications in energy storage, catalysis, adsorption, and environmental remediation [25,26]. Fakhar et al. linked improvements in biochar properties to their effects on agricultural applications. In this regard, they noted that specific physical, chemical, biological, or mechanical factors could affect the soil's future attributes [27].

Furthermore, the use of agricultural waste as a raw material gives biochar a competitive advantage from a life cycle assessment (LCA) perspective, through long-term sequestration of biogenic carbon and reduced dependence on fossil precursors. The aromatic stability of the resulting structure contributes to carbon retention on timescales ranging from decades to centuries, making biochar a relevant tool for climate change mitigation strategies. As Yu et al. noted, the agro-food industry can be seen as a sector with two valences: a source of biochar raw materials and a field of remediation applications [28].

### 1.3. The Concept of Biochar-Based “Supermaterials”

The term “supermaterials” is used in the materials science literature to describe materials that exhibit exceptional performance relative to conventional analogs, whether mechanically, electrochemically, catalytically, or functionally. In this context, biochar-based supermaterials refer to engineered structures in which the carbon matrix derived from agricultural biomass is optimized or modified to achieve performance parameters comparable to those of advanced materials based on graphene, carbon nanotubes, or metal oxides. According to research by Fazi et al., biomass-based coal could be considered a feasible alternative to graphite as a feedstock for graphene [29].

The engineering of these materials often involves chemical or physical activation to increase the specific surface area, doping with heteroatoms to improve electrochemical properties, and integration into nanocomposites with metals or metal oxides for catalytic applications. In the field of energy storage, modified biochar is used as an electrode material for supercapacitors and batteries, where specific capacitance, cycle stability, and energy density are critical metrics. In environmental applications, performance is evaluated by adsorption capacity, capture kinetics, and material regenerability. Conceptually, these supermaterials achieve a convergence of sustainability and technological performance, demonstrating that residual biomass can be a strategic resource for developing high-value functional materials [30].

In this review, the term biochar-based supermaterials is used in an operational sense rather than an absolute one. It does not imply a universal class defined by a single threshold value. Still, it refers to biochar-derived materials whose functional performance is significantly enhanced relative to unmodified biochar through deliberate control of pore architecture, surface chemistry, electronic structure, or multifunctional hybridization. Depending on the intended application, the relevant performance descriptors may include adsorption capacity and regenerability, electrical conductivity and electrochemical reversibility, or catalytic and photocatalytic activity. As an indicative rule of thumb, the designation is most defensible when at least two performance dimensions are simultaneously improved, for example, surface area plus  $q_{\text{max}}$ , or adsorption capacity plus regeneration stability, instead of a single isolated metric.

### 1.4. Objectives and Structure of the Analysis

The purpose of this review article is to critically summarize the current state of research on the conversion of agricultural waste into biochar and its subsequent development into functional supermaterials, with an emphasis on their relevance to sustainability. The analysis

aims to (i) correlate the types of agricultural biomass with the properties of the resulting biochar, (ii) evaluate processing and modification technologies, (iii) study post-use valorization and dual functionality, and (iv) analyze performance evaluation and sustainability.

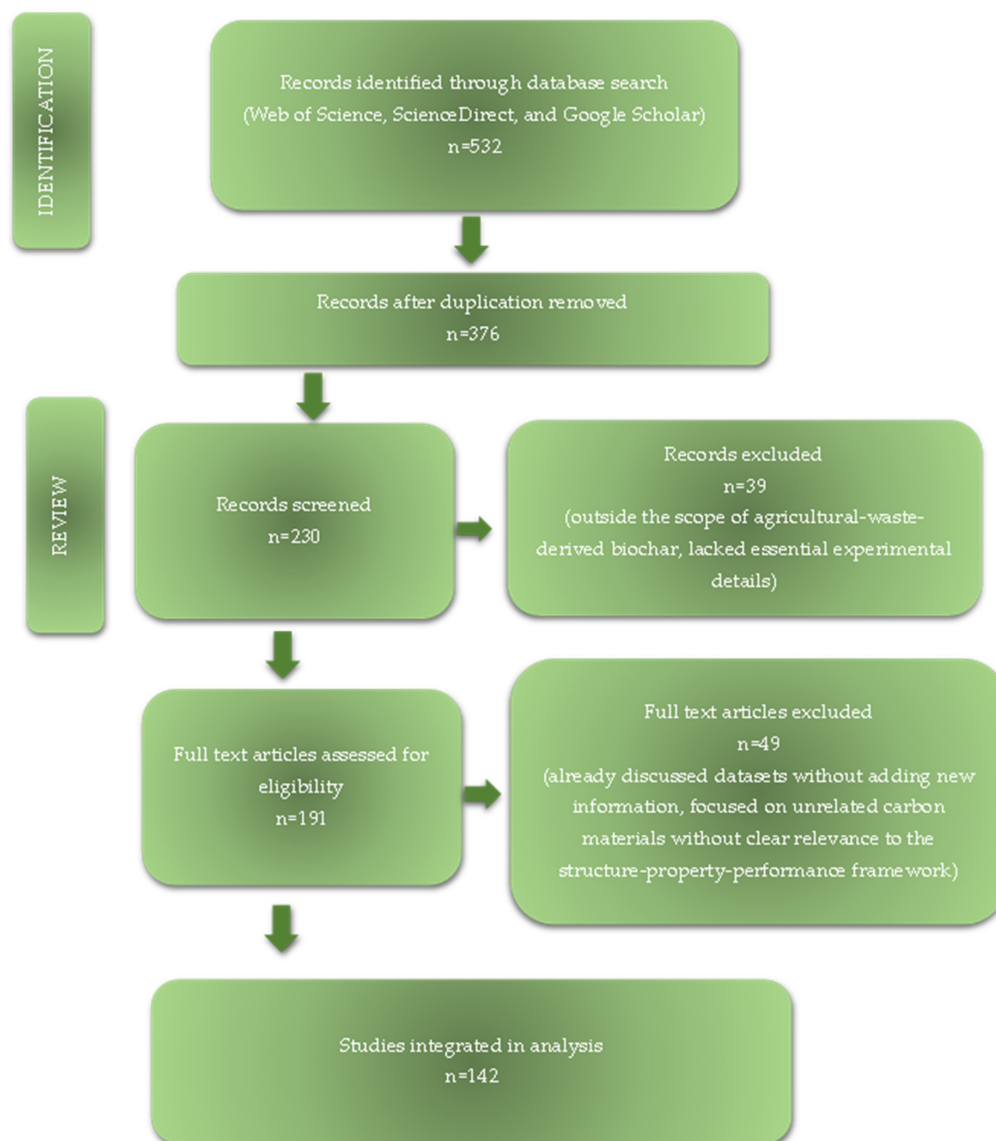
To sharpen the analytical focus, this review addresses four specific questions: (Q1) How do the chemical composition and mineral content of agricultural residues, especially the cellulose/hemicellulose/lignin balance and ash fraction, influence biochar yield, aromatization, porosity development, and surface chemistry? (Q2) How do pyrolysis conditions and post-treatments, including activation, oxidation, heteroatom doping, and hybrid composite formation, modify the physicochemical descriptors most relevant to performance? (Q3) Which structural and chemical characteristics are most consistently associated with high performance in water treatment and in emerging advanced applications such as electrochemical energy storage or catalytic systems? (Q4) Under what conditions can spent biochar be safely and productively valorized in secondary applications such as soil amendment, stabilization systems, or construction materials, and how do sustainability and regulatory constraints affect these pathways?

Methodologically, this review integrates studies published in international scientific databases, such as ScienceDirect and Google Scholar, with a focus on papers published in the last 5–10 years to reflect recent developments in the field. The article is organized progressively: after this introduction, the possible raw materials are presented, followed by an analysis of strategies for producing supermaterials based on biochar, and finally a discussion of post-use valorization, performance evaluation, future research perspectives, and directions.

Although the present article is conceived as a narrative review, the literature selection was guided by a transparent search procedure to reduce arbitrariness. The primary search was conducted in major scientific databases (Figure 1), using combinations of keywords such as “agricultural waste”, “crop residue”, “biochar”, “activated biochar”, “modified biochar”, “surface functionalization”, “heteroatom doping”, “adsorption”, “photocatalysis”, “energy storage”, “life cycle assessment”, and “carbon accounting”. The main time window emphasized publications from the last 5–10 years, while earlier landmark studies were retained where necessary to explain foundational mechanisms or widely adopted preparation routes. Studies were included if they reported at least one of the following in a sufficiently explicit manner: feedstock identity, conversion conditions, material characterization, application-relevant performance, or post-use/regeneration information. Studies were excluded when they were deemed beyond the scope of the topic developed here (Figure 1). Through this integrated approach, this article aims to highlight the role of biochar derived from agricultural waste as an interface between sustainable biomass management, advanced materials development, and global decarbonization goals. The originality of this work lies in the integration of the concept of “biochar-based supermaterials” into a clear procedural framework, the systemic approach to sequential use as adsorbent-stabilizing material-construction material, the mechanistic correlation between structure, property, and performance, and the integration of the sustainability perspective. This paper goes beyond the traditional descriptive approach and proposes a conceptual model geared towards industrial implementation and the circular economy.

The present review addresses a specific gap in the biochar literature: although numerous studies and reviews describe biomass sources, pyrolysis conditions, activation methods, and environmental applications, these elements are often discussed separately rather than as a continuous design chain. The specific contribution of this manuscript is to organize agricultural-waste-derived biochar as a configurable materials platform in which feedstock composition, thermochemical processing, structural evolution, functional performance, and post-use valorization are interpreted within a single integrative framework. Accord-

ingly, this review is intended not only to summarize previous results but also to provide a design-oriented perspective for selecting biomass, tailoring conversion conditions, and aligning modification strategies with target functionality and end-of-life constraints for materials chemists, process engineers, and environmental scientists.



**Figure 1.** Flow diagram of study identification, screening, eligibility, and inclusion.

## 2. Agricultural Wastes as Raw Material for Biochar

### 2.1. Predominant Biomolecules and Influence on Biochar Properties

Most agricultural waste consists predominantly of a lignocellulosic matrix, composed of cellulose, hemicellulose, and lignin, in a complex three-dimensional structure that provides mechanical strength and chemical stability to plant tissues. Cellulose is a linear homopolymer formed from  $\beta$ -(1 $\rightarrow$ 4)-D-glucose units, organized into crystalline and amorphous regions, which influence the thermal behavior of biomass. Qiu et al. highlighted the promising attributes of cellulose-based materials in several fields, among which water treatment and separations stand out [31]. Hemicellulose is an amorphous heteropolymer composed of xylan, mannan, arabinoxylan, and other saccharide units, with lower thermal stability compared to cellulose. As Mathrura et al. noted in their study, this polymer's use may be limited by its properties. Improvements could be obtained upon its incorpo-

ration into composites such as edible films, fillers, or emulsifiers [32]. Lignin is a three-dimensional aromatic polymer composed of phenylpropanoid units (p-hydroxyphenyl, guaiacyl, and sinapyl), responsible for the structural rigidity and increased fixed carbon content of biomass. Vinod et al. emphasized the possible role of lignin as an intermediate in carbon fiber synthesis [33]. Also, Creteanu et al. reported the potential adaptability of this biopolymer across different application fields [34].

Table 1 presents data on the compositional variability of vegetable wastes. The observed difference could serve as a starting point for understanding differences in pyrolysis behavior and the need for standardization mechanisms.

**Table 1.** Typical composition of main agricultural wastes.

Raw Material	Cellulose	Hemicellulose	Lignin	Reference
wheat straw	48.34	22.64	18.86	[35]
	45.43	36.50	21.61	[36]
	47.60		20.10	[37]
corn stalks	39.00	42.00	7.30	[38]
	36.50	23.50	19.30	[39]
sunflower seed hull	29.80		26.40	[40]

For interpretation and comparison purposes, these feedstocks may also be grouped into herbaceous field residues, agro-industrial processing residues, woody pruning residues, and mineral-rich or manure-associated agricultural by-products, since this classification more accurately reflects both thermochemical behavior and potential end-use constraints than crop name alone.

In residues such as wheat straw, corn stalks, sunflower hull, or rice husks, typical proportions vary between  $\approx 30$ –45% cellulose, 20–35% hemicellulose, and 7–27% lignin, depending on the species and pedoclimatic conditions. These variations could lead to significant differences in pyrolysis behavior and in the properties of the resulting biochar [41], depending on the treatment parameters used [42]. The study by Lin et al. highlighted the potential use of such by-products across several domains [43]. Batista et al.'s principal component analysis showed that variables related to biomass chemical composition exhibit strong correlations with biochar yield, accounting for approximately 67% of the first component's variation [44].

In addition to the lignocellulosic fraction, agricultural waste contains extractives (soluble phenolic compounds, lipids, resins), residual proteins, and mineral fractions. Extractives can participate in secondary reactions during thermal treatment, contributing to the formation of volatile compounds or altering the surface chemistry of biochar. Ash content is a critical parameter, ranging from 2% to over 20%, depending on the raw material. For example, rice husks are characterized by a high silica content, which influences the solid residue and final porous structure. The presence of alkaline and alkaline-earth elements (K, Ca, Mg) can catalyze devolatilization and aromatization reactions during pyrolysis.

The compositional information summarized in Table 1 is useful as a first-order descriptor of feedstock variability, but, by itself, it does not provide a complete predictive basis for biochar structure. Ultimate-analysis descriptors, such as H/C and O/C ratios, are often more directly related to thermal transformation and carbon-network evolution than are cellulose, hemicellulose, and lignin contents alone. Biomass fractions rich in lignin generally favor higher fixed-carbon yield and more condensed aromatic structures after pyrolysis. In contrast, cellulose- and hemicellulose-rich feedstocks tend to generate higher volatile release and stronger primary pore-forming effects [45,46]. However, this relationship is not strictly linear because extractives, ash content, and mineral catalysis also influence devolatilization and carbon rearrangement. Mineral matter deserves particular

attention: SiO<sub>2</sub>-rich feedstocks may constrain accessible porosity or alter the apparent surface area, while K, Ca, and related minerals can catalyze dehydration, devolatilization, and secondary char-forming reactions. The principal component analysis cited from the literature is retained here as supportive evidence, but no original multivariate meta-analysis was performed in this review; a formal PCA based on harmonized feedstock–process–property data remains a worthwhile future direction.

## 2.2. Important Properties of the Conversion Process

The chemical composition of agricultural biomass determines not only the solid yield obtained through pyrolysis but also the carbon architecture and functionality of the biochar surface. A high lignin content promotes the formation of condensed aromatic structures, thereby increasing fixed carbon and improving thermochemical stability. In contrast, fractions rich in hemicellulose and cellulose undergo rapid decomposition via depolymerization and dehydration, generating increased volumes of volatile compounds and contributing to the development of primary porosity.

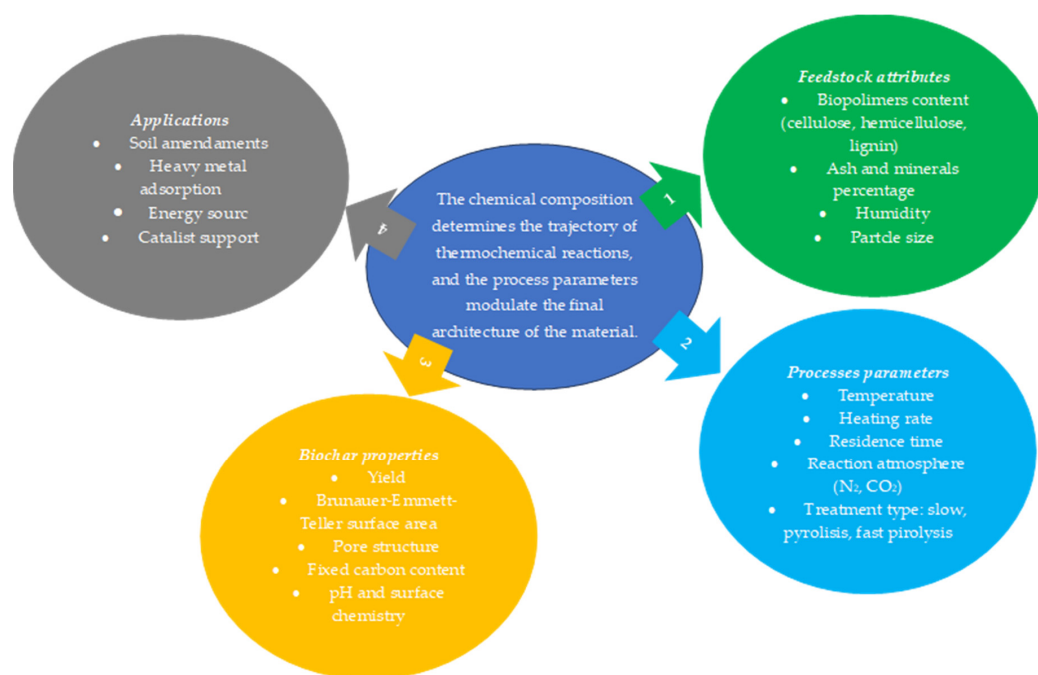
The H/C and O/C atomic ratios are essential structural indicators for assessing the degree of aromatization and long-term stability of biochar. The reduction of these ratios with increasing temperature reflects the progression of aromatic condensation reactions and the elimination of oxygenated functional groups. The biomass type could also influence the future use of the biochar obtained. Zhang et al.'s study suggests that leaf-derived biochar could be preferred to increase soil total nitrogen content and improve plant assimilation [47].

The processes for obtaining biochar could impact the application domain. Sathyabama and Firdous' study suggests that biochar produced at moderate to high temperatures (around 350 °C) has improved physicochemical and structural properties. Such findings may indicate a possible sustainable resource in eco-friendly environmental management [48].

The conversion temperature controls the transition from a functionalized carbon structure to a predominantly aromatic one. At moderate temperatures (≈500 °C), biochar retains carboxyl and phenolic groups, which are relevant for cation exchange capacity. At high temperatures (>650 °C), dehydrogenation and aromatization reactions lead to the formation of a more ordered carbon network with increased specific surface area but reduced chemical functionality. Baniasadi et al. concluded that increased pyrolysis temperature drives specific processes, including systematic carbon enrichment in biochar, loss of oxygenated groups, and progressive aromatization [49]. Parameter optimization must be achieved by correlating the desired properties with the transformation mechanisms of the main constituent biomolecules.

