



Review



# Engineered Biochar for Tetracycline Removal under Realistic Water Matrices: Structure–Performance–Deployment Framework

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**Abstract:** The widespread presence of tetracycline (TC) in aquatic environments poses serious risks to ecosystems and public health due to its persistence and role in promoting antimicrobial resistance. Engineered biochar has become a promising and sustainable material for removing TC because of its adjustable physicochemical properties, low cost, and multiple interaction mechanisms. This review examines the current state of biochar-based TC removal through a structure–performance–application framework that integrates material design, mechanistic insights, and real-world applications. The analysis shows that choices of feedstock, pyrolysis conditions, and modification methods—such as chemical activation, doping with heteroatoms, and metal impregnation—shape the structural features that influence adsorption and catalytic breakdown through mechanisms like pore filling,  $\pi$ – $\pi$  interactions, hydrogen bonding, electrostatic attraction, and metal–ligand complexation. Although engineered biochars can achieve exceptionally high adsorption capacities (occasionally exceeding 1000 mg/g) under optimized laboratory conditions, most reported values fall within a broader range depending on feedstock, modification, and experimental conditions. However, their effectiveness can vary significantly in real water systems, where factors such as pH, ionic strength, natural organic matter, and other contaminants introduce competitive and inhibitory effects. Additionally, issues related to regeneration, stability, and declining performance pose major challenges for long-term use. Our review also highlights the huge gap between laboratory research and real-world implementation, stressing the importance of standardized testing, pilot-scale trials, and integration into continuous treatment systems. By linking material structure to function and operational practicality, our work offers a comprehensive guide for designing and scaling up engineered biochar technologies to effectively remove tetracycline from complex aquatic environments.

**Keywords:** engineered biochar; tetracycline removal; adsorption mechanisms; catalytic degradation; regeneration and reuse

## 1. Introduction

The widespread occurrence of antibiotics in aquatic environments has become a major environmental and public health issue, driven by extensive pharmaceutical use in human medicine, livestock, and aquaculture [1–3]. Among these pollutants, tetracycline (TC) is one of the most commonly found compounds in surface water, groundwater, and wastewater, often at levels from nanograms to micrograms per liter [4–7]. Its persistence mainly results from incomplete metabolism in humans and animals, with large amounts excreted unchanged into the



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environment, where it remains biologically active for long periods [1,6,8]. The environmental impact is significant, TC disturbs microbial communities, influences ecosystem functions, and encourages the spread of antibiotic resistance genes through ongoing selective pressure [9–11]. Additionally, its ability to move across environmental compartments, aided by interactions with natural organic matter and coexisting ions, enables it to extend beyond discharge points into sensitive ecosystems [12,13]. These combined traits make TC both a persistent pollutant and an important factor in the global antimicrobial resistance crisis, highlighting the need for effective and sustainable removal methods.

Conventional wastewater treatment technologies have shown limited success in removing tetracycline because of its complex chemical structure, high solubility, and resistance to biodegradation [6,10]. Biological treatment processes often do not achieve complete removal, while physicochemical methods such as coagulation and filtration perform inconsistently, especially under different environmental [14–17]. Advanced oxidation processes can improve degradation; however, their effectiveness is often limited by high costs, energy needs, and sensitivity to substances like chloride ions and natural organic matter, which can consume reactive species and decrease degradation efficiency [18,19]. Additionally, these methods may produce transformation products that are as toxic as or more toxic than the original compound, complicating risk assessments and treatment results [20]. These limitations emphasize the need for alternative treatment approaches that are not only effective but also affordable and resilient in real-world environmental conditions.

In this context, biochar has become a promising adsorbent for removing tetracycline because of its low cost, plentiful feedstock, and adjustable physicochemical properties [21,22]. Made through the pyrolysis of biomass, biochar shows a porous structure, high surface area, and various functional groups that support multiple interactions with TC molecules, including pore filling,  $\pi$ - $\pi$  interactions, hydrogen bonding, electrostatic attraction, and metal–ligand complexation [23–27]. Early research showed moderate adsorption performance for pristine biochars made from agricultural residues and sludge [28–31], while newer studies focus on engineered biochars modified with chemical activation, heteroatom doping, and metal impregnation to boost adsorption capacity and enable catalytic degradation pathways [32–34]. These engineered materials have achieved much higher performance, often exceeding 1000 mg/g in adsorption capacity under optimal conditions, thanks to synergistic effects between their structural features and surface chemistry [35–38]. Despite these benefits, some limitations still exist, such as performance variation based on feedstock and preparation methods, vulnerability to fouling by co-occurring contaminants, and uncertainties about long-term stability and regeneration efficiency [24,28].

Although a growing body of research has examined biochar's ability to remove tetracycline, existing reviews mainly focus on adsorption capacity, modification methods, and mechanisms tested under controlled lab conditions. These studies often use simplified systems with single-solute TC solutions, which don't fully represent the complexity of real wastewater that contains natural organic matter, inorganic ions, heavy metals, and other organic pollutants [39,40]. These components can significantly affect adsorption via mechanisms such as site competition, pore blockage, and electrostatic effects, leading to discrepancies between lab results and actual field performance [12,29,41]. Additionally, little attention has been paid to regeneration, long-term stability, and scaling up, with most studies limited to bench-scale tests and lacking validation in continuous or pilot-scale setups [42]. These gaps highlight a disconnect between material research and practical application, hindering the transition of promising lab findings into deployable treatment solutions.

To address these limitations, our review presents a structure–performance–deployment framework for engineered biochar used in tetracycline removal from complex water matrices. This framework incorporates three main dimensions: (i) the structural design of biochar, including feedstock selection, pyrolysis conditions, and modification strategies that influence physicochemical properties; (ii) the performance of these materials in terms of adsorption and catalytic mechanisms under different environmental conditions; and (iii) the deployment potential, covering regeneration, stability, and scalability in real-world treatment systems. By systematically linking material structure to functional performance and practical use, this review moves beyond traditional descriptive analyses to offer a mechanism-based, application-focused perspective. Its goal is to bridge the gap between laboratory research and field application, providing a clear pathway for the rational design of engineered biochar systems that achieve effective and sustainable tetracycline removal in real environmental settings.

### Review Methodology

This review's references were identified through a systematic search in December 2025, using the Scopus and Web of Science databases. The focus was on studies about biochar-based removal of tetracycline from aqueous environments, emphasizing material design and mechanisms. Boolean search strings combining keywords related to biochar, tetracycline, and removal processes were utilized. An example search query is: (“biochar” OR

“engineered biochar” OR “modified biochar”) AND (“tetracycline” OR “antibiotic”) AND (“adsorption” OR “removal” OR “sorption” OR “degradation”) AND (“water” OR “wastewater” OR “aqueous system”).

The initial search produced 2446 records, which were then filtered based on specific inclusion and exclusion criteria. Duplicate entries were removed, leaving only peer-reviewed articles that reported experimental studies on tetracycline removal using biochar in water or wastewater systems. Studies not related to tetracycline, lacking experimental data, or focusing on non-aqueous systems were omitted. Furthermore, preprints, conference papers, non-English publications, and review articles (170 in total) were excluded, resulting in a final set of 248 articles. Of these, about 150 were selected for systematic analysis. To ensure thorough coverage, additional relevant studies were identified through backward and forward citation analysis of key publications. The literature screening process did not include a formal quantitative meta-analysis; however, the studies were qualitatively assessed based on their experiments, relevance to tetracycline removal, and completeness of the reported adsorption parameters. Also, selection was based on their relevance to structure-performance relationships, mechanistic insights and applicability under real world water matrices. The database search was conducted in December 2025, and all included studies were published up to this date.

After screening, the chosen articles were assessed for their relevance to biochar design, adsorption mechanisms, environmental influences, and application potential. They were then grouped according to structural features, removal processes, and performance under real water conditions, aiding the creation of a structure–performance–deployment framework.

## 2. Structure: Biochar Design and Engineering Strategies

The performance of engineered biochar in tetracycline (TC) removal mainly depends on its structural features, which are influenced by feedstock choice, pyrolysis conditions, and post-synthesis modifications. These factors collectively shape key physicochemical properties such as surface area, pore structure, functional group distribution, and surface charge, all of which directly affect adsorption mechanisms and catalytic activity. Understanding these design factors is crucial for creating biochar systems that can sustain efficiency in real-world water environments.

### 2.1. Biomass Feedstocks and Their Influence On Biochar Properties

Biomass feedstock selection is crucial in determining the structural and chemical properties of biochar. Agricultural residues like rice husks, corn straw, and bamboo provide lignocellulosic frameworks that produce biochars with developed porosity and aromatic carbon structures, which enhance  $\pi$ – $\pi$  interactions with tetracycline molecules [43]. Wood-based feedstocks similarly generate biochars with high carbon content and stable graphitic domains, supporting hydrophobic interactions and long-term structural stability [44]. Conversely, manure and sewage sludge-derived biochars often contain higher ash content and mineral phases, creating additional adsorption sites and promoting metal–ligand complexation [29,45]. These variations emphasize that feedstock origin not only impacts baseline adsorption capacity but also affects the primary removal mechanisms, especially in complex environmental conditions where multiple contaminants interact.