Figure 2 presents a vertical-flow conceptual diagram highlighting the causal relationships among raw material characteristics, conversion process parameters, and final biochar properties, with an extension to application performance. It is organized into four distinct levels, connected by downward-pointing arrows, suggesting a sequential, deterministic relationship.

The first level defines the intrinsic parameters of biomass that govern its thermochemical behavior. Conceptually, lignocellulosic composition and mineral content determine degradation mechanisms, solid yield, and the potential for porosity development. The second represents the technological control stage. The process parameters modulate the trajectory of the dehydration, devolatilization, aromatic condensation, and structural reorganization reactions. The third stage suggests that biochar properties result from the interaction between the initial composition and the process parameters. The final step illustrates that application performance is directly dependent on the properties generated in the previous stage, which in turn are determined by the feedstock and conversion parameters.



**Figure 2.** Conceptual framework linking agricultural feedstock composition, thermochemical process parameters, and biochar properties and applications.

### 3. Strategies for Obtaining Supermaterials Based on Biochar

Transforming conventional biochar into a multifunctional “supermaterial” requires moving beyond the traditional paradigm of simple carbonization and adopting an integrated process approach. The structural properties and functional mechanisms discussed in the next chapter are directly dependent on the strategies applied during the conversion and modification stage. Thus, controlling the carbon architecture, surface chemistry, and heteroatomic composition is essential for obtaining materials with advanced performance in adsorption, redox processes, or photocatalysis.

In this context, four major technological directions can be identified: controlled pyrolysis, activation, chemical functionalization, and hybridization in composites.

#### 3.1. Controlled Pyrolysis

Controlled pyrolysis is the primary stage in defining the carbon structure and pore distribution. Operational parameters such as temperature, heating rate, residence time, and process atmosphere determine the degree of aromatization, porosity development, and structural stability.

Temperature is the dominant variable. Ouahabi et al.’s study describes five possible processes depending on the temperature. The highest char yield, ~85%, is obtained after flash carbonization. The temperature range is ~300 °C to 600 °C, with an exposure time of less than 30 min [50]. A higher pyrolysis temperature appears to be negatively correlated with biochar production yield. The regime may be shifted to increased carbon content and decreased hydrogen content in the final material. The observations were highlighted by the research on beech wood chips, walnut shells, and wheat-rye straw in the study by Wystalska et al. [51]. In the intended use for remedial purposes, besides the temperature regime, other parameters also appear to influence biochar’s capacity.

The wheat straw biochar was tested for nitrate adsorption efficiency and variation in pyrolysis temperature from 300 to 500 °C. The results showed a significant decrease in hydrogen, oxygen, and nitrogen. At the same time, it was found that carbon content, surface area, density, and water solubility in biochar were positively correlated. Regarding

absorption efficiency, the maximum adsorptive capacity for nitrate was observed at pH 6 after 120 min of contact [52]. The product derived from the same raw material could also be used to preserve soil moisture. A temperature of 550 °C resulted in the largest mean weight diameter, the most water-stable aggregates, and the highest available water content compared to the control [53]. The biochar's intended use can be an important consideration when establishing the temperature regime. Secondly, other reaction parameters may also influence biochar characteristics under different element ratios.

The heating rate and dwell time influence the mechanisms of devolatilization and structural reorganization. Moderate speeds favor the development of a stable network of micropores, while extended holding times allow additional aromatic condensation and increased structural ordering. The use of CO<sub>2</sub> can induce in situ activation via controlled gasification reactions, thereby developing porosity without an additional activation step. Controlled pyrolysis establishes the structural basis for the functional properties discussed in the following chapters.

The term controlled pyrolysis should be understood as the deliberate adjustment of the thermal history to regulate the sequence of dehydration, devolatilization, fragmentation, repolymerization, and aromatic condensation reactions that determine the final carbon structure. At relatively low temperatures, biomass first undergoes dehydration and cleavage of weakly bound oxygenated structures, especially from hemicellulose and the amorphous cellulose fraction. As temperature increases, depolymerization and devolatilization intensify, releasing condensable and non-condensable products while leaving behind an increasingly carbon-rich solid matrix. Varol et al. included valuable data in their analysis on the thermal behavior of different biopolymers, which underlie their specificities [54]. Those were related to the constitutive polymers. Between intermediate and high pyrolysis temperatures, the remaining carbonaceous fragments undergo polycondensation and aromatization, leading to the nucleation and growth of fused aromatic clusters. Progressive dehydrogenation and decarboxylation reduce the H/C and O/C ratios and promote the formation of more condensed sp<sup>2</sup>-rich domains. The process atmosphere also contributes to structure development because CO<sub>2</sub> or steam can induce partial gasification of less-ordered carbon domains, creating or widening pores and increasing the accessible surface area.

A more quantitative discussion of aromatization and structural ordering can be built from Raman spectroscopy, particularly through the D and G bands and their intensity ratio. In principle, increasing pyrolysis temperature from approximately 300 to 700 °C promotes deoxygenation, condensation of aromatic clusters, and evolution toward more ordered sp<sup>2</sup>-rich carbon domains [55]. However, interpreting the ID/IG ratio is not always straightforward in biochar systems, as it may reflect both the formation of new aromatic ring systems and the persistence of structural defects in turbostratic carbon.

### 3.2. Activation of Biochar

For advanced applications in water treatment or catalysis, specific surface area and pore distribution become critical parameters. Activation is the main strategy for enhancing these characteristics.

Physical activation, carried out at higher temperatures in the presence of different gases or vapors, is aimed to increase the specific surface area. The mechanisms could involve selectively oxidizing amorphous carbon and enlarging micropores. This process leads to a predominantly microporous structure, favorable for physical adsorption.

Chemical activation, particularly with KOH, via complex mechanisms involves redox reactions and alkali-metal intercalation into the carbon network. The optimal conditions presented in the study by Nazbakhsh et al. of 800 °C, 120 min, and 1:1 KOH impregnation

ratio resulted in an increased BET surface area of 1149 m<sup>2</sup>/g and a total pore volume of 0.53 cm<sup>3</sup>/g. The biochar raw material was sugarcane bagasse [56].

Although KOH activation at 800 °C for 120 min with a 1:1 impregnation ratio can yield very high surface areas in some systems, these parameters should not be interpreted as universally optimal across biomass types. The apparent optimum depends on the precursor's lignin content, ash fraction, mineral composition [57], initial pore-forming tendency, and resistance of the carbon skeleton to burn-off. A condition that maximizes surface area in one feedstock may cause excessive pore widening, structural collapse, or low yield in another. Therefore, KOH activation must be optimized as a feedstock-specific trade-off between surface development, carbon yield, structural integrity, and post-treatment cost. The performance of biochars used for decontamination depends on several factors, including the raw material used for their preparation, the production parameters utilized, and the environmental conditions of the application [58].

Activation with H<sub>3</sub>PO<sub>4</sub> promotes the development of mesoporousness and can simultaneously introduce phosphorus doping, subsequently influencing redox mechanisms. Biochars resulting from peanut shell, corncob, and cotton exhibited increased surface areas after phosphorus acid activation and thermal treatment at 600 °C. The product was shown to adsorb ciprofloxacin efficiently in real lake water [59]. Thus, activation not only increases the specific surface area but also shapes the pore-size distribution, which is decisive for the accessibility of active sites and the kinetics of adsorption [60].

Surface-sensitive techniques such as XPS are particularly important for distinguishing whether H<sub>3</sub>PO<sub>4</sub> treatment merely changes porosity or also introduces new chemically active sites. In P-modified biochars, XPS deconvolution can reveal phosphorus environments such as P-O-C, P=O, and phosphate-like species, which are relevant because they alter electron density, acidity, hydrophilicity, and coordination behavior. Accordingly, phosphorus activation should not be interpreted only as a textural treatment. It also creates chemically distinct surface functionalities whose distribution may influence adsorption, redox activity, and interfacial charge transfer.

Premchand et al.'s research suggested that chemical activation during CO<sub>2</sub> pyrolysis results in increased levels of chemical activation reactions. Such a situation led to increased formation of oxygen functional groups and to enhanced specific surface area and pore volume in the biochar obtained from rice husk. As activators, sodium and potassium alkali were considered [61].

From a sustainability perspective, in situ or physical activation routes, including CO<sub>2</sub>-assisted activation, may reduce the need for corrosive chemicals and extensive washing compared with conventional chemical activation. However, this does not automatically guarantee a lower carbon footprint because gas-phase activation often requires higher temperatures and longer residence times to achieve comparable porosity. Conversely, chemical activation can generate a high surface area at lower apparent thermal severity but may incur substantial burdens from reagent production, washing water, neutralization, and waste treatment. For this reason, the environmental comparison between CO<sub>2</sub>-based in situ activation and chemical activation should be assessed on a case-by-case basis, using explicit life cycle boundaries rather than inferred from process labels alone. Jiang et al.'s study suggests better performance of aqueous-activated biochar compared to CO<sub>2</sub>. A significant synergistic mechanism between the two triggers was not observed in the studied situations [62].

### 3.3. Chemical Functionalization

While activation optimizes the material's physical architecture, chemical functionalization modulates its molecular interactions and electronic properties. Controlled oxidation introduces carboxyl, lactone, and phenol groups, increasing the density of sites capable of

complexation or ion exchange. This modification directly affects adsorption mechanisms, with chemical interactions dominant for metal ions. Wood chip biochar functionalized with potassium hydroxide underscored its potential for carbon dioxide capture [63].

Doping with heteroatoms (N, S, P) alters the surface electronic density. Pyridine and pyrrole nitrogen groups enhance conductivity and promote electron transfer, making them relevant for redox processes and electrocatalytic applications. The presence of such molecules could contribute to an increase in Pb (II) adsorption [64]. Doping with phosphorus can generate additional active centers for advanced oxidation reactions [65]. Therefore, functionalization transforms biochar from a passive adsorbent into a chemically active and selective material [66]. Investigations of poplar biochar revealed correlations between oxidative treatment conditions and its final attributes. The functionalization conditions seem to determine structural modifications and water dynamics within the porous network [67].

### 3.4. Hybridization and Composite Formation

The next stage of development involves integrating biochar into hybrid or composite systems to achieve functional synergies. Composite-based biochars are becoming viable solutions for various bioremediation applications and agricultural uses [68]. Use of such products could result in up to 99% of toxic metals, such as Cr(VI) and Pb(II), being present. This shows good perspectives for energy storage and increased soil fertility [69]. He et al.'s research on a biochar–microorganism hybrid showed the potential to decrease hydraulic retention time and improve aerobic digestion efficiency. The biochar raw materials were phoenix tree branches, coconut shells, and corn straw. The pre-couple with the considered microorganisms was developed in anaerobic granular sludge [70]. The technique was observed at the level of increased methanogenic efficiency.

Magnetic composites enable rapid recovery via magnetic separation and can achieve significant adsorption capacities for heavy metals. In these systems, biochar provides the porous surface, and the metal phase furnishes the additional active sites.

Integration with semiconductor oxides leads to hybrid photocatalytic materials. Biochar acts simultaneously as an adsorbent and electronic mediator, facilitating charge separation and reducing electron–hole recombination. This synergy is essential for photocatalytic mechanisms. Integrating metals into biochars increases their weight, enabling sedimentation–separation processes, an attribute that could be exploited in aqueous environments for remediation purposes [71]. Bregadiolli et al.'s study underlined that a biochar electrode could be considered for energy preservation. The composite elaboration began with the sugarcane-based biochar. The nanostructures were obtained after a hydrothermal synthesis [72]. In structural applications, incorporation into polymer or cement matrices enables post-use recovery, directly connecting this chapter to the sections dedicated to the circular economy and sequential use.

## 4. Structural Properties and Functional Mechanisms

### 4.1. Physicochemical Characterization

To highlight the direct relationship between the synthesis strategies discussed above and the functional behavior of the resulting materials, a systematic analysis of the structural and chemical properties of the modified biochar is necessary. Physicochemical characterization is an essential step in validating the porous architecture, elemental composition, and nature of functional groups, parameters that control adsorption mechanisms, redox processes, and biological interactions.

Techniques such as BET analysis (determination of specific surface area and pore distribution), SEM/TEM electron microscopy (morphology and texture), FTIR and XPS spectroscopy (identification of functional groups and oxidation states), and Raman spec-

troscopy (degree of structural ordering and D/G ratio) provide complementary information on the material structure. Correlating these parameters allows for a mechanistic interpretation of performance in water treatment or catalysis applications.

Table 2 summarizes the main characterization methods used, the parameters determined, and their relevance to the functional mechanisms, thereby facilitating the integration of the structure–property–performance relationship.

**Table 2.** Characterization techniques for activated biochar properties.

Technique	Characterization	Reference
BET	N <sub>2</sub> /CO <sub>2</sub> adsorption isotherms help determine surface area, pore volume, and pore-size distribution. After activation with KHCO <sub>3</sub> , KOH, ZnCl <sub>2</sub> , or microwave treatment, the BET surface area and micropore volume increase, thereby enhancing adsorption capacity. Activated tea waste biochar with KHCO <sub>3</sub> had a higher surface area and micropore volume.	[73]
SEM/TEM	In KOH-activated and other chemically activated agricultural biochars, SEM/TEM shows random holes, fractures, and hierarchical porosity that promote mass transfer and pore filling.	[74]
FTIR	As reported across rice-husk and modified biochars, FTIR shows oxygen-, nitrogen-, and other heteroatom-containing functional groups (carboxylate, hydroxyl, carbonyl, C–O) that mediate hydrogen bonding, electrostatic interactions, and surface complexation.	[75]
XPS	XPS can measure surface elemental composition and chemical states, including C 1s, O 1s, and N 1s speciation. Activation or functionalization may increase or decrease the quantity of O- and N-containing species and carboxylates, thereby affecting the material's adsorption chemistry and ion-exchange capacity.	[75]
Raman	Raman spectroscopy uses the D and G bands and their intensity ratios to analyze the ordering of graphite. Pyrolysis and activation may improve graphitization and reduce defect density, impacting $\pi$ – $\pi$ electron–donor–acceptor interactions and electrical conductivity in redox and photocatalytic processes.	[73]

#### 4.2. Adsorption Mechanisms

Understanding the adsorption mechanisms of biochar-based supermaterials requires direct correlation of structural properties and surface chemistry with the type of interactions involved in contaminant retention. Adsorptive performance is not determined solely by specific surface area but by a combination of hierarchical porosity, pore-size distribution, functional group density, and the nature of heteroatoms incorporated into the carbon network. For heavy metals, the dominant mechanisms include ion exchange, surface complexation, and pH-dependent electrostatic interactions. In contrast, for aromatic organic pollutants,  $\pi$ – $\pi$  interactions, van der Waals forces, and hydrophobic effects are frequently at play. In doped or hybrid materials, redox processes can further facilitate the chemical transformation of contaminants (e.g., the reduction of Cr(VI) to Cr(III)). To systematize these correlations, Table 3 summarizes the main adsorption mechanisms associated with them.

For aromatic organic pollutants, adsorption cannot be interpreted only in terms of pore filling or generic hydrophobicity. The aromaticity and electron density of the adsorbate also influence uptake, especially when the biochar surface contains condensed aromatic domains capable of  $\pi$ – $\pi$  interactions. In such cases, the adsorption tendency may increase with the pollutant's greater aromatic character, although this relationship is modulated by substituent effects, ionization state, steric accessibility, and competition with water.

**Table 3.** Adsorption mechanisms of pollutants on activated/modified biochars.

Technique	Characterization	Reference
Physisorption	Besides pore filling, physisorption, van der Waals forces, micropore and mesopore confinement, these factors enable tiny-molecule absorption. Biochars with substantial micropore volumes and pores ranging from 1.2 to 10 nanometers, suitable for molecules such as oxytetracycline and other organic chemicals, exhibit dominant pore-filling.	[76]
Chemisorption	Chemical adsorption involving coordination or hydrogen bonding may be characterized using pseudo-second-order kinetics and D–R studies. Uptake and selectivity are improved by surface complexation and specific interactions, such as metal coordination or functional-group binding, in modified biochars.	[75,76]
Ion exchange	Inferred ion exchange in methylene blue absorption, PFAS, metal interactions demonstrating electrostatic, complexation contributions, and adsorption dependency on pH and ionic strength have been found. Ionic pollutants are taken up by swappable surface cations and charged functional groups.	[75,76]
Complexation	The adsorption of tetracycline on activated charcoal was studied, and the results showed that coexisting cations ( $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , and $\text{Mg}^{2+}$ ) may impede adsorption by either competing for sites or screening electrostatic attractions.	[73]

Likewise, in N-doped systems used for Pb(II) adsorption, mechanistic assignment should not rely solely on improved uptake values. A stronger interpretation is obtained when adsorption is accompanied by shifts in XPS binding energies, particularly in N 1s, O 1s, and Pb 4f regions, indicating coordination or complexation between the metal ion and electron-donating surface groups. Accordingly, improved Pb(II) uptake should be linked, where possible, to spectroscopic evidence rather than to performance data alone.

The use of the Langmuir and the Freundlich models in the biochar literature should be interpreted with caution. Langmuir behavior is often reported when adsorption appears to approach a finite apparent capacity under relatively controlled single-solute conditions. In contrast, Freundlich behavior is more commonly observed on heterogeneous surfaces and energy distributions expected for modified biochars. However, because many studies fit both models to limited datasets, differences in  $R^2$  values are often too small to justify strong mechanistic conclusions. The same caution applies to kinetics: although the pseudo-second-order model is frequently associated with chemisorption, a good mathematical fit does not by itself prove that chemical bonding is rate-limiting; intraparticle diffusion, film diffusion, and heterogeneous site occupancy may remain important.

#### 4.3. Photocatalytic Mechanisms and Redox Processes

Biochar is typically a cocatalyst, electron reservoir, or conductive support in photocatalytic and redox systems. Charge dynamics and reactive species change when combined with semiconductors or metal nanoparticles. Agricultural biochar may improve electron transport, inhibit charge recombination, and increase reactive oxygen species that eliminate pollutants [77,78].

Trapping electrons and separating charges, biochar's conductive domains and imperfections capture electrons from photoexcited semiconductors such as  $\text{TiO}_2$ . These defects and domains act as electron sinks, reducing  $e^-/h^+$  recombination and extending charge-carrier lifetimes, thereby boosting photocatalytic degradation rates [77].