### 2.2. Pyrolysis Conditions and Structural Evolution

Pyrolysis parameters regulate how biomass transforms into functional biochar. Temperature is the key factor, influencing the balance between surface functionality and structural order. Low-temperature biochars (<500 °C) keep many oxygen-containing functional groups such as –OH and –COOH, which enhance hydrogen bonding and electrostatic interactions with tetracycline [44]. In contrast, high-temperature biochars (>600 °C) gain increased aromaticity and graphitization, which support  $\pi$ – $\pi$  electron donor–acceptor interactions and better adsorption of organic pollutants [39]. Residence time also affects carbonization efficiency and pore development, with longer times enabling more complete devolatilization and structural stabilization. Heating rate impacts pore formation too; rapid heating can generate hierarchical pore networks, while slower heating promotes uniform carbon structures. In all, these parameters decide whether biochar is optimized for functional group interactions or pore-based adsorption.

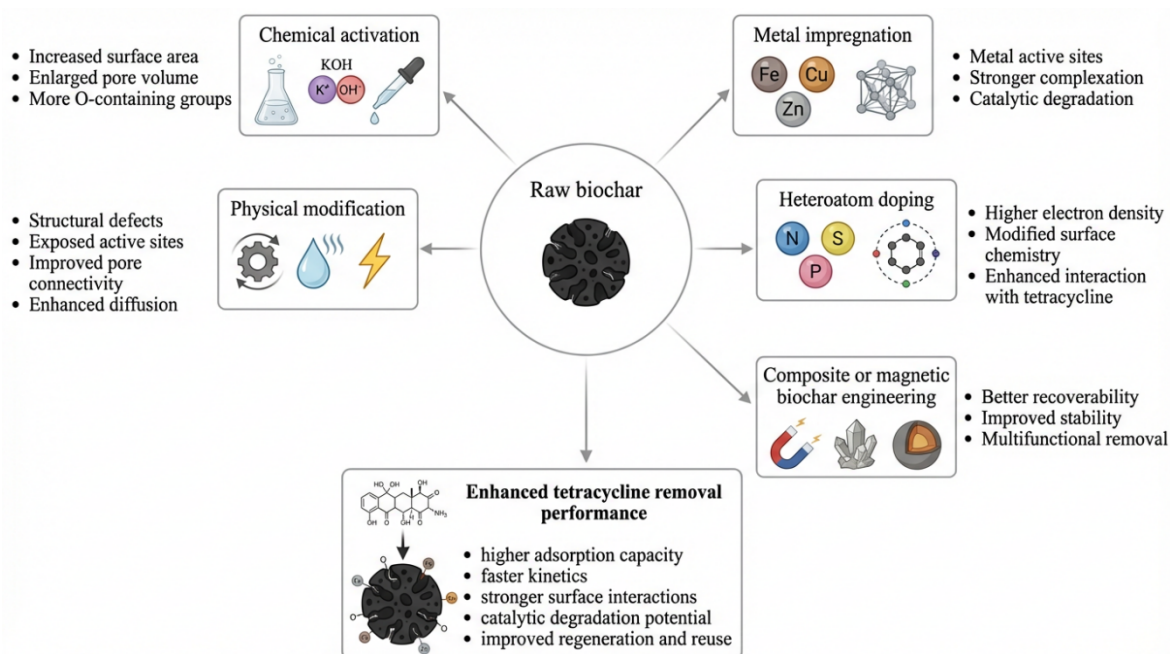
### 2.3. Surface Chemistry and Physicochemical Properties

The adsorption performance of biochar is directly connected to its surface chemistry and physicochemical properties. A high specific surface area and well-developed micro- and mesoporous structures improve pore filling and allow TC molecules to diffuse into internal adsorption sites [12]. Aromaticity and graphitic domains formed

during high-temperature pyrolysis enable strong  $\pi$ - $\pi$  stacking interactions with the conjugated ring structure of tetracycline [13]. Oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups, help with hydrogen bonding and surface complexation, especially under different pH conditions [35,46]. Surface charge characteristics, controlled by pH and the ionization of functional groups, also influence electrostatic attraction or repulsion between biochar and TC species [13]. These combined properties shape the interaction landscape of biochar and determine how effective it is in various environmental conditions.

#### 2.4. Biochar Modification Strategies

To overcome the limitations of pristine biochar, various modification strategies have been developed to improve adsorption capacity and add catalytic functions as illustrated in Figure 1. Chemical activation with agents such as KOH, ZnCl<sub>2</sub>, and H<sub>3</sub>PO<sub>4</sub> greatly increases surface area and pore volume, thus boosting adsorption efficiency [37,47]. Heteroatom doping with elements like nitrogen, sulfur, and phosphorus changes the electronic structure and creates active sites that enhance hydrogen bonding and electron transfer interactions [35,48]. Metal impregnation, involving elements such as Fe, Cu, Zn, and Mn, provides more adsorption sites and enables catalytic degradation via redox reactions and reactive oxygen species production [29,49]. Magnetic modification, often through Fe<sub>3</sub>O<sub>4</sub> addition, allows for efficient separation and reuse of biochar, making water treatment systems operationally more feasible [50]. Combining carbon matrices with materials such as hydroxyapatite or metal oxides to produce composite biochars enhances structural stability and multifunctionality, enabling simultaneous adsorption and contaminant degradation (Figure 1).



**Figure 1.** Strategies for biochar modification and their effects on improving tetracycline removal efficiency.

#### 2.5. Structure–Property Relationships in Engineered Biochar

The effectiveness of engineered biochar for tetracycline removal ultimately depends on the interaction between its structural design and functional performance as summarized in Table 1. A high surface area and hierarchical porosity enable efficient mass transfer and pore filling, while aromatic domains promote  $\pi$ - $\pi$  interactions with TC molecules. Functional groups and doped elements provide specific binding sites for hydrogen bonding, electrostatic attraction, and complexation, whereas metal components facilitate catalytic degradation pathways [23,35]. These structure–property relationships are interconnected; they work together, with optimized biochars combining multiple mechanisms to achieve high adsorption capacities and stability. However, the performance of these materials is highly sensitive to environmental factors, including pH, ionic strength, and coexisting contaminants, which can modify surface chemistry and adsorption behavior. Therefore, rational design of biochar must account for not only the inherent material properties but also their interaction with real water matrices, ensuring that structural benefits lead to consistent performance in practical conditions. The relationship between structural features, dominant mechanisms, and removal efficiency is compiled in Table 1.

**Table 1.** Structure–performance relationships governing tetracycline removal by engineered biochar.

Biochar Type	Structural Feature	Mechanism(s)	TC Removal Performance	Ref
Agricultural residues (rice husk, corn straw, bamboo)	High lignocellulosic carbon, developed porosity	$\pi$ - $\pi$ interaction, pore filling	Enhances adsorption via aromatic interactions and pore accessibility	[29,30,43]
Wood-based biomass	High carbon content, graphitic domains	Hydrophobic interaction, $\pi$ - $\pi$ stacking	Improves structural stability and adsorption of organic TC species	[44]
Manure/sludge-derived biochar	High ash content, mineral phases	Metal–ligand complexation, electrostatic interaction	Provides additional active sites and enhances adsorption in multi-contaminant systems	[45,51]
Low pyrolysis temperature (<500 °C)	Abundant oxygen-containing functional groups (-OH, -COOH)	Hydrogen bonding, electrostatic interaction	Improves adsorption of polar and ionized TC species	[44]
High pyrolysis temperature (>600 °C)	Increased aromaticity, graphitization	$\pi$ - $\pi$ interaction, hydrophobic interaction	Enhances adsorption of neutral TC and improves structural stability	[39,52]
Chemical activation (KOH, ZnCl <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub> )	Increased surface area and microporosity	Pore filling, diffusion-controlled adsorption	Significantly increases adsorption capacity (>900–1000 mg/g)	[37,47]
Heteroatom doping (N, S, P)	Electron-rich functional groups, defect sites	Hydrogen bonding, electron transfer, Lewis acid–base interaction	Enhances adsorption affinity and interaction strength	[35,48]
Metal impregnation (Fe, Cu, Zn, Mn)	Formation of metal active sites	Metal–ligand complexation, catalytic degradation (ROS generation)	Enables dual adsorption–degradation pathways and improved removal efficiency	[29,49]
Magnetic modification (Fe <sub>3</sub> O <sub>4</sub> incorporation)	Magnetic particles embedded in biochar matrix	Adsorption + magnetic recovery (operational advantage)	Improves reusability and separation efficiency without affecting adsorption mechanisms	[50]
Composite biochar (e.g., hydroxyapatite, metal oxides)	Multi-phase structure, enhanced stability	Combined adsorption + catalytic mechanisms	Improves multifunctionality and stability in complex water matrices	[29,49,53]
High surface area & hierarchical porosity	Micro- and mesoporous network	Pore filling, mass transfer enhancement	Increases adsorption capacity and kinetics	[12]
Oxygen-containing functional groups	-OH, -COOH, C=O groups	Hydrogen bonding, surface complexation	Enhances adsorption under variable pH conditions	[35,46]
Aromatic/graphitic domains	Conjugated carbon structures	$\pi$ - $\pi$ stacking interactions	Strengthens adsorption of tetracycline aromatic rings	[39,52]
Surface charge (pH-dependent)	Protonated/deprotonated functional groups	Electrostatic attraction/repulsion	Controls adsorption efficiency depending on TC speciation	[13,52]

### 3. Performance: Adsorption and Degradation Mechanisms

The removal of tetracycline (TC) by engineered biochar involves both adsorption and catalytic degradation mechanisms, which are heavily influenced by material properties and environmental factors. These mechanisms usually work together, with their relative contributions depending on tetracycline's form, the surface chemistry of the biochar, and the complexity of the water matrix involved.