Assistance with nanoparticles and biochar dispersion provides high-surface-area anchoring sites for metal/metal-oxide photocatalysts such as  $\text{Ag}/\text{TiO}_2$  and  $\text{Fe}_3\text{O}_4$ , thereby improving dispersion, interfacial contact, and the synergy between sorption and catalytic degradation. Reactive oxygen species generation of enhanced charge separation enables

the formation of reactive oxygen species (ROS) ( $\bullet\text{OH}$ ,  $\text{O}_2\bullet^-$ ) at the semiconductor–charcoal interface. ROS oxidize dyes and organic substances and kill bacteria when metals like silver are present [77,79,80].

Direct electron transfer and redox cycling may participate in Fenton-like or catalytic redox cycles due to redox-active heteroatoms or transition-metal sites. These cycles transport electrons to oxidants or contaminants, enabling deterioration beyond adsorption [78,81].

Increasing Ag concentration in Ag/TiO<sub>2</sub>-biochar composites accelerated dye degradation and reduced recombination. Multiple rounds of recyclability indicate stable electron-transfer-driven photocatalysis on agricultural biochar substrates. These practical outcomes were realized using biochar.

The datasets lack precise band alignment or charge-transfer rate measurements for agricultural biochars. Thus, molecular-level energetics need electrochemical or spectroscopic studies beyond the reporting [77,80].

In TiO<sub>2</sub>-biochar hybrid systems, the frequently proposed enhancement mechanism is based on improved light utilization, higher pollutant preconcentration near the catalyst surface, and more efficient separation of photogenerated charge carriers at the semiconductor–carbon interface. In the literature, reduced electron–hole recombination is typically supported by photoluminescence quenching, electrochemical impedance spectroscopy, transient photocurrent measurements, and, occasionally, Mott–Schottky analysis. Similarly, ROS pathways involving hydroxyl radicals or superoxide are often inferred from scavenger assays, but stronger evidence is available when spin-trapping or EPR measurements are reported.

#### 4.4. Antimicrobial Activity and Biological Interactions

Biochar made from agricultural waste has antibacterial properties, particularly when combined with biocidal metals or photogenerated reactive oxygen species (ROS). Current research suggests ROS generation, metal-mediated toxicity, and sorption-mediated effects are key antimicrobial pathways.

Reactive oxygen species (ROS) stress in composites with photocatalysts and silver-charcoal-supported materials promotes ROS generation, which damages microbial components and produces bactericidal action [77,82,83].

Silver incorporated or doped into biochar surfaces releases metal ions and interacts with biological components to induce antibacterial effects. Silver/titanium dioxide and biochar composites exhibit enhanced antibacterial activity through sorption, reactive oxygen species, and metal-mediated effects.

Nutrient sorption and sequestration: The sources show no indication that pure agricultural biochar breaks cell walls or bursts membranes. Biochar sorption may reduce food availability or sequester microbial signaling molecules, preventing growth [77,84,85].

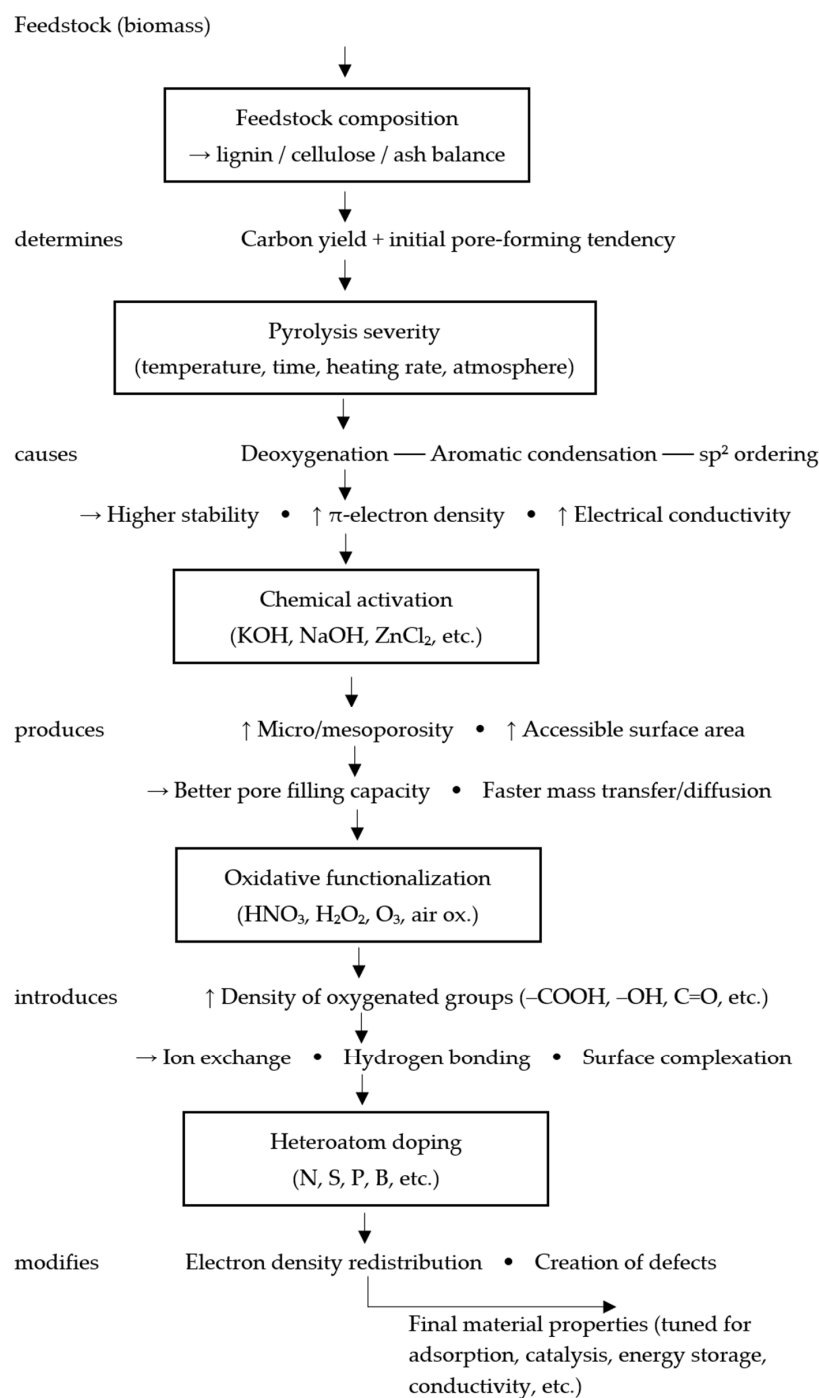
Certain functionalized or magnetic biochar composites have been tested for biocompatibility and antioxidant activity with antibacterial tests. The known molecular theories emphasize ROS and metal impacts above mechanical cell-wall breakage [75,77].

The antimicrobial behavior of modified biochars should not be reduced solely to the release of ROS or metal ions. Surface charge, hydrophobicity, roughness, defect density, and the material's zeta potential may also influence cell adhesion, membrane disruption, and local electrostatic interactions. In silver-doped systems in particular, mechanistic interpretation should ideally include not only total antimicrobial efficiency but also Ag release kinetics and comparisons with relevant toxicity thresholds for the target organism and the surrounding medium.

#### 4.5. Structure–Property–Performance Relationship

Physicochemical characterization has identified measurable structural features that consistently transfer to adsorption, catalysis, and antibacterial activity. Agricultural biochar research has linked structure, property, and performance.

In this review, the structure-property-performance relationship is interpreted as a directional sequence in which feedstock composition and process conditions determine structural descriptors, structural descriptors determine dominant interaction modes, and these interaction modes determine application performance (Figure 3).



**Figure 3.** The process chain for producing carbon-based materials from biomass: effects of pyrolysis, activation, oxidation, and doping.

Pore architecture, body surface area, and hierarchical micro- and mesoporosity increase the number of adsorption sites and the open pore volume for organic molecules. The enhanced surface area of  $\text{KHCO}_3/\text{KOH}$ -activated biochars improved tetracycline and antibiotic adsorption [73,74].

Pore-size distribution, compaction, and van der Waals forces help pores between 1 and 10 nanometers capture small organic contaminants. Organic trace impurities are removed differently by coir, rice husk, and other biochars, depending on their porous structures [86].

Polarity, hydrogen-bonding capacity, ion-exchange potential, and surface complexation for ionic or polar pollutants increased with rich oxygen- and nitrogen-containing groups (carboxyl, hydroxyl, and carbonyl). Chemisorption and ion exchange enabled the modified carboxylate-appended biochars to absorb methylene blue readily [73,77].

High aromatic content and enhanced graphitic ordering in photocatalytic and redox systems enhance  $\pi$ - $\pi$  interactions, electrical conductivity, and adsorption of aromatic contaminants, supporting electron transfer [87].

Ash and mineral content, surface charge, inorganic content, and zeta potential affect electrostatic attraction, which may involve surface complexation sites for oxyanions such as arsenic. Due to the presence of oxygen functional groups and mineral content, mineral-rich colloids absorbed more [76,77].

Adding metals or metal oxides, such as Ag,  $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{ZnCl}_2$ , alters chemical affinity (surface complexation and catalytic sites) and physical trapping (increased porosity). This creates combined adsorption, photocatalysis, and antibacterial action.

Following  $\text{KHCO}_3$  activation, increasing surface area and micropore volume led to a 15-fold increase in tetracycline adsorption.  $\text{KOH}$ -activated bagasse biochar with hierarchical porosity removed norfloxacin due to pore-filling and electrostatic attraction [73,74]. Examples show that quantitative structural properties can predict practical removal efficiency and catalytic activity.

## 5. Applications in Water Treatment

### 5.1. Removal of Heavy Metals, Organic Dyes, and Emerging Contaminants

The applications of modified biochar in water treatment must be evaluated comparatively using quantifiable performance indicators, such as maximum adsorption capacity ( $q_{\text{max}}$ , mg/g), process kinetics, optimal pH range, and regeneration stability. Actual performance depends on experimental conditions (pH, initial concentration, aqueous matrix, ionic competition), which requires a standardized comparative analysis. Table 4 summarizes representative applications of modified biochar for the removal of heavy metals, organic dyes, and emerging contaminants, including the type of material, modification method, operational parameters, and reported performance, facilitating a critical evaluation of efficiency and transferability to the practical scale.

The values for removal efficiency presented in Table 4 should be interpreted as context-dependent performance indicators rather than as directly standardized benchmarks. Reported capacities were obtained under different pH values, initial concentrations, contact times, ionic strengths, and background matrices, which means that cross-study ranking is only approximate. For this reason, Table 4 illustrates the performance range achievable through feedstock selection and modification strategy rather than implying strict comparability among all listed systems.

**Table 4.** The efficiency of removal of heavy metals, organic dyes and emerging contaminants.

Contaminant	Biochar Type or Modification	Removal Efficiency	Mechanisms	Reference
Methylene blue	Carboxylate-functionalized	98% removal; $q_m \approx 261 \text{ mg}\cdot\text{g}^{-1}$	Chemisorption, ion exchange, surface sorption	[73]
Tetracycline	$\text{KHCO}_3$ -activated tea biochar	$q_m = 293.46 \text{ mg}\cdot\text{g}^{-1}$	Pore filling, $\pi$ - $\pi$ EDA interactions	[74]
Norfloxacin	KOH-activated sugarcane bagasse	$q_m$ up to $157.4 \text{ mg}\cdot\text{g}^{-1}$	Pore filling, electrostatic attraction	[76]
PFOS (PFAS)	$\text{ZnCl}_2$ -modified litchi biochar	$q_m = 29.6 \text{ mg}\cdot\text{g}^{-1}$ ; >95% removal	Surface complexation, electrostatics, H-bonding, hydrophobic	[88]
Atrazine	Corn straw biochar colloids (700 °C)	$139.33 \text{ mg}\cdot\text{g}^{-1}$	Oxygen functional groups, adsorption on colloids	[77]
Chloroquine	Microwave-activated cassava biochar	$q_m = 39 \text{ mg}\cdot\text{g}^{-1}$	Physisorption; spontaneous endothermic	[87]
As(III)	Thermally/chemically modified husk biochar composites	High capacities reported; pH 7.5–9.0 favored	Surface chemistry-driven sorption/complexation	[81]

### 5.2. Batch vs. Continuous Flow Systems

As a result, batch and column assessments address distinct design concerns, and research offers metrics and models to characterize biochar performance. It is possible to quantify equilibrium and rate parameters for material comparison via batch testing. On the other hand, column tests simulate continuous treatment and provide dynamic behavior and realistic design parameters [73,74].

In batch measurements, it is usual practice to investigate maximal adsorption capacities and to fit isotherm models such as Langmuir and Freundlich, as well as kinetic models such as the pseudo-second-order model, to characterize sorption rates.

Mechanistic inference from batch data: In scientific experiments, it was used to fit isotherms and kinetics, as well as to perform spectroscopic characterization, to infer processes such as pore filling,  $\pi$ - $\pi$  interactions, electrostatic attraction, and chemisorption in batch experiments [74,76,77].

For each column, metrics and models are used to determine bed capacity under flow and predict breakthrough time and service life. Continuous tests employ breakthrough curves and dynamic models, such as the Thomas model. A study reported that approximately  $267.09 \text{ mg}\cdot\text{g}^{-1}$  was obtained from column data and that the method maintained an efficiency of more than 80% over two cycles in a methylene blue column test [86,89,90]. When discussing the design and scaling-up of industrial wastewater treatment, it is emphasized that continuous adsorption trials are important. Engineered biochars were described as easy and scalable for the removal of emerging contaminants in continuous modes [91].

A further limitation in the available literature is the imbalance between batch adsorption studies and column-based or continuous-flow tests [92–95]. While some studies report metrics such as breakthrough time, bed capacity, and various model parameters, these metrics are not yet sufficiently harmonized to support robust cross-study meta-analysis. Likewise, liquid-film and intraparticle mass-transfer coefficients are rarely reported in a consistent format. Competitive adsorption and ionic-strength effects are also underexplored in many studies using real wastewater matrices, even though coexisting ions, natural organic matter, and variable conductivity can materially reduce apparent performance relative to synthetic solutions.

### 5.3. Regeneration and Reuse

Regeneration and reuse are essential to the economy; however, the most recent scientific studies have provided little data on the processes involved in regeneration. Never-

theless, the works now accessible describe varying levels of performance retention across reuse cycles without consistently detailing regeneration mechanisms [75,91].

After eight cycles of reuse, coir biochar achieved complete oxytetracycline treatment, indicating that its dynamic performance was maintained over a significant number of cycles [75].

Approximately 70% of the original adsorption capacity of microwave-activated cassava biochar was retained after five desorption cycles [96].

After five regeneration cycles in PFAS testing, the biochar made from litchi seeds treated with  $ZnCl_2$  remained reusable. The biochar's performance was reported as resilient across pH and in actual waterways [87].

During dye testing, Ag/TiO<sub>2</sub>-doped biochar photocatalysts were regenerated and reused for up to five cycles without significant loss of activity.

Over 80% of the removal effectiveness was maintained by leached rice straw biochar that had been carboxylate-functionalized for two MB adsorption cycles in the column test [76].

Future research should specify regeneration procedures (including chemicals, concentrations, temperatures, and contact times), report cycle-by-cycle quantitative capacities, and couple regeneration with characterization to link loss mechanisms to method choices. Several studies in the dataset demonstrate that reuse is feasible, but they lack the procedural detail that is required for reproducible scale.

#### 5.4. Critical Evaluation of Current Evidence and Unresolved Research Needs

Although the available literature demonstrates the versatility of agricultural-waste-derived biochars in adsorption, photocatalysis, redox systems, and multifunctional composite design, the evidence base remains uneven in quality and scope. A large proportion of published studies report high removal efficiencies or favorable adsorption capacities under controlled laboratory conditions. Still, their results are often difficult to compare directly because testing protocols, water matrices, and reporting standards vary substantially from one study to another. A second major limitation is the predominance of batch-scale experiments using synthetic solutions. Continuous-flow studies, multicomponent matrices, and realistic wastewater conditions remain underrepresented, even though they are essential for assessing practical feasibility. Another important shortcoming concerns reproducibility and transparency of production conditions. These shortcomings define several priorities for future research: more harmonized reporting of feedstock characteristics and thermal history, greater use of realistic matrices and continuous-flow operation, quantitative reporting of regeneration, and explicit life cycle and carbon-accounting assumptions.

#### 5.5. Emerging Advanced Applications Beyond Water Treatment

Although water treatment remains the most mature application field discussed in this review, the same structure-guided design principles also support the use of biochar-based materials in more advanced technological sectors, including electrochemical energy storage, conductive composites, electrocatalysis, and sensor platforms. A representative study on biochar derived from the aquatic macroalga *Ahnfeltia tobuchiensis* and carbonized at 700 °C reported a reversible capacity of 391 mAh g<sup>-1</sup> in the initial cycles, which remained close to 300 mAh g<sup>-1</sup> after 25 cycles [97]. From the perspective of the present review, such advanced applications reinforce the same structure–property–performance logic: high aromatic carbon content improves stability and electron transport, developed porosity increases accessibility to ions, molecules, or electrolytes, and heteroatoms such as N, P, or S modify charge density and create additional active sites.

## 6. Post-Use Valorization and Dual Functionality

Post-use management of biochar should be addressed as an integral part of process design instead of a terminal disposal step. After adsorption, saturated biochar often retains a porous carbon matrix, mineral phases, and reactive surface functionalities that can support secondary applications in soils or construction materials. The recent review literature has increasingly framed spent biochar as a multifunctional material with potential for agronomic reuse, contaminant stabilization, thermochemical valorization, or incorporation into engineered products, which supports the concept of dual functionality in biochar-based treatment systems.

However, secondary valorization cannot be justified solely based on residual porosity or retained sorption capacity. The feasibility of reuse depends on the identity, concentration, mobility, and regulatory status of the adsorbed contaminants, as well as on the intrinsic quality of the biochar itself. For this reason, post-use routing should be assessed through a risk-based framework that distinguishes between nutrient-loaded or relatively benign spent materials, which may be suitable for controlled agronomic or material reuse, and contaminant-laden biochars, which may require stabilization, thermal reprocessing, or restricted use.