#### 3.1. Tetracycline Speciation and Environmental Chemistry

Tetracycline is an amphoteric compound with multiple ionizable functional groups, leading to different pH-dependent species that greatly influence its interaction with biochar surfaces [54,55]. Under acidic conditions, TC mainly exists as a cationic species (TCH<sup>+</sup>), while near-neutral pH shifts it to a zwitterionic or neutral form (TCH<sup>0</sup>). Under alkaline conditions, it becomes anionic (TC<sup>-</sup> and TC<sup>2-</sup>) [13,56]. These changes in speciation directly impact adsorption by altering electrostatic interactions and binding affinity. For example, positively charged TC species tend to interact with negatively charged biochar surfaces rich in deprotonated functional groups, whereas anionic forms may face electrostatic repulsion unless specific binding sites, like metal centers, are available [57–59]. Environmental factors such as ionic strength and coexisting ions further influence speciation and mobility, affecting adsorption efficiency in complex environments [12,57–59]. Therefore, understanding TC speciation is essential for predicting adsorption performance under real-world water conditions.

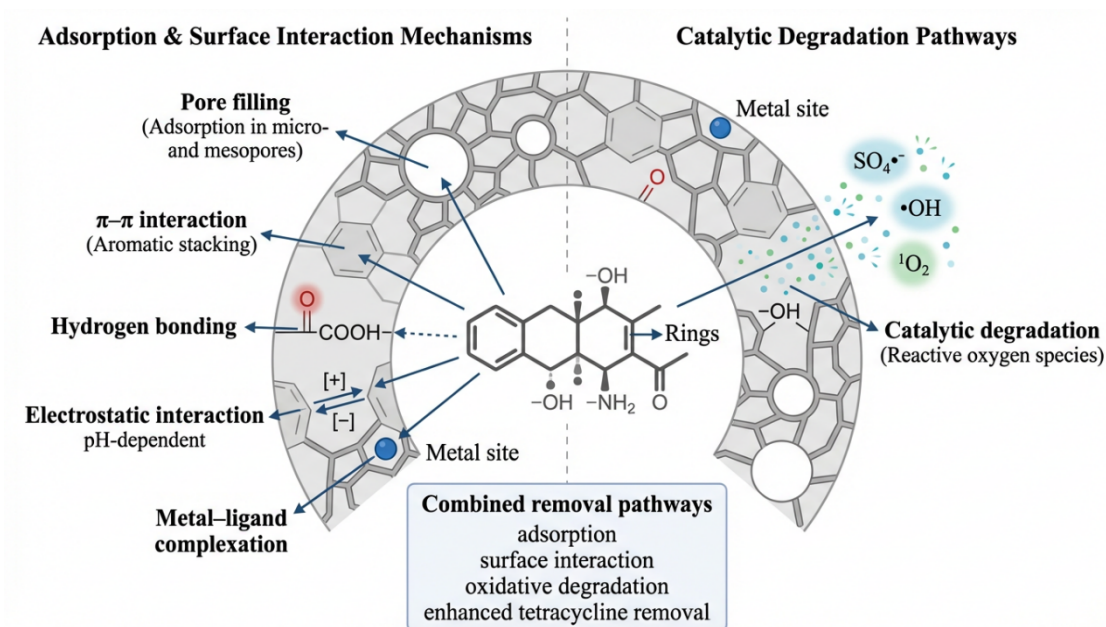
#### Adsorption Modeling

In adsorption modeling, adsorption behavior is described using isotherm models such as the Langmuir and the Freundlich models, which provide insights into monolayer adsorption and surface heterogeneity, respectively. Kinetic models, including pseudo-first-order and pseudo-second-order equations, are frequently used to describe adsorption rates and mechanisms. Many studies report that TC adsorption onto biochar follows pseudo-second-

order kinetics, indicating chemisorption as the most common mechanism, while Langmuir isotherms often provide the best fit, suggesting monolayer adsorption of TC on homogeneous surfaces.

### 3.2. Primary Adsorption Mechanisms

The removal of tetracycline by engineered biochar involves both adsorption and catalytic degradation mechanisms, as illustrated in Figure 2, which highlights the connections among multiple interaction pathways.



**Figure 2.** Mechanisms of tetracycline (TC) removal by engineered biochar, including adsorption (pore filling,  $\pi$ - $\pi$  interaction, hydrogen bonding, electrostatic interaction), surface complexation, and catalytic degradation via reactive oxygen species (ROS).

#### 3.2.1. Pore Filling (Micro- and Mesopores)

Pore filling is a primary mechanism in biochars with well-developed micro- and mesoporous structures [60–62]. Tetracycline molecules diffuse into internal pores where they are physically confined and held through multiple weak interactions [58,63,64]. Studies on Fe-modified Hydrochar show that micropores with diameters like TC molecular size enable effective trapping, which significantly boosts overall adsorption capacity [12,65,66]. High surface area and hierarchical pore structures improve accessibility and diffusion, making pore filling especially important in chemically activated biochars. These mechanisms, summarized in Figure 2, include both physical and chemical interactions that determine adsorption behavior and capacity.

#### 3.2.2. $\pi$ - $\pi$ Interactions (Aromatic Stacking)

$\pi$ - $\pi$  interactions result from the overlap between the aromatic rings of tetracycline and the graphitic domains of biochar [58,67]. These interactions are especially significant in biochars produced at high pyrolysis temperatures, where increased aromaticity boosts electron donor–acceptor interactions [13,30,39,54]. As summarized in Figure 2, such interactions are most effective when TC remains in a neutral form, as electrostatic influences are minimized, allowing  $\pi$ - $\pi$  stacking to control adsorption behavior.

#### 3.2.3. Hydrogen Bonding

Hydrogen bonds form between functional groups in tetracycline, like  $-OH$  and  $-NH_2$ , and oxygen-based groups on biochar surfaces such as  $-COOH$  and  $-OH$  [68,69]. These bonds play a key role in adsorption, especially in biochars with numerous surface functionalities. And these are typically produced at lower pyrolysis temperatures or modified by oxidation [30,35,46,49]. The strength of hydrogen bonds is highly pH-dependent because changes in pH cause protonation or deprotonation of the functional groups, affecting their bonding ability and this is shown in Figure 2.

### 3.2.4. Electrostatic Interactions

Electrostatic attraction or repulsion between biochar surfaces and TC species plays a crucial role in adsorption. The surface charge of biochar, determined by its functional groups and solution pH, controls interactions with charged TC species [70,71]. Under acidic conditions, negatively charged biochar surfaces attract cationic TC species, increasing adsorption efficiency, while under alkaline conditions, repulsion may occur unless offset by other mechanisms [13,55]. Ionic strength and competing ions can also influence electrostatic interactions by compressing the electrical double layer and decreasing effective attraction [72–74].

### 3.3. Advanced Interaction Pathways

Both metal-ligand complexation and surface complexation involve coordination interactions; however, they differ in the nature of their binding sites. While metal-ligand complexation involves coordination between tetracycline and functional groups and metal ions introduced during biochar medication, surface complexation refers to interactions between the tetracycline molecule and native oxygen-containing functional groups on a particular biochar surface.

#### 3.3.1. Metal–Ligand Complexation

Demonstrated at the bottom left of Figure 2, metal-doped biochars create extra adsorption pathways through complexation between metal ions (e.g., Fe, Cu, Zn) and functional groups in tetracycline molecules [75–77]. These interactions involve coordination between metal centers and electron-donating groups such as phenolic or diketone parts in TC, forming stable complexes that boost adsorption capacity [29,49]. Metal–ligand complexation is especially important in multi-contaminant systems where metal ions may either compete with or help TC adsorption depending on system conditions [78–80].

#### 3.3.2. Surface Complexation Mechanisms

Surface complexation entails the creation of either inner-sphere or outer-sphere complexes between TC molecules and biochar surface functional groups [81–83]. Oxygen-containing groups like carboxyl and hydroxyl can form robust chemical bonds with TC, particularly under suitable pH conditions [33,46]. These interactions often resemble chemisorption, leading to increased adsorption stability and a lower likelihood of desorption compared to physical adsorption.

### 3.4. Catalytic Degradation Pathways

Beyond adsorption, engineered biochars can enable catalytic degradation of tetracycline through advanced oxidation processes (AOPs) [84,85]. Metal-modified and heteroatom-doped biochars can activate oxidants like persulfate or peroxymonosulfate to produce reactive oxygen species (ROS), including hydroxyl radicals (OH), sulfate radicals (SO<sub>4</sub><sup>-</sup>), and oxygen (O<sub>2</sub>), which break down TC molecules into less harmful products [18,86,87]. These catalytic pathways often work alongside adsorption, creating dual-function systems that both capture and transform contaminants. Biochar acts as both an adsorbent and a catalyst support, providing active sites for ROS generation and improving degradation efficiency [88–90]. However, extended catalytic use may cause structural degradation or a loss of active sites, emphasizing the importance of balancing adsorption and catalytic performance. Despite these advances, most catalytic degradation studies remain limited to controlled laboratory conditions, with limited validation in continuous systems or real wastewater matrices, which is a key barrier to practical deployment.

### 3.5. Mechanism Dominance under Varying Conditions

The primary mechanisms for removal vary considerably based on environmental conditions and biochar properties as detailed in Table 2. pH plays a key role because it influences the speciation of total carbon (TC) and the biochar surface charge, affecting electrostatic interactions, hydrogen bonding, and  $\pi$ - $\pi$  stacking [13,26,51,59]. Surface chemistry, including functional groups and metal dopants, determines whether adsorption is dominated by physical or chemical interactions. In complex water environments, co-existing ions and natural organic matter can hinder certain mechanisms by competing for active sites or blocking pores, reducing overall efficiency [12,29]. Additionally, catalytic degradation becomes more prominent in modified biochars that generate reactive species, especially under oxidative conditions. These interactions highlight that biochar effectiveness results from a dynamic interplay of various processes influenced by both material design and environmental conditions. A

comprehensive summary of how environmental factors influence adsorption mechanisms and performance is presented in Table 2.

A comparative evaluation of various modified biochar systems, including the modification, adsorption capacities, dominant mechanisms, and regeneration performance, is presented in Table 3.

**Table 2.** Adsorption mechanisms of tetracycline under varying environmental conditions.

Environmental Condition	Mechanism(s)	Reason	Effect on TC Removal Performance	Ref.
Low pH (acidic conditions)	Electrostatic attraction, hydrogen bonding	TC exists mainly as cationic (TCH <sup>+</sup> ); biochar surface often negatively charged	Enhanced adsorption due to strong electrostatic attraction	[13,91]
Neutral pH	$\pi$ - $\pi$ interaction, hydrogen bonding	TC exists in zwitterionic/neutral form, reducing electrostatic effects	Balanced and often optimal adsorption performance due to multiple mechanisms	[46,51]
High pH (alkaline conditions)	Metal-ligand complexation, $\pi$ - $\pi$ interaction	TC becomes anionic (TC <sup>-</sup> /TC <sup>2-</sup> ), leading to electrostatic repulsion	Reduced adsorption unless compensated by complexation or $\pi$ - $\pi$ interactions	[29,51]
High ionic strength	Reduced electrostatic interaction	Compression of electrical double layer and charge screening	Decreased adsorption efficiency, especially for electrostatic-driven systems	[12]
Presence of natural organic matter (NOM)	Reduced pore filling, reduced hydrogen bonding	NOM competes for active sites and blocks pores	Significant decline in adsorption capacity due to fouling and competition	[12,29]
Presence of divalent metal ions (e.g., Cu <sup>2+</sup> , Zn <sup>2+</sup> )	Metal-ligand complexation (enhanced or competitive)	Formation of TC-metal-biochar complexes or competition for sites	Can enhance or inhibit adsorption depending on system conditions	[29,39]
Multi-contaminant systems	Competitive adsorption across mechanisms	Coexisting organics compete for $\pi$ - $\pi$ , H-bonding, and pore sites	Reduced selectivity and lower TC removal efficiency	[92,93]
High surface area biochar	Pore filling, diffusion-controlled adsorption	Increased availability of micro- and mesopores	Improved adsorption capacity and kinetics	[12]
High aromaticity biochar	$\pi$ - $\pi$ interaction	Graphitic domains interact with TC aromatic rings	Stronger adsorption, especially under neutral conditions	[39,52]
Functional group-rich biochar (-OH, -COOH)	Hydrogen bonding, surface complexation	Abundant reactive sites for TC interaction	Enhanced adsorption under variable pH conditions	[35,46]

**Table 3.** Comparing biochar types with adsorption capacity, mechanism, and regeneration.

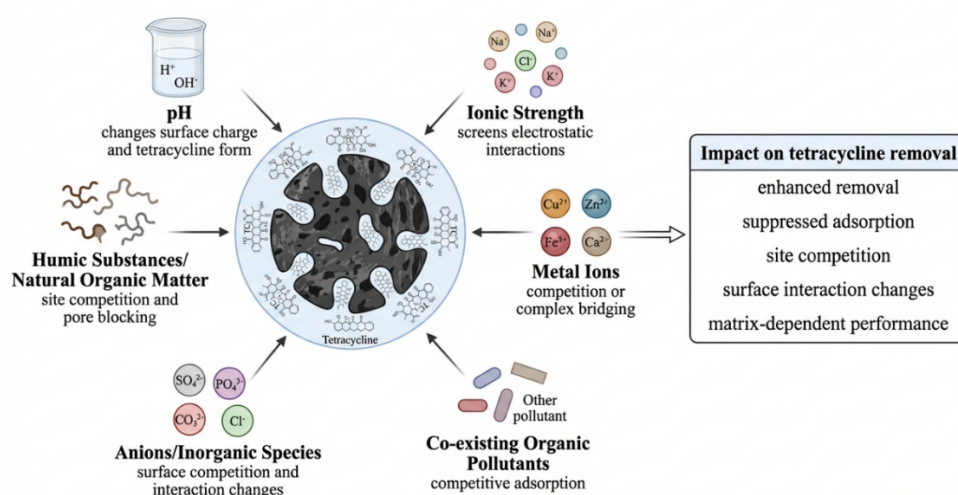
Study	Biochar Modification	Adsorption Capacity (mg/g)	Removal Mechanisms	Co-Contaminant Influence	Regeneration & Stability
[47]	Periodate activation, pyrolysis temperature effect	~100 (BC-700)	Electron transfer, reactive species	Minimal interference by anions and the water matrix	Good reusability, stable performance
[94]	Metal-free biochar from biogas residue, pyrolysis at 800 °C	97.9	Non-radical pathways, electron transfer	Stable presence of organic/inorganic compounds	High stability and recyclability
[37,95]	One-step pyrolytic porous biochar from antibiotic residue	1096.87	Chemical adsorption, electron exchange, and monolayer adsorption	Not reported	Not reported
[96]	Hydrochar from co-hydrothermal carbonization of PVC and garden waste	Increased by 28–406% vs. feedstocks	Carbonyl $\pi$ - $\pi$ electron interaction, dechlorination effects	Not reported	Regeneration cycles studied
[37]	Hydrothermal carbonization with ZnCl <sub>2</sub> activation	930.3	Pore diffusion, $\pi$ - $\pi$ interaction, electrostatic attraction, hydrogen bonding	Insignificant effect of coexisting ions (10–100 mg/L)	>77% removal after 10 cycles
[49]	Sequential iron impregnation at low-temperature pyrolysis	891.37	Hydrogen bonding, coordination with iron oxides/hydroxides	Not reported	High recyclability
[52]	Microwave-assisted porous graphitized biochar with KOH/KCl activation	1033.06	Pore filling, electrostatic attraction, hydrogen bonding, $\pi$ - $\pi$ interaction	Not reported	Not reported
[35]	N, S co-modified biochar with tunable micro-mesoporosity	1480.1	Pore filling, hydrogen bonding, $\pi$ - $\pi$ stacking, Lewis's acid-base interaction	Evaluated cation strength, actual water, fixed-bed column	Good regenerability

#### 4. Realistic Water Matrices

The performance of engineered biochar for tetracycline (TC) removal is greatly affected by the complexity of actual water samples as summarized in Table 4, where many physicochemical factors interact at the same time. Unlike controlled laboratory settings, environmental waters have varying pH levels, dissolved ions, natural organic matter (NOM), metals, and other organic contaminants, all of which can change how adsorption occurs and which mechanisms are dominant. These interactions as shown in Figure 3 often lead to lower efficiency compared to ideal conditions, emphasizing the need to assess biochar performance under real-world situations.

**Table 4.** Discrepancies between laboratory conditions and real water matrices in tetracycline removal.

Parameter	Laboratory Conditions	Wastewater Conditions	Impact on TC Removal Performance	Affected Mechanism(s)	Ref
Contaminant	Single-solute TC solutions	Multi-contaminant systems (antibiotics, organics, metals)	Competitive adsorption reduces TC removal efficiency	All mechanisms (site competition)	[29]
pH conditions	Controlled and constant	Variable and fluctuating	Alters TC speciation and biochar surface charge, shifting adsorption mechanisms	Electrostatic, $\pi$ - $\pi$ , hydrogen bonding	[51,91]
Ionic strength	Low or negligible	High (presence of salts and ions)	Electrostatic screening reduces adsorption efficiency	Electrostatic interaction	[12]
Natural organic matter (NOM)	Absent	Present (humic/fulvic substances)	Pore blockage, site competition, surface fouling	Pore filling, hydrogen bonding	[12,29]
Co-existing inorganic ions	Minimal or absent	$\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$ , $\text{CO}_3^{2-}$ present	Competition for adsorption sites, altered solution chemistry	Electrostatic, complexation	[26,97]
Metal ions	Often excluded	Present ( $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , etc.)	Can inhibit adsorption via competition or enhance via complex bridging	Metal-ligand complexation	[29,39]
Organic co-contaminants	Absent	Present (pharmaceuticals, dyes, organics)	Reduced selectivity and adsorption efficiency	$\pi$ - $\pi$ , hydrogen bonding	[40,98]
Hydrodynamic conditions	Static (batch systems)	Dynamic (continuous flow systems)	Reduced contact time leads to lower adsorption capacity	Pore diffusion, mass transfer	[12]
Contact time	Extended (equilibrium conditions)	Limited (real operational systems)	Incomplete adsorption due to insufficient interaction time	Kinetics-controlled adsorption	[39]
Temperature variability	Controlled	Fluctuating environmental temperatures	Affects adsorption kinetics and thermodynamics	All mechanisms	[39]

**Figure 3.** Effects of other water components on tetracycline (TC) removal by biochar, highlighting the roles of pH, ionic strength, natural organic matter, inorganic ions, metal ions, and co-existing organic pollutants in affecting adsorption behavior and effectiveness.