Spent biochar is typically reused as nutrient-loaded soil amendments, managed as contaminant-bearing waste requiring stabilization or disposal or diverted to non-agronomic products such as construction composites and energy/catalytic materials. Each route carries distinct performance needs, release risks, and policy gaps.

Spent biochar that carries recovered nutrients is increasingly discussed as a post-use product with agronomic value rather than as a residue requiring disposal. In this context, saturated biochar can be used directly as a slow-release fertilizer or incorporated into blended soil amendments, provided that its nutrient loading, post-processing, and field application strategy are compatible with crop requirements. Reviews and life cycle-oriented studies report encouraging agronomic outcomes and provide explicit examples, such as phosphate-saturated and Mg-modified biochars used as fertilizer carriers, supporting the relevance of this pathway for circular nutrient management [94,98,99].

The agronomic function of nutrient-loaded spent biochar is inherently dual: it serves as both a nutrient carrier and a soil conditioner. Beyond nutrient supply, the biochar matrix can improve soil structure, moisture retention, and related physical properties, thereby enhancing nutrient-use efficiency and crop response over time [94,98]. However, these benefits are not automatic. Evidence indicates that agronomic performance is sensitive to post-processing, particularly particle-size distribution. Plant responses appear to improve when particle size is controlled, with favorable ranges reported around 0.5–1.0 mm, and additional treatments such as heating or aeration may further influence performance [100]. Likewise, nutrient form and loading chemistry are critical. The nutrient must remain sufficiently plant-available while avoiding rapid leaching losses, and studies on Mg-modified phosphate-loaded biochars illustrate how material-specific loading strategies can be designed to balance retention and release [98].

For this route to be credible in a process-oriented framework, agronomic reuse must be supported by consistent material characterization and release testing. At minimum, nutrient-loaded spent biochar should be evaluated for nutrient content, pH, electrical conductivity, and soluble fractions, along with its release behavior under conditions relevant to crop management [94]. Without this level of characterization, field performance is difficult to predict and integration into fertilization programs remains uncertain.

At the same time, the risks associated with direct land application must be stated clearly. When biochar is sourced from wastewater or polluted streams, contaminant carryover becomes a major concern. Heavy metals, organic contaminants, pathogens, and

antibiotic resistance genes (ARGs) may persist in spent material and pose risks to soil health and food safety if applied without adequate screening [100]. In addition, leachate chemistry from post-processed biochars has been reported to be heterogeneous across studies, suggesting that short-term release behavior can vary substantially depending on feedstock, treatment history, and post-processing conditions [101]. This variability underscores the need for end-use-specific leaching and release assessments rather than assuming uniform behavior across materials.

Regulatory and governance aspects remain significant limitations. Although the direct application of nutrient-loaded spent biochar is recognized in the policy and sustainability literature as a promising circular pathway, harmonized standards and application thresholds remain limited, and practical implementation generally depends on local regulations and case-specific testing [99]. Based on the supplied literature, there is not yet sufficient evidence to define universally applicable regulatory limits or a standardized certification framework for nutrient-loaded spent biochars; accordingly, regulatory compliance must currently be addressed on a jurisdiction-by-jurisdiction basis.

In contrast to nutrient-loaded materials, biochar that has sorbed contaminants from wastewater treatment, remediation systems, or industrial process streams often cannot be safely returned to soil without further treatment. In these cases, the post-use challenge is no longer nutrient recovery but contaminant containment, and the spent biochar should be managed through stabilization, encapsulation, controlled disposal, or transfer to engineered sinks. Reviews on biochar in wastewater treatment and remediation consistently emphasize that end-of-life handling of contaminant-laden biochar remains a major operational and environmental constraint [100,102].

This management challenge is directly linked to the mechanisms by which biochar captures pollutants. Adsorption, ion exchange, pore entrapment, filtration, and biofilm-mediated biodegradation can all contribute to contaminant accumulation on or within the biochar particles [100]. As a result, the spent material becomes a concentrated solid matrix in which contaminant speciation, binding strength, and mobility determine downstream risk. From a process perspective, this means that the success of the primary treatment stage cannot be evaluated independently of the fate of the loaded sorbent.

Several management routes are discussed in the literature. Stabilization and immobilization approaches aim to reduce contaminant leachability through chemical or physical treatment, including further modification of the biochar surface or incorporation into binding matrices [103]. These strategies build on the same materials science principles used to enhance adsorption—namely, changing surface chemistry and strengthening sorption interactions—but apply them to containment rather than uptake. Encapsulation in construction or composite materials is another option, particularly where the goal is to isolate contaminants while generating a secondary-use product; however, such approaches require clear evidence of long-term containment and acceptable material performance [94,103]. When safe reuse cannot be demonstrated, controlled disposal in engineered landfills or secure recovery pathways remain necessary. Reviews repeatedly identify disposal and containment as unresolved issues for contaminant-bearing biochars, particularly at scale [94,102].

Regardless of the route chosen, safe management requires performance criteria that go beyond adsorption capacity. Reduced leachability is essential: contaminant release rates must remain low under the environmental conditions relevant to the intended end use or disposal setting [98,100]. Physical integrity is also important, especially for materials that are handled, transported, or weathered. Abrasion, fragmentation, and disintegration can increase the risk of particle mobilization and contaminant exposure [4]. In addition, life cycle thinking is needed when comparing reuse and disposal options, since environmental

burdens can shift downstream depending on how the spent biochar is treated within the broader nutrient recovery or remediation chain [98].

The decision criteria are therefore risk-centered. Improper reuse may result in the release of metals, organic contaminants, or biological hazards into soil and water, undermining the original environmental benefits of the treatment process [100,102]. Although the literature clearly identifies disposal and containment as policy-relevant challenges, it does not yet provide standardized regulatory thresholds that apply across jurisdictions. As with agronomic reuse, specific regulatory requirements must therefore be determined locally, and the current evidence base is insufficient to support a single universal compliance framework.

When agronomic reuse is unsuitable or risky, non-agronomic valorization offers an alternative route to recover value from spent biochar. The current literature describes several pathways, including incorporation into building materials, polymer or cement composites, and conversion into catalytic or energy-related materials, such as electrodes. These routes are attractive because they may either immobilize contaminants within engineered matrices or extend the functional life of biochar through higher-value applications. Reviews covering construction additives, biocomposites, and energy and catalytic applications consistently show that the feasibility of these routes depends on targeted functionalization and end-use-specific material design [94,103,104].

Construction-related uses are among the most developed non-agronomic options. Biochar has been incorporated into cementitious systems, asphalt, and insulation-type materials, where it may contribute to moisture regulation, thermal behavior, and electromagnetic properties, in addition to its role as a filler [98]. From the perspective of spent biochar management, these applications are particularly relevant because they may combine valorization with containment, especially when contaminant-bearing biochar is embedded in a stable matrix. Related composite strategies use polymeric or mineral binders to encapsulate the particles while also contributing to the mechanical or functional performance of the final product [103].

Catalytic and energy-related applications represent a more specialized yet technologically significant class of end uses. Functionalized biochars, including nanoscale or chemically activated variants, are being developed for catalytic systems and electrochemical energy storage, where conductivity, surface chemistry, and stable active sites are essential [103,104]. These applications usually require additional modifications—such as the activation or incorporation of metal oxides—to achieve the required performance, which means they are more processing-intensive than direct reuse in soil or in basic construction matrices.

Because these pathways move spent biochar into engineered products, their performance requirements are correspondingly strict. For construction and composite uses, the material must satisfy mechanical and durability criteria (e.g., strength, stiffness, fire resistance, and long-term stability) appropriate to the target application and relevant building standards [94]. For catalytic and energy applications, the requirements shift toward conductivity, accessible surface area, and stable reactive sites, which are generally achieved through tailored functionalization [103,104]. When the application's purpose is partly to sequester previously captured contaminants, containment verification becomes a central requirement. In such cases, leaching tests under accelerated weathering and service-life simulation conditions are needed to demonstrate long-term immobilization [94,103].

The literature supports the promise of these non-agronomic routes but also highlights important evidence gaps. Although benefits have been reported, comprehensive long-term datasets on leaching behavior and structural safety of contaminant-bearing biochar in engineered products remain limited. As a result, long-term risk and standardized regulatory acceptance cannot yet be considered fully established [94,103]. In addition, policy and market barriers continue to affect scale-up, especially for more engineered materials such

as magnetic or highly functionalized biochars, indicating that nontechnical factors may be as important as material performance in determining industrial adoption [99].

The climate relevance of sequential or post-use application depends on whether the secondary route merely delays disposal or actually displaces a more emission-intensive product or process. Recent case studies show that the net GHG effect can shift substantially depending on the accounting scenario, functional unit, and substitution credit used. The key implication is that sequential use should be presented as a potentially advantageous strategy, rather than an automatically carbon-negative outcome; illustrative case studies and scenario-based quantification should be incorporated into future revisions, where possible.

Conclusions regarding the reuse or environmental performance of manure-derived, sludge-derived, or otherwise contaminant-bearing biochars should be considered substantially more uncertain than those for relatively clean lignocellulosic residues. These materials may contain higher ash fractions, concentrated trace metals, salts, phosphorus-rich mineral phases, residual organic contaminants, or mobile toxic species whose behavior depends strongly on pyrolysis temperature, feedstock heterogeneity, and post-treatment history. Accordingly, the present review does not generalize conclusions from crop-residue-derived biochars to manure- or sludge-based systems without qualification; future LCAs should explicitly address this uncertainty through scenario analysis, sensitivity analysis, and separate inventory modeling for contaminant control steps.

#### *6.1. Use of Saturated Biochar as a Soil Amendment*

The use of saturated biochar as a soil amendment is most appropriate when the sorbed phase is beneficial (e.g., nutrient-enriched biochar) or when contaminant release is demonstrably controlled. Even after adsorption, biochar typically preserves key structural characteristics (porosity, surface area, aromatic carbon backbone) that can improve soil water retention, aggregation, cation exchange behavior, and nutrient retention.

From a process perspective, this route can be described as a two-stage valorization strategy: adsorption serves as the primary treatment function. In contrast, soil application provides a secondary agronomic and carbon-management function. This framing is particularly relevant for systems designed to recover nutrients or condition effluents before land-based reuse. The sustainability value of this pathway increases when it reduces mineral fertilizer demand or improves nutrient-use efficiency in degraded soils.

Saturated biochar can be safe and beneficial if sorbed contaminants are immobilized and nonextractable, but risks exist from intrinsic contaminants (e.g., PAHs) and from fractions mobilized under environmental conditions. Eligibility requires targeted desorption testing under field pH and rhizosphere conditions, and limits on total and extractable contaminants before soil reuse.

The use of saturated biochar in soil systems requires a balanced interpretation of both its immobilization potential and its residual risk. In many cases, saturated biochar can reduce contaminant bioavailability and alleviate pollutant-induced phytotoxicity, particularly when sorption is strong, and the bound fraction remains stable under soil conditions. At the same time, safety assessment must distinguish between two fundamentally different issues: (i) beneficial immobilization of contaminants captured during treatment, and (ii) harmful intrinsic contaminants already present in the biochar due to feedstock type or production method. This distinction is essential for any review of post-use biochar management.

Several studies support the immobilization benefit of saturated biochar under appropriate conditions. In sludge-amended soils, biochar addition has been shown to increase adsorption capacity while reducing desorption and bioavailability of metals such as Cd, Cu, Ni, and Zn relative to non-amended systems, indicating a clear stabilization effect for multiple potentially toxic elements [105]. Similarly, experiments using metal-saturated soft-

wood biochar reported improved plant growth and reduced phytotoxicity compared with controls, suggesting that sorbed metals can, under some conditions, be retained in forms that are less bioavailable and less harmful to plants [106]. Comparable trends have also been reported for organic contaminants: biochar can strongly adsorb pesticides, thereby reducing desorption, limiting their mobility, and reducing bioavailability in soil [92]. Taken together, these findings support the view that saturated biochar can provide a genuine environmental benefit when sorption is persistent and contaminant remobilization is low.

However, the presence of intrinsic contaminants in the biochar itself may offset or even negate these benefits. Some biochars, particularly those produced from certain feedstocks or under poorly controlled thermal conditions (e.g., traditional kilns), may contain elevated concentrations of polycyclic aromatic hydrocarbons (PAHs). In such cases, soil application has been associated with marked increases in soil PAH concentrations, demonstrating that biochar may act not only as a sorbent but also as a contaminant source [107]. In addition, even when contaminants are captured during treatment, only part of the sorbed fraction may be strongly retained. A measurable proportion can remain loosely bound or become mobilizable in the presence of environmentally relevant extractants such as salts or organic acids. This necessitates distinguishing between total contaminant content and extractable or remobilizable fractions when evaluating safety [106].

For these reasons, the benefits of saturated biochar should be interpreted conditionally rather than assumed. Evidence supports reduced bioavailability and phytotoxicity in many systems, but only when contaminant retention is robust and intrinsic contamination is adequately controlled [92,105–107].

Desorption behavior under field-relevant conditions is central to the safe reuse of saturated biochar, as contaminant retention is not static. Sorption strength and release potential vary with soil chemistry, particularly pH, ionic strength, ligand availability, and rhizosphere activity. As a result, laboratory adsorption data alone are insufficient to predict long-term safety after land application. A more appropriate assessment requires desorption testing under conditions that simulate realistic soil environments, including pH shifts and biologically relevant extractants.

Experimental evidence shows that sorption capacity and affinity are strongly pH-dependent. Controlled studies have reported clear pH effects on retention behavior, including differences in sorption trends among elements (e.g.,  $Pb > Cu > As > Sb$  under some conditions), with substantial sorption quantified at around pH 6 [106]. These results indicate that changes in soil pH can alter contaminant retention and therefore modify the risk of release over time. This is particularly relevant in agricultural soils where pH may vary due to liming, fertilizer inputs, root activity, or seasonal changes.

Organic ligands provide an additional, often underestimated, desorption pathway. Extraction tests using  $Ca(NO_3)_2$  and environmentally relevant organic acids have shown that only a relatively small fraction of some potentially toxic elements may be released as loosely exchangeable material (approximately 6–11%), while much larger fractions—up to about 60% of total PTE mass in some cases—can be mobilized in the presence of organic acids [106]. This finding is highly important for post-use evaluation because it suggests that rhizosphere compounds can substantially increase desorption risk even when conventional salt extractions indicate relatively low mobility.

At the same time, matrix effects may partially mitigate remobilization. In sewage-sludge-amended soils, the inclusion of biochar reduced desorption of several potentially toxic elements relative to sludge-only or unamended soils, indicating that interactions between soil, sludge, and biochar phases can improve retention [105]. However, this reduction should not be interpreted as complete immobilization. Rather, it supports the

need for system-specific testing that accounts for the full soil matrix rather than only biochar in isolation.

One notable gap in the available evidence concerns moisture dynamics. While the supplied studies provide useful data on pH and ligand effects, they do not offer quantified field-scale evidence on how wetting–drying cycles influence desorption and transport of sorbed contaminants. Because soil moisture fluctuations can alter redox conditions, pore-water chemistry, and transport pathways, moisture-specific desorption behavior remains insufficiently documented in this corpus.

Based on the reviewed evidence, desorption assessment for saturated biochar intended for land application should prioritize a set of field-relevant assays, including pH-dependent sorption/desorption testing, determination of ionic-exchangeable pools (e.g.,  $\text{Ca}(\text{NO}_3)_2$ -extractable fractions), organic acid leaching to simulate rhizosphere conditions, and plant uptake or bioassays to evaluate biologically relevant remobilization [92,105,106]. These approaches provide a more realistic basis for judging whether apparent sorption stability in laboratory systems will translate into safe performance in soil.

The reviewed literature does not provide a single set of universal numeric threshold values for the agricultural reuse of saturated biochar. Instead, it consistently indicates which contaminant classes, fractions, and exposure-relevant metrics should be monitored to avoid transferring contaminants from treatment systems into soils. In this context, regulatory criteria should not rely solely on total contaminant concentrations; they should also account for environmentally mobile fractions, particularly for metals and persistent organic pollutants (POPs).

A recurring theme in comparative studies and policy-oriented discussions is the lack of harmonized limits for spent or saturated biochar. Existing national guidance examples may be informative, but they are not uniform, and some biochars fail available country-level criteria due to elevated metal contents, such as Ni [93,107]. Importantly, the cited studies do not establish internationally harmonized numeric thresholds for reuse. This limits the ability to recommend fixed, universal cutoffs based solely on the current evidence base.

The case of PAHs illustrates why contaminant-specific limits are necessary. Reported  $\Sigma 16\text{PAH}$  concentrations in biochar vary widely, ranging from hundreds to thousands of  $\mu\text{g kg}^{-1}$ , and field-relevant application rates (e.g.,  $10\text{--}40 \text{ t ha}^{-1}$ ) can produce measurable and sometimes substantial increases in soil PAH concentrations. In some treatments, kiln-produced wood biochar caused up to a tenfold increase in soil PAH levels [107]. These findings demonstrate that limits for PAHs should be defined not only in terms of biochar content but also in terms of the resulting changes in soil concentration after application.

The literature also makes clear that total concentration alone is an incomplete safety metric. A substantial portion of sorbed contaminants may remain weakly bound or become mobilizable under environmentally relevant ligands, particularly organic acids [106]. For this reason, regulatory evaluation should include multiple contaminant descriptors: total contaminant content, exchangeable or ionic-extractable fractions (e.g.,  $\text{Ca}(\text{NO}_3)_2$ -extractable), and organic-acid-leachable fractions that simulate rhizosphere conditions. This multi-fraction approach is more consistent with actual environmental exposure pathways than a total-mass-only criterion.

In practical terms, the available evidence supports a precautionary pre-reuse assessment framework. Before agricultural deployment, saturated biochar should undergo (i) feedstock and production characterization to identify intrinsically contaminated materials, including problematic feedstocks or poorly controlled kiln products, (ii) analysis of total metals and POPs, and (iii) extractability testing under pH- and ligand-relevant conditions to demonstrate low mobilizable fractions [93,105–107]. These requirements are

well supported by the reviewed studies, even though they do not converge on a single numeric threshold.

Accordingly, the current corpus is insufficient to justify specific universal cutoffs for heavy metals or POPs in saturated biochar intended for agricultural reuse. The development of numeric thresholds will require regulatory decisions informed by local background soil conditions, human and ecological risk criteria, and field-scale evidence linking extractable contaminant fractions to plant uptake, soil health, and long-term environmental outcomes.