#### 4.1. pH Effects and Tetracycline Speciation

Solution pH is a critical factor that influences TC adsorption, as it affects both tetracycline speciation and biochar surface charge. Tetracycline can exist as cationic ( $\text{TCH}^+$ ), zwitterionic ( $\text{TCH}^0$ ), or anionic ( $\text{TC}^-/\text{TC}^{2-}$ ) species depending on pH, which leads to shifts in adsorption mechanisms [99–101]. At low pH, electrostatic attraction between positively charged TC species and negatively charged functional groups on biochar enhances adsorption. Conversely, at higher pH levels, electrostatic repulsion may become dominant, decreasing adsorption efficiency unless balanced by  $\pi$ - $\pi$  interactions or metal complexation [51,59,100]. Studies have shown that adsorption capacity can vary greatly across pH levels, with the best performance typically seen under mildly acidic conditions where multiple mechanisms work together [29,91]. These results highlight that pH not only influences the strength of adsorption but also determines which interaction pathways are predominant.

#### 4.2. Ionic Strength and Electrostatic Screening

Ionic strength plays a key role in the electrostatic interactions between TC molecules and biochar surfaces. Dissolved salts compress the electrical double layer around biochar particles, which decreases the effective range

of electrostatic attraction and lowers adsorption efficiency [13,76,78]. Higher ionic strength also leads to competition between ions and TC molecules for adsorption sites, especially in systems primarily driven by electrostatic mechanisms. Monovalent ions usually have weaker effects, while divalent cations like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can greatly change adsorption behavior through charge screening and complex formation [12,58,102,103]. Consequently, adsorption capacities measured in low-ionic-strength lab conditions are often overestimated compared to actual wastewater systems, where ionic concentrations are much higher [58,59].

#### 4.3. Natural Organic Matter (NOM) and Humic Substances

Natural organic matter, including humic and fulvic acids, adds significant complexity to biochar-mediated TC removal. NOM competes directly with tetracycline for adsorption sites, especially those with oxygen-containing functional groups, which decreases adsorption capacity [12,51,55,104]. Besides competing for sites, NOM can block pore entrances and internal adsorption sites, limiting access and reducing the effective surface area. Surface fouling caused by NOM adsorption further changes biochar's surface chemistry, potentially covering active sites and altering surface charge characteristics [55,104]. Studies indicate that humic substances can greatly lower TC removal efficiency, especially in biochars that depend on pore filling and electrostatic interactions [29,104]. These effects emphasize the importance of designing biochars that are more resistant to fouling and competitive adsorption in real water samples.

#### 4.4. Co-Existing Inorganic Ions and Anions

The presence of inorganic ions and anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{CO}_3^{2-}$  affects TC adsorption behavior [99,100,102,103]. These species compete with tetracycline for active sites on biochar surfaces or modify solution chemistry in ways that decrease adsorption efficiency. For example, anions like phosphate and carbonate can hinder TC adsorption by occupying binding sites or raising the solution pH, which shifts TC into less favorable forms [97]. Sulfate ions may also interfere with adsorption through competitive interactions or by changing ionic strength. Although some modified biochars show resistance to ionic interference (especially those with hierarchical pore structures or strong chemical binding sites) many systems experience reduced performance under high ionic conditions [26,100,102,103]. These observations highlight the importance of testing adsorption under conditions that reflect real wastewater chemistry.

#### 4.5. Metal Ions and Complex Bridging Effects

Metal ions in wastewater can have both inhibitory and synergistic effects on tetracycline removal, depending on system conditions and biochar properties. Divalent metal ions like  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  can compete with TC for adsorption sites, lowering removal efficiency [39,105–107]. However, in some cases, these metals aid adsorption through complex bridging mechanisms, forming ternary complexes between TC, metal ions, and biochar surfaces [29,105,106]. These interactions can improve adsorption by stabilizing TC binding or creating new coordination pathways. The dual role of metal ions underscores the complexity of multi-component systems, where adsorption behavior can't be predicted solely from single-solute experiments. Therefore, effective biochar design must consider both competitive and cooperative interactions in environments rich in metal ions.

#### 4.6. Co-Existing Organic Pollutants

In wastewater systems, tetracycline exists together with a variety of organic contaminants, including other antibiotics, PFAS, dyes, and pharmaceuticals. These substances compete for adsorption sites, which reduces selectivity and lowers the removal efficiency for each pollutant [10,17,108]. Interactions among multiple contaminants can also change how adsorption works, as different compounds tend to favor specific binding pathways. For example, aromatic compounds may compete for  $\pi$ - $\pi$  interaction sites, while polar organics compete for hydrogen bonding sites [109–111]. Research shows that engineered biochars with diverse functional groups and layered pore structures are more resilient in such conditions, maintaining relatively high adsorption performance despite competition effects [95,98]. However, competition still remains a significant challenge in complex wastewater systems.

#### 4.7. Laboratory vs. Real Wastewater Performance Gap

One major challenge in applying engineered biochar is the gap between laboratory results and real-world outcomes. Most studies are done under simplified conditions, using single-solute systems, controlled pH, and low ionic strength, which do not reflect the complexity of actual wastewater [39,50,51,59,112,113]. In real water

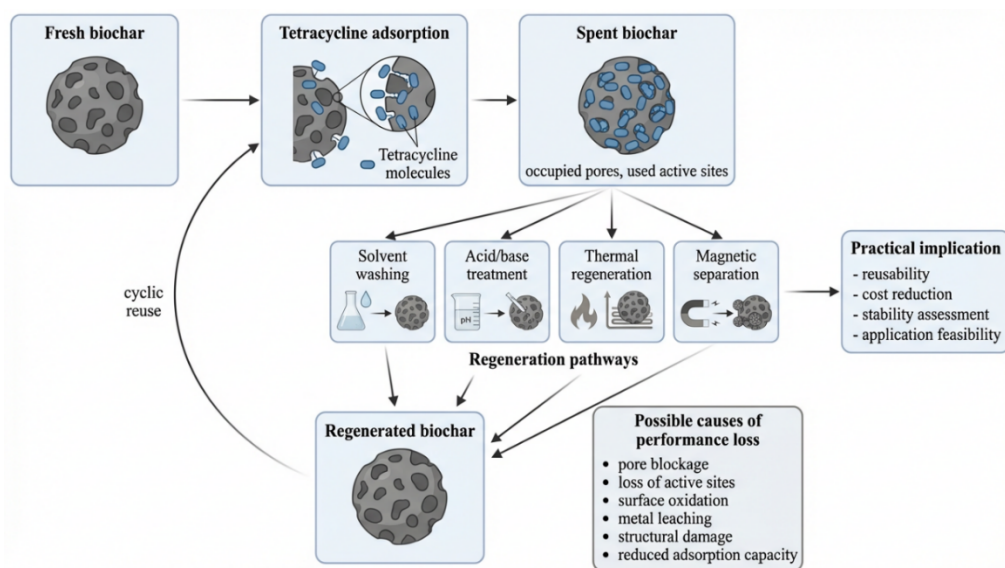
samples, factors like pH changes, ionic competition, NOM fouling, and multi-contaminant interactions often cause much lower adsorption efficiency. Also, hydrodynamic factors such as flow rate and residence time affect performance, with higher flow rates decreasing contact time and limiting adsorption capacity [12,59,106]. These differences highlight the need for standardized testing protocols that include realistic water chemistry and operational conditions. Closing this gap is vital to turn laboratory successes into practical water treatment solutions.

### 5. Regeneration, Stability, and Reusability of Biochar

The long-term effectiveness of engineered biochar for tetracycline (TC) removal depends not only on its initial adsorption capacity but also on its ability to maintain performance across multiple use cycles. The regeneration, stability, and reuse potential of engineered biochar are critical for sustainable application, as summarized in Table 5. Regeneration, structural stability, and resistance to performance decline are essential factors for practical application. Although many engineered biochars show promising reusability in laboratory settings, their stability in real water conditions remains a significant challenge that needs systematic investigation. The processes of regeneration are illustrated in Figure 4.