In the European context, agronomic valorization must also be considered in light of the contaminant thresholds applicable to fertilizing products and soil improvers. Under Regulation (EU) 2019/1009, pyrolysis and gasification materials intended for EU fertilizing products are subject to compositional restrictions, including a PAH16 limit of  $6 \text{ mg kg}^{-1}$  dry matter. For organic soil improvers, relevant contaminant limits include Cd  $2 \text{ mg kg}^{-1}$  DM, Hg  $1 \text{ mg kg}^{-1}$  DM, Ni  $50 \text{ mg kg}^{-1}$  DM, Pb  $120 \text{ mg kg}^{-1}$  DM, inorganic As  $40 \text{ mg kg}^{-1}$  DM, Cu  $300 \text{ mg kg}^{-1}$  DM, and Zn  $800 \text{ mg kg}^{-1}$  DM. These benchmarks underscore that soil reuse of spent biochar should be considered conditional rather than automatic.

### 6.2. Stabilization and Immobilization of Contaminants in Soil

For contaminant-loaded biochar, a major post-use pathway is controlled application for stabilization/immobilization in contaminated soils. In this case, the biochar matrix can reduce contaminant mobility and bioavailability through multiple mechanisms, including pore adsorption, ion exchange, electrostatic attraction, surface complexation, and mineral-associated precipitation. The effectiveness of these mechanisms depends on pH, ash content, cation exchange capacity, and the abundance of oxygen-containing surface functional groups.

It has to be retained that immobilization performance in soil cannot be inferred directly from batch adsorption tests in water. Soil systems introduce competing ions, variable redox conditions, interactions with organic matter, and microbial effects that may alter sorbate stability over time. Therefore, claims of long-term immobilization should be supported by soil-specific evidence (e.g., fractionation, leaching tests, plant uptake data, and aging studies), rather than solely by aqueous adsorption isotherms. Composite strategies further improve safety and performance.

Combining biochar with mineral-rich industrial residues is increasingly recognized as a practical strategy for contaminated-soil remediation as it couples metal immobilization with waste valorization. Rather than relying on a single sorbent mechanism, these co-amendments bring together complementary chemical and physical functions: biochar provides porous carbon surfaces and functional groups for adsorption and complexation. In contrast, mineral residues provide alkalinity and reactive mineral phases that promote precipitation and convert metals into less labile forms. In parallel, the amendment can improve soil structure, cation exchange capacity (CEC), and nutrient availability, thereby supporting vegetation recovery and reducing long-term remobilization risk. From a circular-process perspective, this approach is particularly attractive because it simultaneously reuses industrial by-products and biomass-derived carbon, thereby closing material loops in remediation systems.

A central advantage of these combined amendments is the presence of synergistic immobilization pathways. Biochar provides a condensed aromatic structure and porous matrix that adsorb dissolved metal ions and facilitate the formation of organic carbon–metal complexes, especially during co-treatment with metal-rich residues [27]. At the same time, metals may coordinate with oxygen-containing functional groups on the biochar surface while also being transformed into less bioavailable mineral forms, such as oxides, when the residue component catalyzes oxidation or provides reactive metal/oxide nuclei [27,108]. In this way, immobilization does not depend on a single interaction but on a network of

parallel processes, which generally improves robustness under variable soil conditions. Another key mechanism is pH buffering. Alkaline residues such as carbide slag, apatite, and fly ash raise soil pH, increasing negative surface charge, reducing metal solubility, and promoting precipitation or adsorption onto oxide-rich surfaces [109,110]. Across the reviewed studies, this pH-driven pathway appears to be a dominant contributor to reduced metal mobility in combined amendments [109,110].

The specific role of the mineral residue varies with composition, and the literature highlights several representative functions. Fly ash contributes reactive oxides and supports precipitation and ion-exchange processes, making it a low-cost component in sorbent mixtures designed for metal immobilization [108]. Red mud plays a more chemically active role in some systems, where co-pyrolysis with biomass promotes aromatic condensation in the carbon phase and facilitates the conversion of free metals into oxide-associated forms, thereby reducing bioavailability [27]. Carbide slag and metallurgical slags are particularly effective as buffering agents: they increase soil pH and CEC, improve acid neutralization, and have been shown to reduce DTPA-extractable Cu, Pb, and Zn in mine-affected soils [110]. Apatite contributes phosphate and increases negative surface charge, enhancing adsorption and precipitation-based immobilization, particularly for Pb and Zn, while also stabilizing exchangeable metal fractions [109]. These differences are important for process design because they show that residue selection should be matched to the target contaminant and the desired soil functions.

Beyond direct immobilization, biochar-residue amendments improve soil physical and chemical properties in ways that further support remediation performance. Several studies report enhanced aggregate formation and improved aggregate stability when biochar is co-processed with red mud or applied as part of composite amendments, which contributes to both soil structural recovery and greater stability of the biochar phase itself [27]. Improved aggregation can reduce erosion and particle transport, which indirectly lowers the risk of contaminant redistribution. Mineral-enriched biochars have also been associated with increased pore volume, higher CEC, and better water-holding capacity, all of which help retain metals in less mobile forms while supporting plant establishment on degraded soils [108]. In addition, residues such as apatite or Ca/P-rich mineral sources can provide beneficial nutrients (especially Ca and P) that serve a dual role: they participate in metal immobilization through adsorption and precipitation while also improving nutrient availability for plants [108–110]. This dual function is particularly important in contaminated soils, where fertility constraints and toxicity often co-occur.

The agronomic and ecological benefits of these co-amendments extend to the rhizosphere. Studies indicate that mineral-enriched biochar formulations can reduce DTPA-extractable Cu, Pb, and Zn and improve plant growth in contaminated soils, suggesting that chemical immobilization translates into lower biological exposure [108–110]. At the same time, changes in rhizosphere microbial composition have been reported, including increases in beneficial microbial taxa and reductions in heavy-metal uptake by plants, suggesting ecological recovery alongside physicochemical remediation [108].

From a circular-process design standpoint, integrating biochar with industrial residues provides a strong justification for scale-oriented remediation systems. Co-pyrolysis or blending of residues such as red mud, fly ash, slag, or apatite with biomass can generate composite amendments that immobilize metals while also stabilizing industrial by-products that might otherwise require disposal [27,111]. This is explicitly framed in the literature as resource-efficient reuse and a promising pathway for synergistic valorization of multiple waste streams [27,111]. In situ application of these composite sorbents is also described as a relatively low-cost and low-impact remediation option, particularly suitable for large contaminated areas where conventional excavation-based treatments are economically or

environmentally burdensome [108]. Field and pot-scale studies provide further support by showing measurable reductions in extractable metal fractions, stabilization of soil pH, and improvements in plant health when reclaimed residues are used as part of biochar-based soil amendments [108–110]. Together, these findings support the positioning of biochar–mineral residue composites as a practical circular remediation step that can restore both environmental quality and land productivity.

At the same time, the evidence base remains incomplete in one important respect: quantitative system-level comparisons are still limited. Although the literature supports the technical and agronomic promise of these co-amendments, the supplied sources do not report detailed life cycle assessments or large-scale economic analyses directly comparing circular composite pathways with conventional remediation alternatives. As a result, claims regarding full cost–benefit performance or life cycle superiority should be made cautiously and identified as priorities for future research rather than established conclusions.

### 6.3. Integration into Construction Materials (Cement, Concrete, Composites)

When soil reuse is not suitable, or higher-value reuse is desired, incorporating biochar into construction materials is a promising alternative. In the literature, it is reported that biochar has been used in cementitious composites, concrete, asphalt, and polymer-based materials, where it can influence mechanical performance, durability, thermal behavior, and moisture regulation. These studies also highlight the potential of biochar-containing materials to contribute to carbon-oriented construction strategies.

For saturated biochar, construction integration is particularly attractive because it can serve both as a valorization route and as a containment strategy. In properly designed matrices, the solid phase may encapsulate contaminant-loaded biochar, thereby reducing release risk; however, this must be verified through leaching and durability testing under realistic service conditions. The suitability of this route depends on biochar particle size, ash content, residual sorbate chemistry, and compatibility with the host matrix.

Coupling biochar adsorption units to downstream materials manufacturing creates sequential product streams that recover adsorbed resources, monetize biochar services, and cut disposal needs while improving circularity and supply chain resilience. Process integration and coproduct strategies increase resource efficiency and industrial symbiosis.

A process-oriented discussion of post-use biochar should not treat adsorption as an isolated unit operation. In practice, the value of biochar-based treatment systems increases substantially when adsorption is linked to downstream manufacturing or reuse pathways, creating what the literature increasingly describes as sequential biochar systems. In this framework, biochar is not viewed simply as a consumable sorbent but as a carrier of environmental services that can move across sectors while retaining functional value. Depending on how it is loaded and processed, the same material may act first as an adsorbent, then as a nutrient carrier or carbon sink, and finally as a feedstock for another industrial or agrarian use [112]. This sequential logic is central to circular-process design because it reduces reliance on single-use pathways and supports material cascading.

One of the most promising settings for this approach is the integrated biorefinery. Embedding biochar production and adsorption functions within biorefineries or related biomass-processing industries (including pulp and paper value chains) creates opportunities to co-produce energy and multiple material streams, which can then be routed into downstream manufacturing [113,114]. In such systems, biochar is no longer a side product with uncertain value but part of a coordinated process network in which by-products and intermediates are intentionally directed toward secondary uses. This integration also enables sidestream routing, in which feedstocks and process residues from bioenergy or

biorefinery complexes are redirected to adsorption and subsequent material conversion steps, thereby closing loops and supplying secondary value chains [115].

To implement these links effectively, process integration cannot rely on ad hoc decisions. The literature highlights the importance of formal process design and supply chain tools for identifying optimal routing strategies, coproduct combinations, and logistics for coupling adsorption units with downstream manufacturing [116,117].

Once biochar has been used as an adsorbent or environmental service carrier, several material valorization pathways become possible, and the literature increasingly documents these as viable secondary product streams rather than residual disposal options. The suitability of each pathway depends on the chemical and physical state of the post-use biochar, including whether it is nutrient-loaded, contaminant-bearing, or structurally intact enough for further conversion.

One important route is upgrading to activated carbon or other advanced carbon materials. Spent biochar or biochar precursors can be further processed into activated carbon and engineered carbon products suitable for high-value applications, including electrochemical systems such as supercapacitors [114]. This pathway is particularly relevant when the carbon matrix remains structurally valuable and can be functionalized or activated to meet stricter performance requirements. In this case, the biochar is not only reused but transformed into a higher-value carbon material, extending its functional lifetime within the process chain.

A second major route is agronomic reuse, especially when the biochar carries recovered nutrients or immobilized elements that can be safely returned to soil. In these cases, the spent material can function as a soil amendment that supports nutrient cycling while retaining the carbon-related benefits of biochar application [113]. This route is especially attractive in circular systems because it links treatment processes back to agricultural productivity, allowing nutrients captured from one stream to be reintroduced into another.

Integrated biorefineries provide a broader platform for valorization, enabling recovered biochar streams to be used as manufacturing feedstocks rather than waste residues. Within this setting, biochar can be routed into coproduct generation systems that produce energy, chemicals, or materials, thereby embedding the spent sorbent into a wider portfolio of value-added outputs [113,117]. This aligns closely with the broader concept of resource transfer and transformation described in sequential systems: pollutants, nutrients, and carbon captured by biochar are not seen as fixed burdens but as transformed resources that can enter downstream material processes under controlled conditions [112].

Linking adsorption to downstream biochar valorization has implications that extend beyond waste reduction. At the process level, sequential reuse creates measurable gains in resource efficiency, improves economic resilience through product diversification, and can strengthen sustainability performance when compared with single-use or disposal-based systems. The core principle is straightforward: the more functional stages a material passes through before disposal, the greater the value extracted per unit of biomass input.

One immediate benefit is the reduction in disposal demand. Routing spent biochar into secondary manufacturing or reuse pathways avoids single-use endpoints and keeps the material in circulation across multiple life stages [112]. This directly reduces the burden on disposal infrastructure and lowers the risk that a potentially useful carbon-rich material is prematurely treated as waste. In systems where disposal is costly or environmentally sensitive, this alone can justify additional integration effort.

A second benefit lies in the economics of coproducts. Techno-economic and life cycle studies of integrated biorefineries indicate that profitability and environmental performance improve when value-added coproducts are produced alongside primary outputs [117]. In this context, spent biochar becomes part of a diversified product portfolio rather than a

cost center. The ability to generate additional materials, energy products, or agronomic inputs from the same biomass processing chain can improve process economics and buffer volatility in individual product markets [113,117].

The literature also emphasizes the importance of monetizing multifunctionality. When biochar is treated as a provider of environmental services—such as adsorption, carbon sequestration, and nutrient retention—its value is no longer limited to its initial sale as a material. Instead, sequential applications create opportunities for new pricing structures and business models that capture value across multiple use phases [112]. This is a crucial shift in circular bioeconomy thinking because it reframes post-use management as part of value creation rather than cost minimization.

At the system level, these integration strategies support broader sustainability gains. Co-production and optimized coproduct portfolios can improve the overall performance of biomass processing systems by reducing net waste, intensifying resource use, and increasing the functional output derived from a single feedstock stream [113,117].

Sequential routing of biochar across sectors is also a practical mechanism for industrial symbiosis. By connecting wastewater treatment, agriculture, materials manufacturing, and biomass processing, biochar-based systems can enable exchange relationships in which the output of one process becomes the input of another. This cascading use of biomass-derived resources is a defining characteristic of circular bioeconomy models and is increasingly described in the literature as a realistic pathway for cross-sector integration [112,115].

In this context, biochar acts as a transfer medium between sectors. A biochar stream may capture contaminants or nutrients in one industrial setting, then be redirected into remediation, agriculture, or materials production, creating a chain of interdependent value exchanges [112]. This strengthens industrial symbiosis not only by reducing waste but also by increasing coordination between actors that would otherwise operate separately.

However, the literature also makes clear that technical feasibility alone is not sufficient to achieve implementation. Governance and institutional design play a major role. Policy incentives, institutional innovation, and coordinated value-chain governance are repeatedly identified as necessary conditions for unlocking waste valorization opportunities and scaling symbiotic exchange models in the bioeconomy [118]. Without these enabling structures, even technically sound biochar pathways may remain fragmented or economically uncompetitive.

Several practical barriers also remain. Reviews point to limited economic attractiveness relative to fossil-derived alternatives, difficulties in monetizing biochar's combined climate and material services, and bottlenecks in downstream valorization pathways as recurring obstacles to scale-up [112,114]. These challenges are especially relevant for more complex sequential systems, where value depends on coordination across multiple stages and markets rather than a single product transaction.

For this reason, implementation of sequential biochar systems must be supported by robust design and logistics planning. The literature consistently recommends combining process integration tools, supply-chain design, and life cycle assessment to optimize routing decisions, evaluate trade-offs, and verify that secondary uses genuinely reduce net environmental burdens rather than shifting impacts downstream [116,117]. Therefore, the success of industrial symbiosis in biochar systems depends on integrating technical design with governance, logistics, and life cycle evaluation from the outset.

#### *6.4. Potential Risks and Long-Term Stability*

A balanced review must address the potential risks associated with post-use biochar deployment. The main concern is not only the biochar itself but also the long-term fate of the adsorbed species. Reported risks in recent reviews include heavy metals inherent to

some biochars, dust exposure during handling, greenhouse gas emissions under certain soil conditions, and uncertainties regarding contaminant remobilization during aging.

For saturated biochar, desorption and leaching are critical risk parameters. The adsorption literature emphasizes that regeneration/desorption studies are relevant not only for process reuse but also for environmental risk screening, as they reveal the stability of sorbed contaminants and the likelihood of release under changing conditions. Repeated use or regeneration may also alter pore structure and functional groups, affecting both adsorption performance and downstream stability.

Long-term stability should be assessed using field-relevant evidence whenever possible. While many studies report positive effects of biochar on soil properties and plant performance, long-term outcomes vary with feedstock, pyrolysis conditions, soil type, and climate. Accordingly, post-use applications should be supported by site-specific risk assessment and monitoring protocols, particularly when contaminant-loaded materials are involved.

Field evidence shows that biochar stability is highly variable, ranging from substantial short-term losses to measurable persistence over a decade or more. This variability is not a minor methodological issue; it reflects real differences in feedstock properties, pyrolysis conditions, soil texture, climate, and landscape processes. As a result, field-scale persistence cannot be reliably inferred from laboratory incubation studies alone, and any assessment of long-term biochar behavior—particularly for post-use or contaminant-bearing biochars—must be site-specific and supported by monitoring.

The field literature clearly illustrates this divergence. In a subtropical field study in Florida over 15 months, biochar-C losses ranged from 17.5% to 93.3% yr<sup>-1</sup>, depending on feedstock and production temperature, with lower losses generally observed for chars produced at 650 °C (14.0% to 51.5% yr<sup>-1</sup>) [119]. By contrast, multi-year temperate field trials have shown both dissipation and persistence depending on soil type. In one German study, a sandy site lost most of the initial soil organic carbon (SOC) gain over nine years, whereas a loamy site retained elevated SOC after eleven years [120]. A 13-year UK field experiment likewise found that biochar-amended plots maintained higher organic C density than controls and exhibited only limited loss of chemical stability, supporting medium- to long-term persistence under those conditions [121]. Shorter-duration studies also show mixed outcomes: a four-year corn trial reported greater SOC decline with pine-chip biochar than with poultry-litter biochar. In contrast, a two-year vineyard study found no significant degradation but high variability among plots [120,122]. Taken together, these results indicate that persistence is strongly conditional and should not be generalized across sites or biochar types.

The main drivers of persistence are consistently linked to feedstock, pyrolysis temperature, soil type, and climate. Feedstock influences the elemental composition and the proportion of labile carbon, which, in turn, affects microbial accessibility and weathering behavior [120,122]. Pyrolysis temperature is also a strong determinant: higher-temperature chars (e.g., 650 °C) generally show lower short-term mineralization, which is commonly attributed to greater aromatic condensation and smaller labile carbon pools [119]. Soil texture modifies retention through physical protection, aggregation, and transport behavior, with loamy and clay-rich soils often showing better long-term SOC retention than coarse sandy soils where gains may dissipate more quickly [95,120]. Climate further shapes outcomes, as subtropical environments with higher temperatures and greater moisture variability have been associated with greater short-term losses than temperate systems, where longer persistence has been documented [119,121]. These drivers act in combination, which explains why field outcomes remain heterogeneous even when similar application rates are used.