**Table 5.** Comparison of regeneration strategies for engineered biochar in tetracycline removal.

Regeneration Method	Mechanism of Regeneration	Regeneration Efficiency	Structural Impact on Biochar	Advantages	Limitations	Ref.
Solvent washing (e.g., ethanol, alkaline solution)	Desorption via disruption of weak interactions (H-bonding, van der Waals)	Moderate (partial recovery)	Minimal structural damage	Simple, low-cost, easy to implement	Incomplete desorption, residual accumulation over cycles	[26]
Alkaline treatment (e.g., NaOH)	Alters surface charge and breaks chemical bonds between TC and functional groups	High (~70–80% recovery after multiple cycles)	Moderate alteration of surface chemistry	Effective regeneration, restores active sites	Possible structural modification and gradual efficiency loss	[114]
Acid treatment	Removes metal complexes and restores binding sites	Moderate to high	Can induce structural changes and leach components	Effective for metal-doped biochar regeneration	Risk of metal leaching and structural instability	[114]
Thermal regeneration	High-temperature desorption and volatilization of contaminants	High (initial cycles)	Significant damage to pore structure and functional groups	Removes strongly bound contaminants	Energy-intensive, pore collapse, reduced long-term performance	[87]
Magnetic recovery (Fe <sub>3</sub> O <sub>4</sub> modified biochar)	Physical separation using magnetic field (not true regeneration)	N/A (recovery-focused)	No structural damage from separation	Rapid recovery, minimizes material loss	Requires additional regeneration step for reuse	[38,50]
Combined chemical and magnetic regeneration	Chemical desorption and magnetic recovery	High (improved cycle stability)	Moderate structural impact	Efficient recovery and reuse	Increased operational complexity	[50]
Mild regeneration approaches (low-intensity chemical washing)	Partial desorption while preserving structure	Moderate	Low structural damage	Preserves long-term stability	Lower regeneration efficiency	[47]



**Figure 4.** Regeneration and reuse pathways of biochar after tetracycline (TC) adsorption, showing treatment methods, performance decline mechanisms, and implications for long-term use.

### 5.1. Regeneration Pathways

Regeneration strategies focus on restoring adsorption capacity by removing adsorbed tetracycline and reactivating surface sites [115–117]. Solvent washing is among the most common methods, using organic solvents like ethanol or alkaline solutions to desorb TC molecules from biochar surfaces. This method effectively breaks weak interactions such as hydrogen bonds and van der Waals forces, allowing partial recovery of adsorption capacity [26,107]. However, repeated use of solvents may lead to incomplete desorption and residual contaminants, reducing long-term efficiency [118,119]. Acid and base treatments are also common for regenerating biochar by modifying surface charge and breaking chemical bonds between TC and functional groups [120,121]. Alkaline regeneration with NaOH has been shown to restore a significant portion of adsorption capacity, often achieving 70–80% efficiency after multiple cycles [114,120,122]. Acid treatments can remove metal complexes and restore binding sites but may also cause structural changes or leach active components depending on the biochar's makeup [123].

Thermal regeneration involves heating used biochar to detach contaminants and regenerate its pore structure. Although effective at removing strongly bound substances, this approach is energy-intensive and can damage surface functional groups or cause pore collapse, leading to reduced porosity [87,119]. As a result, thermal regeneration is often less preferred for sustaining long-term adsorption performance compared to chemical alternatives. Magnetic separation presents an alternative regeneration method for metal-modified biochars, especially those with Fe<sub>3</sub>O<sub>4</sub> or similar magnetic particles. These materials can be quickly recovered from water using an external magnetic field, which minimizes material loss and facilitates reuse [23,38,50,51,117]. However, while magnetic recovery enhances operational convenience, it does not naturally restore adsorption capacity and typically requires additional chemical or solvent-based regeneration techniques.

### 5.2. Performance Decay Mechanisms

Although regeneration techniques are effective, their repeated use can cause performance to gradually decline because of different degradation mechanisms. One major issue is pore blockage, where residual tetracycline, co-contaminants, or natural organic matter buildup inside micro- and mesopores, limiting access to active sites [12,124]. This problem is especially acute in actual wastewater systems, where fouling agents are plentiful. Additionally, the loss of active sites significantly hampers performance. During adsorption–desorption cycles, functional groups responsible for hydrogen bonding, electrostatic interactions, and complexation may be depleted or changed, decreasing effective binding site availability [47]. Surface oxidation from regeneration or catalytic reactions can further alter the chemical composition, affect adsorption behavior, and reduce efficiency [117,119,125].

Structural degradation is a significant limitation, especially for biochars subjected to aggressive regeneration techniques like thermal treatment or advanced oxidation. Repeated contact with reactive oxygen species can damage aromatic structures and weaken the structure, reducing their adsorption capacity [87]. In metal-doped biochars, metal leaching may happen during regeneration, causing loss of catalytic activity and posing environmental risks due to secondary contamination [126].

### 5.3. Regeneration Efficiency vs. Structural Stability Trade-Offs

One concern in biochar regeneration is balancing the recovery of its adsorption capacity with the preservation of its structural integrity. Methods such as thermal treatment or strong chemical washing can quickly restore adsorption abilities but often accelerate structural damage and the loss of functional groups over time. Conversely, gentler regeneration techniques help maintain biochar's structure but may not fully remove contaminants, leading to their gradual accumulation. Studies indicate that chemically modified biochars, particularly those with extensive pore networks and stable functional groups, outperform unmodified ones in regeneration [47]. Magnetic biochars provide advantages in recovery and reuse, though their long-term stability depends on the durability of metal components and their resistance to leaching [13,33,50,51]. These findings suggest that regeneration methods should be tailored to the type of biochar, balancing efficiency with durability to ensure consistent performance in practical applications.

### 5.4. Post-Adsorption Fate of Tetracycline-Loaded Biochar

The fate of tetracycline-loaded biochar after adsorption is a crucial yet often neglected factor in environmental risk assessment. Improper disposal or incomplete regeneration of used biochar can cause the released TC to re-enter the environment, reducing the effectiveness of treatment [127]. This issue is especially important in systems where adsorption relies on weak physical forces, which are more prone to reversal under environmental changes. Besides desorption, spent biochar may serve as a carrier for tetracycline and microbial

communities, potentially spreading antibiotic resistance if released into water systems [15]. Metal-doped biochars pose additional risks because metal ions may leach during disposal or reuse, creating secondary pollutants. To reduce these risks, safe disposal and reuse methods are essential. Possible solutions include incorporating biochar into soil amendments to stabilize contaminants or combining adsorption with catalytic degradation to break down tetracycline before disposal [87]. These approaches emphasize the importance of a life-cycle perspective in biochar use, ensuring treatment methods do not cause new environmental problems.

## 6. Bringing Laboratory Insights to Real-World Applications

Transferring engineered biochar from lab research to actual water treatment uses is a major challenge, despite progress in designing materials and understanding mechanisms. Compared to conventional adsorbents like activated carbon, metal-organic frameworks (MOFs), clays, and zeolites, engineered biochar offers a balance between cost, sustainability, and performance [128,129]. While activated carbon often demonstrates comparable or higher adsorption capacities [130], its production cost and regeneration requirements are relatively higher. MOFs also have high surface areas and tunable functionality, but they are limited by stability and scalability challenges [131–133]. On the other hand, biochar provides a low-cost, feedstock flexibility and moderate to high performance as well as environmental sustainability [134,135]. However, its adsorption capacity is more sensitive to water effects, highlighting the need for targeted material design. Furthermore, although experiments show high tetracycline (TC) removal in controlled settings, real-world application involves factors like system setup, operational changes, costs, and environmental impact and these are summarized in Table 6. Closing this gap requires assessing biochar performance outside batch tests and tackling challenges related to continuous systems and complex wastewater compositions.

**Table 6.** Barriers to practical deployment of engineered biochar for tetracycline removal and proposed solutions.

Barrier	Cause	Impact on TC Removal	Proposed Research Direction	Ref.
Matrix interference	Presence of NOM, ions, and co-contaminants	Reduced adsorption efficiency due to competition, pore blockage, and electrostatic screening	Conduct testing under realistic water matrices; design fouling-resistant biochar	[12,29]
Overestimation in laboratory studies	Use of single-solute systems, controlled conditions	Inflated adsorption capacities not representative of real systems	Standardize testing protocols with multi-contaminant systems and variable conditions	[39]
Regeneration inefficiency	Incomplete desorption, structural degradation	Declining adsorption capacity over reuse cycles	Develop optimized regeneration methods balancing efficiency and stability	[87,114]
Structural degradation	Thermal and chemical stress during regeneration	Loss of pore structure and functional groups	Use mild regeneration methods; design structurally robust biochar	[47,87]
Fouling by natural organic matters	Adsorption of humic substances on biochar surface	Blockage of active sites and reduced adsorption capacity	Develop surface-modified or anti-fouling biochar materials	[12,51]
Metal leaching (in modified biochar)	Weak binding of impregnated metals	Secondary contamination and reduced catalytic performance	Stabilize metal incorporation; assess leaching under real conditions	[126]
Scale-up limitations	Lack of pilot-scale and continuous system studies	Uncertainty in real-world performance and design parameters	Increase pilot-scale studies and reactor design optimization	[39]
Hydrodynamic constraints	Reduced contact time in flow systems	Lower adsorption efficiency compared to batch systems	Optimize flow rate, bed depth, and reactor configuration	[12]
Cost of modification	Use of chemical activation and metal doping	Increased production cost limits large-scale adoption	Utilize low-cost feedstocks and green modification techniques	[39]
Lack of standardization	Variability in experimental conditions across studies	Difficulty comparing results and designing systems	Develop unified evaluation metrics and protocols	[39]
Post-adsorption environmental risks	Potential desorption of TC and contaminant release	Secondary pollution and environmental risk	Integrate adsorption with degradation; develop safe disposal strategies	[15,87]

### 6.1. Batch vs. Continuous Systems

Most research on biochar-mediated TC removal relies on batch experiments, which offer valuable insights into adsorption kinetics, equilibrium, and mechanisms. Yet, these experiments often do not mirror real treatment conditions, where water flows continuously and contaminant levels vary [39]. Extended contact time and controlled environments in batch systems can lead to exaggerated performance estimates, as they don't consider hydrodynamic factors like flow velocity and mass transfer limitations essential in real applications. Consequently, materials showing high adsorption in lab tests may perform less effectively in continuous flow setups, underlining the importance of adopting more realistic evaluation methods.

## 6.2. Fixed-Bed and Column Systems

Fixed-bed and column systems are effective options for applying biochar in water treatment. In these configurations, contaminated water passes through a packed bed of biochar, allowing continuous adsorption under controlled hydraulic conditions. Performance is typically assessed with breakthrough curves, which depict the relationship between effluent concentration and time. Research shows that higher flow rates reduce the contact time between TC molecules and biochar surfaces, leading to earlier breakthrough and decreased adsorption capacity [12]. For example, increased flow velocities significantly cut down breakthrough times and lower total sorption capacity in Fe-modified hydrochar systems [66,96], emphasizing the importance of residence time for system efficiency. Hydraulic factors like bed depth, flow rate, and particle size are crucial for optimizing column operation. Deeper beds enhance contact time and adsorption but may also cause higher pressure drops, affecting system performance. Smaller particles improve surface area and adsorption efficiency but can cause clogging and lower permeability, especially in wastewater containing suspended solids or organic matter. These trade-offs underscore the significance of careful system design to translate material performance into operational effectiveness.

## 6.3. Pilot-Scale and Real Wastewater Applications

Pilot-scale studies are crucial in bridging laboratory research and full-scale implementation by assessing biochar performance under real environmental conditions [136]. Despite their importance, such studies are limited, with most research still at the bench scale. Existing pilot applications reveal that biochar's effectiveness often diminishes and becomes more variable compared to laboratory results, mainly due to competing ions, organic matter, and fluctuating contaminant levels. In actual wastewater systems, pollutants like heavy metals and organic compounds create competitive adsorption effects that reduce TC removal efficiency [29]. Additionally, natural organic matter can block adsorption sites and change surface chemistry, while variations in pH and ionic strength influence both TC forms and biochar surfaces. These factors cause performance inconsistency, complicating predictions based solely on lab data. However, studies that combine biochar with advanced oxidation or membrane filtration—hybrid treatment methods—show improved removal and system stability [27,137]. Such integrated approaches demonstrate biochar's potential as part of multi-barrier systems rather than a stand-alone treatment.

## 6.4. Economic and Environmental Considerations

The economic feasibility of biochar deployment largely depends on feedstock availability, production methods, and regeneration needs. One key benefit of biochar is its low production cost, since it can be made from plentiful and inexpensive biomass like agricultural residues and industrial waste [39]. However, advanced modification techniques, such as chemical activation and metal doping, can significantly raise production costs and may limit large-scale use.

Also, despite promising lab-scale performance, the scalability of engineered biochar remains a major challenge. Large-scale production requires a continuous feedstock supply, which may be constrained by regional biomass availability. Apart from feedstock supply, high-temperature pyrolysis and chemical activation processes (e.g., KOH, ZnCl<sub>2</sub>) are energy-intensive [138–140] and may introduce environmental and economic burdens. It is important then to take into account the environmental footprint associated with chemical modification, secondary pollution and reagent recovery. These factors suggest that while high-performance engineered biochars are achievable, their large-scale deployment requires optimization toward low-cost, energy-efficient, and environmentally benign production pathways.

Regeneration and reuse further affect economic viability. Although many engineered biochars show promising regeneration performance, maintaining adsorption efficiency over multiple cycles often requires chemical or thermal treatments that add costs and energy use [114]. Thermal regeneration, in particular, can consume a lot of energy and may reduce the cost benefits of biochar compared to traditional adsorbents. From an environmental standpoint, biochar provides advantages like carbon sequestration and waste valorization, supporting circular economy principles. However, these benefits must be weighed against potential environmental risks, such as the release of contaminants or metal leaching during use and disposal [126]. A full life-cycle assessment is therefore needed to determine the overall sustainability of biochar-based treatment systems.

## 6.5. Barriers to Practical Implementation

Despite its promise, the widespread use of engineered biochar for TC removal faces several obstacles in real-world scenarios. Matrix interference remains a key issue, as coexisting ions, organic matter, and multi-contaminant interactions decrease adsorption efficiency and make process optimization more complex [12]. The absence of

standardized testing protocols also hampers cross-study comparisons, complicating the establishment of consistent performance benchmarks and design standards [39]. Regeneration issues continue to pose problems, especially in maintaining long-term structural stability and adsorption capacity through repeated cycles. Fouling agents buildup and irreversible contaminant binding can impair performance over time, requiring frequent regeneration or replacement. Furthermore, scale-up challenges such as reactor design, hydraulic management, and integration with existing treatment systems represent significant engineering hurdles. Most critically, the scarcity of pilot-scale and long-term field data limits confidence in the practical deployment of biochar technologies.

To overcome these challenges, it is important to adopt integrated research approaches that combine material design, process engineering, and practical validation. Emphasizing standardized testing under real-world conditions, developing cost-effective regeneration methods, and incorporating biochar into hybrid systems are crucial for broader application. By harmonizing structural enhancements with operational requirements, engineered biochar can serve as a more practical solution for removing tetracycline from complex water treatment environments.

## 7. Future Directions and Research Needs

Although there have been notable improvements in engineered biochar for removing tetracycline (TC), several important research gaps remain that need to be filled to ensure successful application beyond laboratory settings. These include standardizing experiments, designing better materials, integrating systems, developing predictive models, and guaranteeing long-term environmental safety as outlined in Table 7. Overcoming these challenges calls for moving from focusing solely on material optimization to adopting comprehensive, application-oriented research approaches.

**Table 7.** Gaps and future directions.

Gap Area	Description	Future Research Directions	Justification	Research Priority	Ref
Standardization of Biochar Preparation and Modification	The lack of standardized protocols for biochar preparation and modification makes it challenging to compare adsorption performance across studies.	Develop and adopt standardized preparation and modification protocols, including pyrolysis temperature, activation agents, and doping methods, to enable consistent benchmarking of biochar adsorbents.	Diverse methods with varying energy inputs and complexity hinder scalability and reproducibility, limiting practical application	High	[24,47,126]
Mechanistic Understanding in Real Wastewater Matrices	Predominant mechanistic studies are conducted in idealized or synthetic solutions, lacking insights into complex interactions in real wastewater with multiple co-contaminants.	Conduct systematic, mechanistic studies using real wastewater samples to elucidate adsorption and catalytic degradation pathways, including the role of biochar aging and fouling.	Real wastewater matrices contain competing ions and organic matter that affect adsorption and degradation, yet these effects are underexplored	High	[28,47,141]
Influence of Coexisting Pollutants and Natural Organic Matter.	Insufficient data on the impact of coexisting pollutants such as heavy metals, anions, and natural organic matter (NOM) on the adsorption of tetracycline and biochar regeneration.	Investigate competitive and synergistic adsorption mechanisms in multi-contaminant systems, focusing on NOM effects and long-term stability of adsorption sites.	Co-contaminants and NOM can inhibit or promote adsorption, affecting biochar performance and regeneration, but their roles remain inadequately characterized	High	[26,104]
Regeneration and Long-Term Stability of Modified Biochars	Limited studies on regeneration efficiency beyond a few cycles and the impact of repeated use on biochar structural integrity and adsorption capacity.	Develop and optimize regeneration methods that maintain biochar performance over extended cycles; assess structural and functional changes post-regeneration.	Some modifications lead to a rapid decline in regeneration efficiency and potential secondary pollution, impeding practical reuse	High	[87,126]
Scale-Up and Economic Feasibility Assessments	Scarcity of pilot-scale or field studies evaluating biochar application for tetracycline removal, including cost analyses and energy consumption.	Perform pilot-scale experiments and techno-economic analyses to evaluate the scalability, energy requirements, and cost-effectiveness of biochar production and application.	Most studies are lab-scale; energy consumption and preparation costs are significant barriers to commercialization	High	[38,39]

### 7.1. Standardized Testing under Realistic Conditions

A major challenge in current biochar research is the lack of standardized testing methods that replicate real water conditions. Most studies rely on simplified laboratory systems with single-solute TC solutions, controlled pH, and low ionic strength, which do not reflect the complexity of actual wastewater. As discussed in this review, factors such as coexisting ions, natural organic matter, and competing pollutants significantly influence adsorption processes and reduce removal efficiencies. However, differences in experimental setups (initial concentrations, contact times, and solution chemistry) make it difficult to compare adsorption capacities across studies. Future

efforts should focus on creating standardized evaluation protocols that incorporate realistic conditions, including multi-contaminant systems, variable pH, and representative ionic compositions. Moreover, reporting should include metrics beyond maximum adsorption capacity, such as stability over time, fouling resistance, and performance under continuous flow. Developing these standards will improve reproducibility and enable meaningful comparisons of biochar materials, ultimately facilitating their practical use.