An important implication of the field literature is that long-term biochar fate is not controlled only by mineralization. Physical migration and soil interactions can be equally important and may strongly influence apparent persistence. Studies using  $^{13}\text{C}$ -labeled biochar have shown that downward transport can be substantial in some soils within 12 months, with recovery of biochar-C below 30–50 cm varying by soil type and, in some cases, exceeding estimated mineralization losses [95]. This means that declines in topsoil biochar-C cannot automatically be interpreted as decomposition. Biochar also interacts with the surrounding soil environment (the “charosphere”), where it can alter microbial community composition, pH, and nutrient availability. In a 13-year field study, persistent shifts in bacterial and fungal communities were observed near biochar particles, together with elevated local pH and nitrogen availability, indicating that long-term biochar effects extend beyond carbon storage alone [121]. Conversely, some studies reporting SOC dissipation explicitly note uncertainty about whether observed losses reflected microbial breakdown or lateral/vertical movement of biochar particles, underscoring the need to separate transport from mineralization in monitoring designs [119,120].

These findings make a strong case for site-specific risk assessment and monitoring, especially where biochar is used in remediation or carries sorbed contaminants. The literature does not provide a single universal protocol, but it does identify the core elements of robust field monitoring programs. Field studies commonly include baseline soil characterization, depth-resolved measurements of pyrogenic carbon and total carbon, pH, extractable nitrogen, and indicators of soil structure such as aggregation and water-holding capacity, with repeated sampling over multi-year intervals [121,123]. Where physical migration is a concern, depth-resolved sampling to at least 30–50 cm—and in some cases deeper—is recommended, as substantial downward transport of biochar-C and associated constituents has been observed within months to 1 year [95,119]. For remediation applications or contaminant-bearing biochars, authors also recommend feedstock-specific selection and site-scale ecological risk assessment, with monitoring extended beyond soils to include contaminants in solid phases, porewater, and runoff compartments [119,124].

A further methodological point emphasized across studies is the need to distinguish true mineralization losses from physical redistribution. To achieve this, monitoring designs should combine complementary tools, including molecular markers (e.g., BPCA or SPAC/hydrolysis approaches), isotopic tracing, and mass-balance methods, so that fate pathways can be attributed with greater confidence [95,120,121]. Without this distinction, apparent declines in biochar-associated carbon may be misinterpreted, leading to incorrect conclusions about stability or risk.

Overall, the current evidence supports a precautionary, site-tailored approach rather than a standardized universal protocol. Based on the reviewed studies, the most defensible strategy is to develop monitoring programs that combine (i) baseline inventories of pyrogenic carbon and contaminants, (ii) periodic depth-resolved sampling for both carbon and contaminants, (iii) water and leachate monitoring where hydrologic connectivity is relevant, and (iv) multi-year follow-up to capture slow decomposition and transport processes [95,119,123,124].

## 7. Performance, Scale-Up, and Circular Sustainability

Performance evaluation in biochar-based treatment systems should extend beyond adsorption capacity and include reproducibility, environmental burdens, and deployment feasibility. This is especially important when biochar is intended for dual functionality, since the performance of the primary adsorption process and the safety/value of the post-use pathway are interdependent. A process-level framework is therefore more appropriate than a single-metric comparison.

### 7.1. Key Performance Indicators and Post-Use Functionality

A robust KPI framework for biochar-based systems should distinguish between intrinsic material properties, operational process performance, and post-use behavior. These tiers correspond to different decision points in process design: material KPIs support sorbent selection and modification, process KPIs support reactor and operating design, and post-use KPIs determine whether spent biochar can be safely reused or must be stabilized or disposed of. This distinction is especially important because the most commonly reported metrics are highly condition-dependent and therefore have limited value for cross-study comparison unless test conditions are standardized.

Intrinsic material properties define the mechanistic basis for contaminant uptake and therefore belong in the highest KPI tier. These indicators do not directly describe process performance, but they determine which removal mechanisms are likely to dominate and which application niches a given biochar is best suited for.

Surface area is one of the most frequently reported material metrics. It is generally associated with improved adsorption of hydrophobic organic contaminants because it increases the number of available sorption sites. In many studies, higher specific surface area is linked to higher pyrolysis temperatures and activation treatments, although the functional consequences depend on pore accessibility and chemistry [125,126]. Pore structure is equally important, since micropores tend to favor adsorption of small molecules, while meso- and macropores influence accessibility, diffusion, and transport. Feedstock and pyrolysis conditions strongly affect pore-size distribution, which in turn shapes contaminant selectivity [125,126].

Ash content is another key material KPI, particularly for metal removal. Elevated ash fractions may introduce reactive mineral phases that promote precipitation, complexation, or ion exchange and can therefore shift the dominant sorption mechanism from purely carbon-surface adsorption to mineral-assisted immobilization [127,128]. Similarly, bulk pH and point of zero charge (PZC) are critical descriptors because they control electrostatic attraction or repulsion for ionic species. Biochar performance is often strongly pH-dependent across the pH ranges commonly tested in adsorption studies, such as 3–9, and this behavior is directly tied to production conditions and surface chemistry [125,126]. Surface functional groups, especially oxygen-containing groups such as carboxyl and hydroxyl moieties, also play a central role by mediating polar adsorption, complexation, and ion exchange. Lower-temperature biochars typically retain more oxygenated functional groups, which may improve uptake of certain polar inorganic or organic contaminants [125,126].

Taken together, these material KPIs provide the mechanistic context for performance claims. However, they should not be interpreted as substitutes for operational testing, since favorable intrinsic properties do not guarantee performance under realistic process conditions.

Process KPIs describe how biochar performs under defined operating conditions and are the metrics most often used in adsorption studies to support claims of effectiveness. These indicators quantify uptake magnitude, uptake rate, and operational resilience during use and reuse, but they are highly sensitive to test setup and solution chemistry. For this reason, they are useful for process evaluation only when reported together with full experimental conditions.

Adsorption capacity from isotherm fits ( $\text{mg g}^{-1}$ ) remains the most common KPI. However, it is not an intrinsic material constant. Reported  $q_{\text{max}}$  values depend strongly on biochar type, pyrolysis or activation history and batch-test conditions such as pH, contaminant concentration range, and solid-to-liquid ratio [125]. As a result, adsorption capacity is most informative when used for comparison within a standardized test framework rather than across unrelated studies.

Adsorption rate, often represented by fitted kinetic constants or time-to-equilibrium, is similarly condition-dependent. Uptake rate is influenced by surface area, pore accessibility, particle size, and solution chemistry, and modeling studies identify adsorption time and specific surface area as strong predictors under controlled conditions. Reported rate constants can therefore only be meaningfully compared when contact time, mixing intensity, and particle-size distribution are similar [125,129].

Breakthrough behavior is a more relevant KPI for engineered systems, particularly continuous-flow applications. Metrics such as breakthrough time and mass-transfer-zone length in fixed-bed tests provide insight into service life and hydraulic performance, which batch isotherms cannot capture [130,131]. Particle size, porosity, flow rate, and sorption heterogeneity all affect breakthrough, making column data essential for scale-up and application-readiness claims [131].

Regeneration stability is another critical but underreported process KPI. Capacity retention after repeated cycles can vary substantially depending on the sorbate type, regeneration method, and biochar modification approach [129,132]. Because long-term operational viability depends on this stability, regeneration performance should be treated as a formal KPI and reported using a clearly defined and reproducible cycling protocol [129,132].

Overall, process KPIs are indispensable for evaluating application performance, but they must be interpreted as operational metrics rather than universal properties of a biochar material.

Post-use KPIs are essential for determining whether spent biochar represents a risk or a resource. These indicators address environmental fate, secondary-use potential, and durability after service, and they are especially important in sequential biochar systems where the adsorbent is intended for reuse in soil, composites, or other downstream applications.

Leaching resistance is one of the most important post-use KPIs because both sorbed contaminants and native biochar constituents may be released under environmental conditions. Leaching behavior depends on sorbate binding strength, matrix stability, and pH and should therefore be assessed using standardized leaching protocols under conditions relevant to the intended end use [129,133]. For spent biochar intended for land application, leaching resistance directly determines environmental safety; for engineered materials, it informs containment performance.

Soil response is another key post-use KPI when land reuse is considered. Relevant indicators include effects on soil carbon stability, nutrient cycling, and priming of native organic matter. These outcomes are particularly important for evaluating spent biochar in remediation and carbon sequestration contexts, where the post-use pathway must provide agronomic or ecological benefits without causing secondary contamination [129,133].

Composite compatibility becomes important when spent biochar is redirected into construction or polymer matrices. In these cases, performance depends on mechanical stability, surface chemistry, and the potential for leachate formation. Laboratory adsorption metrics do not predict composite behavior, so application-specific compatibility testing is required before industrial use can be justified [125,132].

Secondary-use durability is the final major post-use KPI. Whether the biochar is reused as a soil amendment or as a construction filler, long-term chemical and mechanical stability must be demonstrated, along with continued retention of any sequestered contaminants. Reviews consistently highlight the need for standardized long-term durability testing and note that evidence remains mixed across applications [129,132]. At present, the available literature does not provide a sufficient basis for universal numerical pass/fail thresholds for leaching across multiple environmental scenarios or for long-term durability benchmarks, so these criteria remain context-specific.

Although adsorption, percentage removal, and fitted kinetic constants are widely used because they are relatively easy to generate, they have limited comparability across studies. Experimental conditions strongly constrain their interpretation, and without standardized reporting they can be misleading in process design or meta-analysis.

The most important limitation is that adsorption is conditional, not intrinsic. Isotherm-derived capacities depend on the selected concentration range, solid-to-liquid ratio, pH, and biochar preparation history. They should therefore not be treated as fixed material constants unless testing protocols are standardized [125,130]. Removal efficiency is also concentration-dependent: very high percentage removal at low contaminant concentrations does not necessarily indicate high adsorption capacity or suitability for higher-load systems [125,130]. Kinetic parameters are similarly sensitive to setup. Reported rate constants reflect not only material properties but also particle size, mixing intensity, contact time, and solution chemistry. As a result, comparisons across studies are only valid when these conditions are matched [125,129]. Among the most influential variables, pH and solid-to-liquid ratio are particularly important because they affect contaminant speciation, electrostatic interactions, and the apparent driving force for adsorption in batch systems [129,130].

One area where the current evidence remains insufficient is ionic strength. The supplied literature does not provide enough direct and comparable evidence to quantify how ionic strength systematically alters reported KPIs across different biochar systems, so specific generalized claims on ionic-strength effects cannot be substantiated from these sources alone.

For practical reporting, the implication is clear: KPIs should always be presented alongside standardized test conditions, including pH, solid-to-liquid ratio, ionic composition, contact time, and particle size. In addition, claims of application readiness should include both batch and column metrics, since batch performance alone does not capture the transport and hydraulic limitations relevant to real process systems [129,130,132].

## 7.2. Experimental Limitations, Reproducibility, and Standardization

A major limitation in the literature is the lack of methodological standardization. Biochar properties vary widely with feedstock source, pretreatment, pyrolysis temperature, heating rate, and post-modification, while adsorption protocols often differ in matrix composition and operating conditions. As a result, published adsorption capacities may not be directly comparable, even when the same contaminant is studied.

Reproducibility is further weakened by the predominance of batch experiments using simplified synthetic solutions. Many studies do not include continuous-flow testing, competitive adsorption conditions, or realistic wastewater matrices, which are necessary for scale-up. In addition, uncertainty reporting (replicates, error bars, statistical tests) is often incomplete.

The reproducibility of biochar research begins with transparent reporting of feedstock and pyrolysis conditions because these factors largely determine the structural, chemical, and contaminant-related properties of the final material. For this reason, reports should provide enough detail to allow reconstruction of production conditions and meaningful grouping across studies. Without this information, differences in performance may be incorrectly attributed to “biochar effects” when they are in fact caused by unreported differences in raw materials or thermal processing.

At minimum, feedstock identity should be described clearly, including the species or common name, the biomass fraction used (e.g., wood chips, husks, manure), collection site or provenance, and any pretreatment steps such as drying, grinding, or sieving [128,134]. These details are not minor descriptors: feedstock composition directly influences elemental composition, ash content, and the potential introduction of contami-

nants into the biochar [128,134]. Reactor description is equally important. Authors should report the reactor type (e.g., laboratory muffle furnace, tube furnace, rotary kiln, pilot-scale unit), processing scale (batch size or throughput), and whether the system operated under open or closed conditions relative to air [128,134].

Temperature reporting should go beyond broad labels such as “low” or “high” pyrolysis. The full thermal history is needed, including the heating rate, peak temperature, the method of temperature measurement, and the residence time at peak temperature [128,134]. The gas atmosphere and purge conditions should also be specified, including gas composition (e.g., N<sub>2</sub>, CO<sub>2</sub>, steam, air), flow rates, and any pressure or vacuum conditions, along with the cooling procedure, because these factors affect oxidation, product yields, and final surface chemistry [128,135]. Finally, studies should report production yields and mass balance data, including feedstock mass, biochar mass, and, where possible, bio-oil and pyrolysis gas fractions, so that carbon accounting and process comparisons can be performed [128,134].

These reporting elements are consistent with current standardization and product-testing efforts and are essential for interpreting why biochars differ functionally across applications [128,134,135].

Physicochemical characterization links production conditions to biochar function, and consistent measurement/reporting is necessary for cross-study comparability. To support mechanistic interpretation, studies should report not only measured values but also the analytical methods and conditions used to obtain them.

Specific surface area (SSA) and porosity are foundational descriptors and should be reported with methodological detail, including the adsorption method used (e.g., BET), the adsorbate, degassing conditions, and measurement temperature [134]. Pore-size distribution should also be included, with separation of micro-, meso-, and macropore fractions and the computational method used (e.g., NLDFT or BJH), because pore architecture strongly affects sorption accessibility and contaminant selectivity [134].

Proximate analysis should include moisture, volatile matter, fixed carbon, and ash, with results expressed on a clearly defined basis (dry or wet) and with reference to analytical standards [128,134]. Ash content is particularly important because it strongly influences nutrient content, pH, and metal sorption behavior [128,134]. Elemental (ultimate) analysis should report C, H, N, and S, with oxygen determined directly or by difference and include elemental ratios such as H/C and O/C, which are widely used as indicators of aromaticity and potential aging behavior [127,134].

Surface charge characteristics also require careful reporting. Biochar pH should be measured at a specified solid-to-solution ratio and ionic strength, and the method used to determine the point of zero charge (PZC) should be described explicitly, since pH and PZC govern electrostatic interactions with ionic contaminants [127,134]. Surface functional groups and cation exchange capacity (CEC) should likewise be reported with method details (e.g., FTIR, Boehm titration, CEC protocol) so that reactive-site chemistry can be compared across studies [134,136].

For studies involving environmental reuse or risk assessment, contaminant screening is also essential. Targeted analyses for metals, PAHs, PCBs, and other priority contaminants should be included, together with analytical methods, limits of detection, and QA/QC information (e.g., blanks, standards, duplicates) [6,7]. These characterization practices are strongly supported by analytical handbooks and product-testing standards and are necessary for interpreting biochar behavior across treatments, soils, and materials [137].

Even well-characterized biochar cannot be meaningfully evaluated if the test matrix and statistical treatment are not transparently reported. Many biochar studies differ not only in the sorbent but also in the chemistry of the soil, water, or sludge being tested, and

these matrix effects can dominate observed performance. For this reason, reports must provide full matrix characterization and a clear description of experimental design and statistical analysis.

Matrix composition should be described in sufficient detail to explain likely interactions with biochar. This includes pH, organic matter or dissolved organic carbon, ionic strength, dominant ions or nutrients, redox conditions, and background contaminant concentrations [134,138]. These parameters shape sorption behavior in situ and can strongly affect both adsorption capacity and desorption risk. Experimental conditions must also be fully specified, including solid-to-liquid ratios, contact time, temperature, agitation, and equilibration procedures for batch tests, or hydraulic conditions for column tests, together with a rationale for the selected conditions [134,138]. This is necessary both for comparability and for assessing whether results are relevant to practical applications.

Replication and experimental structure should be reported explicitly. Authors should state the number and type of replicates (biological, technical, analytical), whether blocking or randomization was used, and whether repeated-measures designs were applied [135,138]. QA/QC outcomes for analytical methods should also be included. Statistical reporting should move beyond *p*-values and include the tests used, assumptions checked (e.g., normality, homoscedasticity), effect sizes, confidence intervals, and model-selection criteria, in line with repeated calls in the literature for stronger design and reporting in biochar studies [127,135].

The current literature emphasizes the importance of replication and controls but does not define a universal minimum replicate number suitable for all biochar experiments [127,135]. This is reasonable given the diversity of study designs and variance structures. In practice, what matters most is that authors justify their design choices and report them transparently.

Clear reporting of matrix chemistry and statistical methods is therefore not only a matter of rigor but a prerequisite for meta-analysis and for reducing ambiguity in the interpretation of heterogeneous results [127,135].

When biochar is intended for reuse, or when environmental risk assessment is part of the study objective, desorption, regeneration, and aging tests become critical. These tests determine whether functional performance persists over time and whether secondary emissions or contaminant release may occur. Existing standards and protocol papers provide useful templates, but they do not define a single universal procedure applicable to all biochar uses. This makes detailed reporting especially important.

For sorption–desorption studies, authors should report the sorbate(s) used, initial loadings, desorption solvent or regenerant composition, contact time, number of cycles, and performance metrics such as percent recovery and change in adsorption capacity [134,138]. Any thermal or chemical regeneration steps should be described in detail. Regeneration protocols should also specify regenerant concentration, temperature, mode of contact (batch or continuous), and post-regeneration conditioning steps such as rinsing and drying, since these parameters influence both recovery efficiency and structural degradation pathways [134,138].

Aging simulations require similar transparency. Accelerated aging protocols may include wet–dry cycling, freeze–thaw exposure, oxidative chemical aging, or microbial incubation, but the chosen method, exposure duration, and monitored endpoints must all be documented [134,136]. Relevant endpoints typically include changes in surface chemistry, SSA, CEC, and contaminant release because aging can substantially alter sorption performance and stability [134,136].

Leaching tests should follow standardized elution approaches where possible (batch leach tests or column leaching), with reporting of liquid-to-solid ratios, the number of sequential extractions, solution composition, and cumulative leachate concentration or mass-release profiles. As in other sections, QA/QC information and detection limits for

released contaminants should be included [137,138]. Importantly, performance should be reported as a function of time or cycle number (e.g., capacity after a number cycles, cumulative desorbed mass, changes in key surface indicators) rather than only as initial and final values, since time-resolved data are needed to assess degradation or stabilization trends [134,138].

Overall, standards and protocol papers support a common principle: even when a single universal method is not available, procedures and QA/QC must be reported in sufficient detail so that desorption, regeneration, and aging results can be reproduced and compared across studies [134,137,138].

Taken together, these issues show that the main bottlenecks in the field are not limited to material performance alone but also include inconsistent reporting, insufficient methodological standardization, and weak translation from laboratory screening to realistic operating conditions. For this reason, the limitations of the current evidence are summarized in this section and directly linked to future research priorities, rather than embedded solely in the concluding remarks.

Complete and standardized reporting of production conditions, characterization methods, matrix chemistry, replication, and aging protocols is the foundation of reproducible biochar science. Reviews and standards consistently note that without this information, apparent differences between studies may reflect unreported procedural variables rather than true differences in biochar properties or functions.

Detailed pyrolysis and physicochemical data enable mechanistic linkage between production conditions, structural/chemical features, and observed functions such as sorption, nutrient release, or agronomic effects [134,135]. In turn, full matrix and procedural reporting reduces confounding by clarifying whether performance differences are due to material properties or to differences in pH, ionic composition, reactor atmosphere, or other test conditions [127,128]. This is essential for meta-analysis and for building predictive models that can guide process design.

Standardized reporting also supports certification and regulatory assessment. Adherence to product definitions, contaminant screening requirements, and testing guidelines makes biochar data more interoperable and more useful for quality assurance and policy development [137,138]. At the same time, transparent reporting of replicate structure, QA/QC, and statistical treatment allows readers to assess uncertainty and heterogeneity across studies, which is critical for evidence synthesis and for translating research into practice [127,135].

Where the literature and standards prescribe established methods, those protocols should be followed, and any deviations should be clearly reported. Where universal numeric minima are not defined—for example, for replicate numbers, exact aging durations, or regeneration cycle counts—authors should justify their chosen parameters and provide enough methodological detail for others to reproduce or reanalyze the work [127,135,137]. In this sense, reporting is not a formal requirement at the margins of the study; it is part of the scientific result itself.

### *7.3. Industrial Feasibility and Deployment Constraints*

Industrial feasibility depends on more than adsorption performance. Scale-up requires a stable feedstock supply, process standardization, quality control, logistics optimization, and viable revenue models. The recent literature shows that biochar systems become more attractive when multiple value streams are combined (e.g., treatment services, biochar product sales, carbon-related value, and downstream valorization), rather than relying on a single use case.

Beyond feedstock cost, three economic barriers repeatedly limit the scale-up of modified biochar production: post-pyrolysis modification costs and chemical consumption; energy demand and process integration; and product inconsistency and weak market qualification. The structure–property–performance framework proposed in this review has a practical techno-economic role because it supports fit-for-purpose design rather than assuming that the most severe or expensive modification route is always necessary. This can reduce unnecessary chemical use, improve process selectivity, and integrate post-use routing early in development.

For saturated biochar specifically, feasibility improves when post-use routing is defined during process design. Systems that incorporate planned secondary pathways (soil amendment for eligible materials, construction integration for non-agronomic fractions) are generally more robust than systems that treat spent biochar as a disposal liability. This design principle is central to process intensification and circular manufacturing.

The industrial feasibility of biochar systems is determined by a broader set of techno-economic and life cycle variables than by adsorption performance alone. While sorption capacity, kinetics, and contaminant selectivity are important for technical screening, industrial decisions are often driven more strongly by market price, transport and preprocessing costs, coproduct valorization options, and plant-level energy balances. Empirical studies and case analyses consistently show that these factors can outweigh differences in adsorption metrics when evaluating commercial viability (Table 5).

This has an important implication for process design: biochar systems should not be optimized solely around contaminant uptake but around the full value chain, in which adsorption is one stage among several. In this wider perspective, economic and environmental performance depend on how the material is routed, upgraded, reused, or disposed of after service, as well as how coproducts and energy streams are integrated into the plant design [139,140].

A central feasibility strategy is to define post-use routing for saturated (spent) biochar at the design stage rather than treating it as an end-of-life problem. When downstream pathways are specified in advance—such as regeneration, soil amendment, construction integration, or energy recovery—packaging, handling, storage, and quality control can be built into the process flowsheet from the outset. This reduces uncertainty, supports regulatory compliance, and converts what would otherwise be a disposal cost into a planned value chain.

**Table 5.** Key techno-economic variables influencing the industrial feasibility of biochar-based systems.

Variable	Why It Matters	Evidence
Market price and selling price sensitivity	Sets revenue and determines payback and NPV for plant scales	TEA shows minimum selling price and sensitivity drive payback and probability of positive NPV in slurry fuel scenarios [141].
Logistics and pelletizing costs	High bulk and transport costs can dominate unit costs and GHG footprints	LCA/TEA for forest-residue biochar found logistics and pelletizing materially change MSP and global warming impacts [139].
Coproduct valorization and by-product recovery	Revenues from condensates, syngas, or activated fractions improve plant profitability	An industrial pyrolysis plant recovered condensates and used syngas for heat; converting some biochar to activated carbon increased overall profitability by >3× in value terms [140].
Energy integration and onsite use	Displaces fossil fuel input, lowers operating cost, and creates surplus energy or heat	A farm-scale closed-loop pyrolysis system met milling energy needs and could export electricity or reduce onsite fuel use [142].

The literature suggests that this design choice also changes how value is captured. A service-oriented model, in which biochar is treated as a carrier of staged environmental

and material services rather than a one-time product sale, can improve competitiveness by enabling sequential uses and multiple points of value recovery [141]. In practical terms, the same biochar stream may first deliver adsorption performance, then enter a secondary use pathway that generates additional revenue or offsets another process cost.

Post-use routing can also be integrated directly into process design through planned upgrading. For example, some flowsheets allocate a fraction of biochar production to activation or advanced carbon processing, thereby converting part of the output into higher-value activated carbon and improving overall plant margins [140]. Similarly, when agronomic routing is intended, decisions such as pelletizing, packaging, and field-application logistics should be included during process design because they affect both minimum selling price (MSP) and life cycle emissions [139]. Defining these routes early allows designers to optimize trade-offs between cost, emissions, and operational practicality rather than treating them as downstream constraints.

Systems that include planned secondary pathways for spent biochar are generally more robust than systems that treat spent material as a liability. This robustness arises from several mechanisms identified in case studies and conceptual frameworks, including revenue diversification, reduced disposal exposure, and improved integration with local resource needs.

One of the clearest benefits is diversified revenue. Coproducts and secondary uses reduce dependence on a single market, which can stabilize returns in fluctuating commodity or treatment–service environments. Industrial examples show that valorizing condensates, activated carbon fractions, and other secondary outputs can materially improve the resilience of a biochar plant’s business model [140]. This diversification is especially important for biochar systems, where primary product markets may still be developing and price volatility can be high.

Closed-loop and farm-integrated systems provide another illustration of robustness. Studies show that coupling pyrolysis with on-farm energy needs and soil-amendment use can produce both net income and energy self-sufficiency, reducing exposure to external fuel and input markets [142]. In these systems, biochar is not simply sold into a distant market but retained within a local loop, where it contributes to both agronomic function and process economics.

The same principle is formalized in sequential biochar systems, which explicitly rely on recycling and reuse across multiple sectors (e.g., adsorption, soil use, construction integration) to mobilize multifunctional services and improve value capture [141]. By spreading value across sequential applications, these systems improve price formation and reduce disposal costs, thereby lowering life cycle risk. Reuse pathways may also reduce logistics burdens and landfill liabilities that would otherwise increase MSP and worsen the system’s GHG profile [139].

Embedding post-use routing and secondary pathways is not only an economic strategy; it is also a process-intensification principle. In integrated biochar systems, by-products, energy streams, and secondary uses are designed to reinforce one another, allowing material and energy flows to be internalized rather than lost. This increases the plant’s functional output and strengthens circular manufacturing performance.

Energy integration is a strong example. Industrial plant studies show that syngas and condensates generated during pyrolysis can be reused to supply reactor heat or support activation steps, reducing dependence on external fuels while enabling the production of higher-value activated carbon [140]. In such systems, what would otherwise be considered process by-products become enabling streams that improve both energy efficiency and product value.

Circular resource flows extend this logic beyond the plant boundary. When biochar is intentionally routed into soil amendment, construction materials, or catalyst-support pathways, material loops are closed and new service chains can be monetized across multiple sectors [141,142]. This creates a more resilient and circular manufacturing model in which environmental services, materials performance, and carbon management are integrated into a single process architecture.

Life cycle optimization and coproduct recovery frameworks further support this approach by demonstrating that designing for downstream uses and coproduct capture improves environmental and economic outcomes across the value chain [139,143].

Overall, the literature supports a shift away from single-use, sorption-centered biochar systems toward integrated process designs that specify post-use routing and sequential reuse pathways from the outset. This shift improves industrial feasibility by enabling process intensification, diversifying revenue streams, lowering life cycle costs, and reducing disposal and compliance risk [139–143]. In practice, this means that the most viable biochar systems are likely to be those that combine adsorption performance with planned downstream valorization, energy integration, and circular manufacturing logic rather than treating spent biochar as an afterthought.

#### *7.4. Circular Economy Integration and Sequential Use Design*

Biochar systems are well-suited to circular economy integration because they can connect biomass waste valorization, pollutant removal, nutrient retention, soil remediation, and materials reuse within a single process chain. The circular perspective is strengthened when post-use biochar is kept in productive use rather than landfilled or incinerated.

Biochar's core engineered role in the chain is to capture pollutants from water, gas, or soil via sorption mechanisms; this links waste feedstocks to immediate remediation outcomes. The adsorption capacity depends on surface area, pore structure, surface chemistry, and charge, all of which are tunable through feedstock selection and pyrolysis conditions.

At the core of most biochar process chains is its primary function as an adsorbent. This function is rooted in a combination of physicochemical properties, including high specific surface area, a broad pore-size distribution, reactive surface functional groups, and, in many cases, a net negative surface charge. Together, these features support the adsorption of both organic and inorganic contaminants, which explains why biochar has been widely investigated as a low-cost sorbent for environmental applications [144]. The literature shows that biochar can remove a broad range of pollutants, including emerging contaminants, metals, and other organic compounds, and in some settings it can provide a lower-cost alternative to activated carbon, particularly when performance requirements are moderate and low-cost feedstocks are available [144].

This adsorption role is not only theoretical but has been demonstrated in applied remediation contexts. For example, wood-waste-derived biochar has been evaluated for soils contaminated with polycyclic aromatic hydrocarbons (PAHs) and metal(loid)s, with studies assessing both remediation performance and associated environmental impacts [145]. Such case studies are important because they show how biochar functions under realistic conditions rather than only in simplified laboratory systems. They also reinforce a key implication of process design: biochar performance is highly tunable. Feedstock choice and pyrolysis temperature strongly influence sorption properties and therefore represent primary control points in the process chain when designing materials for specific contaminant targets [144].

In many systems, biochar's role extends beyond adsorption. A second major pathway is its use as a soil amendment, where it contributes to agronomic performance, soil remediation, and carbon sequestration. This secondary function is particularly relevant in

circular-process frameworks because it links pollutant removal and nutrient management to longer-term ecosystem services.

The literature shows that biochar applied to soils can improve nutrient retention, support crop productivity, and, in some cases, reduce soil N<sub>2</sub>O emissions, thereby providing multiple benefits beyond contaminant management [146]. In contaminated soils, biochar can also immobilize metals and hydrophobic organics, reducing their bioavailability and limiting exposure pathways, as documented in remediation-focused assessments [145]. These remediation and agronomic functions often operate simultaneously, which makes soil application one of the most attractive post-use pathways for eligible biochars.

Biochar's stable carbon fraction also contributes directly to the climate mitigation potential of soil use, although the net outcome depends on feedstock type, conversion process, and site conditions [146–148]. In this sense, soil application is not only a disposal or reuse step but an integrated function that combines nutrient retention, contaminant immobilization, and carbon management. Practical implementation, however, depends on logistics and material handling. Studies show that form-factor decisions, such as pelletizing, can improve transport and field application efficiency but may also introduce additional processing emissions; for example, pelletizing reduced outbound logistics emissions in one system while increasing processing emissions [147]. This highlights an important design principle: the soil amendment pathway should be tailored not only to char chemistry but also to soil type, contaminant profile, agronomic goals, and deployment logistics in order to maximize co-benefits without eroding climate gains [146,148].

Where land application is unsuitable or risk-prone, an alternative circular route is to integrate biochar into construction materials. In this pathway, biochar can serve as a material additive while also providing contaminant containment and partial substitution for more carbon-intensive inputs. This extends the useful life of biochar within engineered systems and can strengthen circularity by linking remediation and materials manufacturing.

Studies report promising results when biochar is incorporated into cementitious matrices, including favorable mechanical and adsorption-related properties that support potential structural or functional applications [149]. These findings suggest that biochar-containing materials may serve not only as fillers but also as active components influencing moisture behavior, contaminant retention, or other properties. Sludge- and residue-derived biochars have also been proposed for concrete applications, with integrated life cycle and socio-economic assessments supporting the feasibility of such circular reuse pathways [150].

At the same time, this route involves important trade-offs. Even relatively low biochar additions (e.g., 5–15% *v/v*) can alter material behavior, indicating that performance cannot be assumed based on biochar properties alone [151]. Mechanical durability, long-term stability, and matrix compatibility must all be verified, and environmental benefits should be confirmed through LCA to ensure they are not offset by upstream burdens or reduced product lifespan [151]. From a process-design perspective, construction integration is particularly attractive because it can simultaneously sequester contaminants and fixed carbon in a durable product stream, diverting biochar from direct land application where risks may be higher. However, this pathway requires standardized testing for leachability and long-term stability within the target matrix before it can be considered robust at scale [149–151].

A circular biochar framework is only credible if the proposed pathways are validated at the system level. This requires integrating life cycle assessment (LCA), carbon footprint analysis, techno-economic assessment (TEA), and risk evaluation to compare alternatives such as soil amendment versus material reuse. The available literature shows that feedstock, conversion technology, logistics, and coproduct recovery strongly shape environmental outcomes, making system-level validation essential rather than optional.

Comparative LCA studies clearly illustrate this variability. In one case study, cradle-to-field global warming impacts for biochar systems were estimated at approximately 306–444 kg CO<sub>2</sub>-eq per ton of biochar applied for one portable slow-pyrolysis configuration, compared with 750–1016 kg CO<sub>2</sub>-eq per ton for an alternative system, showing how process design and logistics can significantly alter environmental performance [4]. Modeling studies of distributed co-production systems further suggest that favorable slow-pyrolysis scenarios can achieve net GHG mitigation of up to about 1.4 Mg CO<sub>2</sub>-eq per Mg feedstock when feedstock selection, energy recovery, and biochar stability are optimized [146].

Regional LCA and TEA studies reinforce the importance of feedstock and process optimization. Using residues instead of purpose-grown biomass, and prioritizing pyrolysis conditions that favor char stability rather than maximum energy recovery, have both been identified as strategies that improve sequestration outcomes and overall climate performance [148,152]. For this reason, several authors recommend combining LCA with TEA and site-specific agronomic or materials testing to evaluate circular benefits across environmental, economic, and technical dimensions rather than infer them from a single metric [144,147,152].

Risk assessment remains the least standardized component of this validation framework. Environmental assessments have been conducted for specific contaminants and case-study contexts [145]. Still, the supplied literature does not provide a harmonized, cross-sector protocol for long-term leaching, human exposure, or durability in materials applications. As a result, while risk evaluation is clearly necessary, standardized risk frameworks remain insufficiently developed in the current evidence base.

Taken together, the literature supports a coherent four-node process framework for circular biochar systems. In this framework, waste biomass is first thermochemically converted into a tailored biochar, which is then deployed as an adsorbent for pollutant removal or immobilization [144,145]. After this primary function, the biochar can follow one of two major secondary pathways: it can be applied to soils to deliver nutrient retention, soil remediation, and carbon sequestration services, or it can be embedded in construction materials to support reuse and long-term containment [145–147,149–151]. Across both routes, system-level environmental and economic performance must be validated through LCA, TEA, and context-specific risk assessment to ensure that circularity claims are supported by measurable outcomes [144,146,147,150,152].

### 7.5. Life Cycle Assessment and Carbon Accounting

Life cycle assessment (LCA) attributes the net environmental benefit of biochar systems to the overall balance of emissions avoided, emissions generated, and carbon stored across the full process chain, rather than to biochar carbon stability alone. In this framework, climate performance is a system outcome shaped by feedstock sourcing, thermochemical conversion, coproduct handling, soil processes, and post-use management. For LCA results to be interpretable, studies must define a clear functional unit and apply explicit allocation rules for coproducts and shared process burdens. The literature also shows that robust LCA practice requires uncertainty analysis—typically through sensitivity and Monte Carlo methods—because single-point estimates often obscure the high variability associated with soil responses, coproduct fate, and permanence assumptions [153,154].

To improve comparability and reproducibility, future life cycle assessments of agricultural-waste-derived biochar should be conducted in alignment with the principles and requirements of ISO 14040 [155] and ISO 14044 [156], which define the four core stages of LCA: goal and scope definition, life cycle inventory analysis, life cycle impact as-

assessment, and interpretation. In the context of biochar-based materials, no single boundary is universally best because the preferred scope depends on the question being asked.