### 7.2. Mechanism-Guided Biochar Design

While many studies have shown improved adsorption capacities through chemical activation and doping, material design remains mostly empirical rather than based on prediction. Current methods often focus on increasing surface area or adding functional groups without systematically linking these features to dominant adsorption mechanisms under real-world conditions. However, as discussed earlier, the effectiveness of biochar depends on a complex interaction between its structure and environmental factors, such as TC speciation, ionic strength, and coexisting contaminants [12,13,51,52]. Future efforts should use a mechanism-based design approach that explicitly connects feedstock choice, pyrolysis conditions, and modification techniques to specific interaction pathways like  $\pi$ - $\pi$  interactions, hydrogen bonding, and metal-ligand complexation [23,35]. This approach involves combining experimental data with advanced characterization methods, including spectroscopic analysis and surface chemistry mapping, to find active sites and understand binding mechanisms. Additionally, tailoring biochar properties to specific water matrices (rather than general optimization) will be essential for improved performance in real-world scenarios. These rational design strategies will support the development of materials with predictable, reliable adsorption behavior.

### 7.3. Integration with Existing Water Treatment Systems

While engineered biochar alone may not fully remove tetracycline in complex wastewater systems, integrating it with existing treatments offers a more practical approach. Hybrid systems that combine biochar adsorption with advanced oxidation processes (AOPs), membrane filtration, or biological treatments have shown improved removal efficiency and resistance to matrix interference [18,27,138]. Researchers could aim to optimize these systems by exploring the synergistic interactions between biochar and complementary technologies. For example, pairing adsorption with catalytic degradation can minimize desorption risks and boost contaminant removal. Including biochar in filtration systems or constructed wetlands may also provide cost-effective options for decentralized treatment. Examining reactor design, hydraulic conditions, and operational parameters at the process level will be crucial for scaling these systems. Incorporating biochar into a multi-barrier treatment approach can help overcome its limitations while capitalizing on its adsorption and catalytic properties.

### 7.4. Machine Learning and Predictive Modeling

The growing volume of experimental data on biochar properties and adsorption performance provides an opportunity to apply machine learning (ML) and predictive modeling for optimizing materials. Currently, research mainly depends on trial-and-error approaches, which are slow and may not fully capture complex interactions among various design variables. Nonetheless, emerging studies highlight the potential of data-driven methods to identify key factors influencing adsorption, such as surface area, functional group density, and solution conditions [27,138]. Future research should aim to expand ML applications to predict adsorption capacity and elucidate dominant mechanisms based on biochar characteristics and environmental conditions. These models, trained on existing datasets, could help identify optimal combinations of feedstock, pyrolysis parameters, and modification strategies for specific applications. Combining ML with experimental design can also reduce extensive laboratory testing by guiding targeted synthesis of high-performance materials. Despite challenges like data standardization and model generalization, adopting predictive approaches is a promising way to accelerate innovation in engineered biochar systems.

### 7.5. Long-Term Stability and Environmental Safety

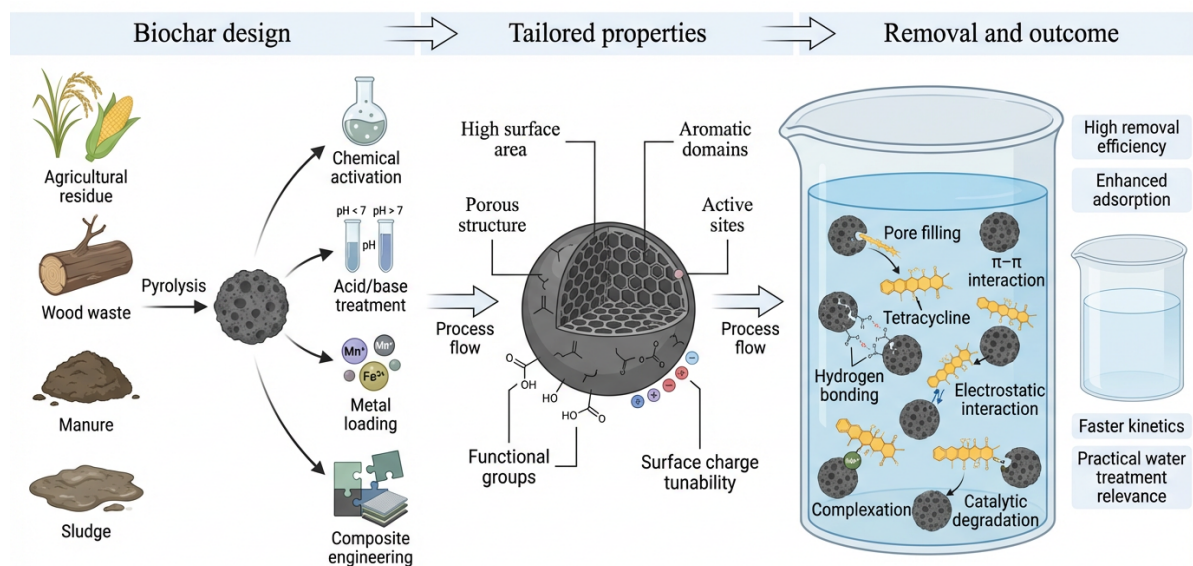
Long-term stability and environmental safety are crucial yet underexplored aspects of biochar application. While short-term studies demonstrate promising regeneration performance, there is limited data on biochar's durability over extended operational periods, especially in complex water matrices [142]. Repeated adsorption-desorption cycles can lead to structural degradation, loss of functional groups, and reduced adsorption capacity. Additionally, fouling by natural organic matter and co-contaminants further impairs performance [12]. Environmental safety concerns also arise from the potential release of adsorbed tetracycline or metal dopants during use and disposal. Metal leaching from modified biochars may introduce secondary pollutants, and

incomplete tetracycline degradation can result in persistent antibiotic residues and resistance risks [15,126]. Addressing these issues requires future research to adopt a life-cycle approach that evaluates long-term stability, leaching behavior, and ecological impacts under real-world conditions. Developing strategies for safe disposal or reuse of spent biochar (combining adsorption with catalytic degradation or integrating biochar into soil systems) is essential to minimize environmental risks. Additionally, implementing comprehensive risk assessments and regulatory frameworks will be crucial to ensure the safe, sustainable use of biochar in water treatment.

## 8. Conclusions

The increasing detection of tetracycline (TC) in water bodies underscores the urgent need for effective, sustainable, and scalable treatment strategies that address both the persistence of contaminants and the threat of antimicrobial resistance. This review highlights engineered biochar as a versatile and promising solution, owing to its customizable structure, multiple adsorption pathways, and catalytic breakdown potential. By examining how feedstock selection, pyrolysis parameters, and modification methods influence biochar, it's evident that its design significantly affects adsorption capabilities through mechanisms like pore filling,  $\pi$ - $\pi$  interactions, hydrogen bonding, electrostatic attraction, and metal-ligand complexation. Nonetheless, a critical insight is that laboratory results often do not directly translate to practical applications, as the complexity of natural water containing organic matter, various ions, and multiple contaminants can hinder adsorption efficiency. Additionally, challenges such as regeneration, long-term stability, and material degradation highlight the necessity of considering lifecycle performance and environmental safety.

This review introduces a structure-performance-deployment framework, summarized in Figure 5, that emphasizes the need to link material design to environmental complexity and practical constraints. To transition engineered biochar from laboratory breakthroughs to real-world applications, we must implement standardized testing, mechanism-based design, integration with current treatment systems, and long-term testing under real conditions. By aligning these elements, engineered biochar can evolve from a promising research material into a reliable, scalable solution for mitigating tetracycline pollution in complex aquatic ecosystems.



**Figure 5.** Conceptual framework of engineered biochar-mediated TC removal from water, illustrating the linkage between material design, physicochemical properties, and removal outcomes.

## Author Contributions

A.M.S.: contributed to conceptualization, literature search, data curation, writing of the original draft, and visualization. M.N.U.: contributed to writing, review and editing, visualization, validation, and technical input. D.H.K.: contributed to supervision, conceptualization, project administration, and writing—review and editing. G.O.: contributed to supervision, conceptualization, review, editing, and literature validation. All authors have read and agreed to the published version of the manuscript.

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## Data Availability Statement

The datasets used or analyzed during the current study are available upon request from the corresponding author.

## Conflicts of Interest

The authors declare no conflicts of interest that could have influenced the work.

## Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used QuillBot and Grammarly for language editing and to organize the document, enhancing the clarity and style of the scientific writing. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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