Claims regarding the sustainability of biochar-based materials depend strongly on the selected system boundaries and should therefore be interpreted with caution [157]. At a minimum, LCA studies should specify whether the analysis is conducted on a cradle-to-gate, cradle-to-use, or cradle-to-grave basis. Carbon accounting also requires careful boundary selection, because the final balance depends on feedstock collection and pre-processing, direct process emissions, the fraction of carbon retained in the biochar, the long-term stability of that carbon in the intended application, regeneration demand, and end-of-life emissions or sequestration outcomes. Generalized claims that all agricultural-waste-derived biochars are inherently carbon-negative or environmentally superior remain insufficiently supported unless these assumptions are made explicit.

The functional unit is one of the most consequential methodological choices. LCA results can differ substantially depending on whether impacts are normalized per ton of feedstock processed, per ton of biochar produced or applied, or per hectare treated, because coproduct credits and soil effects scale differently across these units [153,154]. Likewise, coproduct accounting can significantly alter outcomes. Credits assigned to recovered heat, electricity, or bio-oil may shift a biochar system from net emitter to net sink, particularly when bio-oil is sequestered or when process heat displaces fossil-derived energy [153,154]. Soil emissions and permanence assumptions are equally important. A large share of reported GHG mitigation in process-level LCAs is commonly attributed to the stable carbon retained in biochar—often 60–66%—which means the remaining balance depends on process emissions and coproduct treatment [154]. As a result, assumptions about the longevity of biochar carbon in soil are not secondary details; they are central determinants of net benefit.

The LCA literature consistently shows that feedstock type and conversion technology produce systematic differences in environmental performance. In general, woody and other waste-residue feedstocks tend to show higher carbon sequestration potential and more favorable GHG balances than manure- or sewage-derived feedstocks, which may carry additional contaminant risks or lower stable-carbon yields [158–160]. This feedstock effect is not simply a question of carbon content; it reflects differences in ash composition, moisture, nutrient content, and downstream environmental burdens, all of which influence both biochar quality and life cycle impacts.

Among feedstocks, woody waste and waste wood are frequently ranked as the most favorable in climate terms, with strong sequestration potential and relatively low burdens in many LCA scenarios [158]. Crop residues such as straw and stover often provide moderate sequestration performance and can still produce net-negative GHG outcomes, especially when avoided residue-management emissions are credited [154]. By contrast, manure and sewage sludge biochars generally rank lower in sequestration and may entail greater trade-offs related to nutrient loading, contaminants, or ecotoxicity [158]. Energy crops such as switchgrass show more variable outcomes, ranging from climate benefit to net emissions, depending on land-use assumptions and system boundaries [154].

Technology configuration introduces a second layer of variability. Pyrolysis temperature, energy integration, and plant design affect product yields, external energy demand, and emissions intensity. LCAs indicate that optimized pyrolysis systems, especially those that recover heat or generate electricity while minimizing external fuel use, improve climate performance. In contrast, energy-intensive activation or fossil-powered operation (e.g., diesel-based systems) can degrade it [159,161]. Scale and decentralization also matter. Portable or near-feedstock systems can reduce transport emissions substantially, and several studies show that this can improve global warming potential (GWP) relative to cen-

tralized systems that require long-distance biomass hauling [161]. In broader sustainability assessments, wood- and willow-based systems also tend to outperform manure-based systems across multiple impact categories, partly because they enable avoided fertilizer credits and carry lower contaminant-related risks [158,160].

System boundary definition is one of the strongest determinants of whether a biochar pathway appears climate-neutral, net-negative, or net-positive in emissions. Boundary choices such as cradle-to-gate versus cradle-to-grave accounting, inclusion of coproduct sequestration, and treatment of displaced energy or fertilizers can materially change the result. This is especially important in circular-process designs, where biochar may be integrated with digestate management, bio-oil sequestration, or cascading uses that extend the functional life of the biomass-derived carbon [153,162,163].

LCA studies provide clear examples of boundary sensitivity. Including bio-oil sequestration alongside soil application can substantially increase negative emissions compared with a soil-only system, while assigning credits for displaced fossil electricity from pyrolysis heat yields larger offsets when the marginal electricity mix remains carbon-intensive [153,162]. These examples show that boundary choices are not only methodological preferences; they directly shape the magnitude and direction of reported mitigation.

At regional scales, prospective LCAs suggest that biochar deployment can offset a meaningful share of emissions in some sectors. Still, the achievable contribution depends on locally available residues, competing biomass uses, and land capacity for application [153,154,163]. Studies from national and provincial contexts illustrate this point by showing that biochar potential is highly region-specific and linked to resource availability and infrastructure [153,154,163]. Circularity further modifies outcomes. Cascading uses—such as using biochar first in animal feed or manure systems and then applying it to soil—may increase net mitigation compared with direct soil application, although these effects remain pathway- and region-dependent [153,162]. When biochar is co-generated with bioenergy and applied in systems that reduce fertilizer demand or lower soil-borne GHG emissions, LCAs report combined benefits from carbon storage and emission reductions, supporting carbon-efficient resource circulation in bioenergy and biosolids systems [154,163].

Several recurring uncertainties in LCA significantly influence conclusions about biochar performance, and in many cases, these uncertainties are comparable to or exceed the average reported effect sizes. The most influential factors include transport distance, the energy source used for pyrolysis or activation, assumptions about carbon permanence, and the fate or stability of contaminants associated with the biochar. Because these parameters strongly affect results, they should be treated explicitly through scenario and uncertainty analysis rather than embedded as fixed assumptions [153,154,159].

Transport distance is repeatedly identified as a major sensitivity parameter. Longer hauling distances can significantly erode GHG benefits and, in some systems, may negate them entirely, which is why distributed or near-feedstock production often performs better than centralized processing in LCAs [154,161]. The energy source for pyrolysis or activation is similarly important. Switching from diesel-based power to gasifier-based or integrated onsite bioenergy systems has been reported to reduce global warming impacts by large margins, with improvements of roughly 60–70% in some portable-system case studies [161]. These examples illustrate how infrastructure choices can dominate the climate signal of the biochar pathway.

Carbon permanence remains one of the most consequential uncertainties because a large portion of mitigation is usually credited to stable biochar carbon. Different assumptions about decay rates, persistence horizons, or long-term soil stability can materially alter the GHG balance, and LCAs commonly address this through scenario analysis or

probabilistic treatment, as permanence cannot be directly verified in short-duration experiments [153,154]. In parallel, contaminant stability and post-use risk remain weakly resolved in much of the LCA literature. Some studies report ecotoxicity trade-offs associated with certain feedstocks, but robust, generalizable evidence on the long-term stability of adsorbed contaminants after field use—or after repeated reuse cycles—is still limited [153,158]. This means that LCA-based conclusions about contaminant-bearing biochars should be interpreted cautiously and supplemented with direct risk and leaching evidence.

End-of-life routing introduces an additional trade-off. Many LCA scenarios show that beneficial reuse—especially soil application or cascading reuse pathways—delivers the strongest carbon sequestration and co-benefits. In contrast, energy-intensive regeneration or disposal can reduce net climate gains [154,160,162]. However, direct comparative LCAs that systematically evaluate regeneration versus repeated reuse across different feedstocks and contaminant states remain sparse. As a result, broad generalizations about the superiority of one post-use pathway over another are not yet well supported across all contexts [154,160,162].

### Carbon Accounting Detail

Carbon footprint should be treated as a pathway-dependent metric rather than an inherent advantage of all biochar applications. The net carbon benefit of a biochar route depends on feedstock logistics, energy demand for conversion and activation, transport, and downstream use. In dual-function systems, post-use valorization can improve the carbon balance by avoiding disposal, offsetting the use of conventional materials, or reducing fertilizer demand.

A credible assessment of biochar's climate benefit must begin at the feedstock stage because feedstock sourcing and preprocessing determine the upstream emissions burden, the opportunity cost of biomass use, and the feedstock-specific potential for carbon stabilization. In practice, this means that claims about sequestration cannot rest solely on the recalcitrance of the final biochar; they must be constrained by the emissions and resource choices embedded in collection, transport, and preparation.

Pretreatment operations such as chipping, drying, and size reduction are often treated as secondary process steps, but life cycle studies show they generate measurable, nontrivial CO<sub>2</sub>-equivalent emissions. In cradle-to-gate assessments, these pretreatment emissions reduced the net sequestration benefit in wood-waste-based systems, demonstrating that upstream handling can materially affect the final climate balance [164]. Feedstock identity is equally important. Reviews comparing multiple biomass sources show that waste wood, crop straw, manure, and sludge differ in their physicochemical properties, and these differences propagate through biochar quality and life cycle GHG performance, leading to different sequestration rankings [153].

This is why supply chain integration is essential for LCA and carbon accounting. Studies that include transport, collection logistics, and broader supply-chain processes show that these factors can significantly change the magnitude of net emissions attributed to biochar projects and in some cases may even alter the direction of the result [160]. As a result, feedstock-stage accounting is not simply a preliminary calculation; it sets the boundary conditions for any defensible sequestration claim.

The conversion stage is the core of biochar production, but its climate performance depends strongly on the chosen technology, operating conditions, and coproduct management. Accounting at this stage must therefore go beyond reporting biochar yield and include the amount of carbon stabilized, the amount emitted, and how energy and coproduct streams are handled.

Comparative modeling across slow pyrolysis, fast pyrolysis, and gasification shows that mitigation outcomes vary with process configuration and temperature and that even

favorable slow-pyrolysis pathways deliver substantial climate benefit only when feedstock selection and energy coproduct recovery are also optimized [146]. This finding is important because it shows that conversion technology cannot be evaluated independently of the wider process system.

Life cycle results also indicate that stable carbon in biochar is often the largest contributor to climate benefit, but not the only one. In one study, stable carbon accounted for approximately 62–66% of the total GHG reduction, with the remaining share determined by process emissions and coproduct accounting [165].

The importance of correct coproduct allocation is further illustrated by cases where biochar production is embedded in bioenergy systems. Under certain renewable biomass assumptions, misallocation of bioenergy substitution credits or increased fuel use can cause the overall system to emit higher rather than lower emissions [166]. In other words, the same thermochemical pathway can appear beneficial or harmful depending on how the system boundary and coproduct credits are handled. This reinforces the need for explicit and transparent conversion-stage accounting.

The climate performance of biochar is ultimately realized during use, particularly when applied to soils. At this stage, net outcomes depend not only on carbon stability but also on ecosystem responses, including greenhouse gas fluxes, crop effects, and interactions with native soil organic matter. These effects must be measured or modeled directly; they cannot be inferred solely from biochar persistence.

LCA studies that incorporate soil processes show that use-phase responses can materially alter net-negative-emission estimates. Depending on the context, biochar application may yield co-benefits, such as reduced N<sub>2</sub>O emissions or improved crop yields. Still, it may introduce trade-offs by altering other emissions or ecosystem processes [160]. This variability means that the use phase is not a passive storage stage but an active determinant of climate performance.

A key implication is that biochar stability does not automatically translate into net sequestration. Biochar-induced changes in soil function, such as priming of native soil organic matter or altered nitrogen cycling, can alter the overall carbon and GHG balance at the application site [146,153]. For this reason, robust carbon accounting should combine empirical or modeled soil GHG responses with life cycle emissions rather than assuming that the inert fraction of biochar is fully and uniformly permanent [146,160]. This integrated approach provides a more realistic estimate of climate benefits and avoids overestimating negative emissions based solely on recalcitrance.

Post-use management is the final stage that determines whether carbon benefits are retained, extended, or partially lost. Whether biochar is reused, regenerated, encapsulated, or disposed of, its ultimate fate affects its permanence and must therefore be explicitly tracked in climate accounting. Ignoring this stage risks overstating sequestration by assuming indefinite stability without evidence of actual end-of-life handling.

Methodological guidance on biochar crediting emphasizes the need for realistic baselines, including comparisons with biomass decomposition pathways, and for explicit treatment of permanence, leakage, and reuse when defining credible crediting periods [166]. This is especially relevant for sequential systems in which biochar may move through multiple applications before final disposal or stabilization. Management choices such as reuse, encapsulation in materials, or long-term storage—including alternative sequestration of pyrolysis coproducts—can substantially alter the final residence time of carbon and therefore the net climate benefit [160].

Sustainability governance is also part of post-use accounting. Certification systems and life cycle safeguards across production, application, and disposal stages have been proposed to reduce environmental risks that might otherwise undermine sequestration

claims [159]. In this sense, post-use management is not only a technical issue but also a governance requirement for credible climate reporting.

A four-stage framework—covering feedstock collection and preprocessing, thermochemical conversion, use-phase performance, and post-use management—prevents overstatement by closing the system boundary around all major sources of emissions, credits, and uncertainty. Counting only the stable carbon fraction in biochar risks overcrediting by ignoring upstream emissions, conversion trade-offs, soil-process effects, and end-of-life fate.

LCA evidence shows that stable carbon often accounts for the majority of GHG reductions, but not all of them. The remaining balance comes from other stages of the system and can significantly erode net gains if omitted [165]. Likewise, conversion technology, coproduct allocation, and feedstock sourcing can change the climate outcome of the same biomass pathway from beneficial to neutral or even net positive in emissions, demonstrating that persistence alone is insufficient evidence of mitigation [146,166].

Studies that combine supply-chain accounting with measured or modeled soil effects provide more robust estimates of negative emissions and reveal trade-offs that a stability-only metric would miss [153,160]. The literature also offers methodological safeguards, such as explicit baselines, leakage rules, permanence treatment, and post-use tracking, that can be applied to avoid overcrediting based solely on biochar recalcitrance [159,166].

## 8. Conclusions, Limitations, and Future Developments

Agricultural-waste-derived biochar has evolved from a low-value thermochemical by-product into a versatile platform for the design of functional carbon materials. Across the literature reviewed, performance depends on a linked chain of factors: feedstock composition, pyrolysis severity, activation or functionalization route, resulting pore architecture and surface chemistry, and the requirements of the intended application. Regeneration, post-use valorization, durability, and systems-level sustainability should be considered as integral parts of material design rather than as downstream afterthoughts.

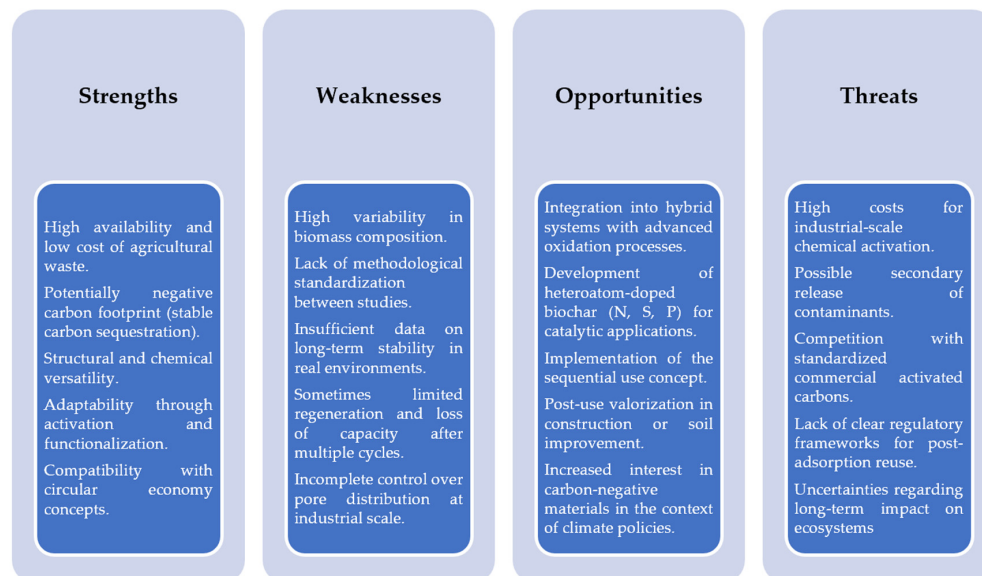
Agricultural waste is a strategic raw material for obtaining biochar, and its lignocellulosic composition directly determines the yield and properties of the final material. The parameters of the conversion process, particularly temperature and residence time, control the degree of aromatization, the development of porosity, and the surface chemistry.

Activation and functionalization strategies transform biochar into an adaptable material platform capable of achieving specific surface areas  $> 500 \text{ m}^2/\text{g}$  and adsorption capacities comparable to commercial materials. The integration of metal nanoparticles or photocatalytic phases extends applications to redox processes and advanced contaminant degradation. However, high performance under laboratory conditions does not automatically guarantee industrial scalability. Raw material variability, lack of standardization, and insufficient life cycle studies remain major challenges. The concept of sequential use and post-use recovery offers a promising direction for integrating biochar into circular resource and carbon management models.

The topic limitations are presented in Figure 4 as a SWOT analysis.

The advantages highlight the material's benefits, including the high availability of residual biomass, its carbon sequestration potential, and its structural versatility achieved through activation and functionalization. The disadvantages highlight current technical limitations, including variability in raw materials, a lack of standardization, and uncertainties about long-term stability. The opportunities are seen as potential for integration into circular economy models, the development of hybrid materials, and growing interest in carbon-negative solutions. The risks considered include the challenges posed by industrial costs, regulations, and competition with established commercial materials. The figure provides an integrated strategic perspective on the positioning of modified biochar between

fundamental research and industrial implementation. The identified guiding lines could be addressed in the future priority research areas that may target development of standardized characterization protocols, advanced kinetic modeling for process optimization, long-term studies on stability and ecotoxicological safety, or the development of scalable processes with low energy consumption.



**Figure 4.** Analysis of the development of biochar-based supermaterials for applications in water treatment and the circular economy.

**Author Contributions:** Conceptualization, F.-D.M.; methodology F.-D.M. and S.G.; writing—original draft preparation, S.G., B.-D.C. and F.-D.M.; writing—review and editing, F.-D.M. and S.G.; supervision, F.-D.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing does not apply to this article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

BET	Brunauer–Emmett–Teller
CEC	cation exchange capacity
CO <sub>2</sub> -eq	carbon dioxide equivalent
DTPA	diethylenetriaminepentaacetic acid
GHG	greenhouse gas(es)
KPI	key performance indicator(s)
LCA	life cycle assessment
MSP	minimum selling price
PAH(s)	polycyclic aromatic hydrocarbon(s)
PFAS	per- and polyfluoroalkyl substances
PZC	point of zero charge
QA/QC	quality assurance/quality control
ROS	reactive oxygen species

SEM	scanning electron microscopy
SOC	soil organic carbon
SSA	specific surface area
TEA	techno-economic assessment
TEM	transmission electron microscopy
XPS	X-ray photoelectron spectroscopy

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