

Review

Biochar-Integrated Nature-Based Solutions for Pesticide Bioremediation in Urban Water Systems: Mechanisms, Applications, and Future Perspectives

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Abstract

Pesticide contamination in urban runoff, stormwater, and peri-urban drainage networks is an increasing concern because of the persistence, mobility, and ecological toxicity of many pesticide residues and their transformation products. Nature-based solutions (NBSs), including constructed wetlands, bioretention systems, biofilters, and permeable reactive bio-barriers, provide low-energy and ecologically compatible platforms for urban water treatment; however, their performance is often constrained by limited sorption capacity, substrate saturation, variable hydraulic loading, and incomplete degradation of persistent pesticides. Biochar offers a multifunctional amendment for strengthening these systems because its tunable porosity, surface functionality, mineral composition, redox activity, and microbial habitat-forming capacity can support pesticide adsorption, catalytic transformation, and biodegradation. This review critically evaluates biochar-integrated NBSs for pesticide-contaminated urban water systems by linking biochar production and modification strategies with pesticide removal mechanisms, biochar–microbe interactions, engineered treatment configurations, and field-scale applicability. A comparative synthesis is provided across material-level mechanisms, system-level performance, machine learning-assisted prediction, techno-economic feasibility, life-cycle impacts, and environmental risk considerations. By integrating material properties, removal mechanisms, NBS configurations, predictive modeling, sustainability assessment, and risk considerations, this review provides a broader comparative basis than previous studies focused mainly on individual aspects of biochar-based pesticide remediation. Future priorities include standardized biochar production, long-term field validation, spent-biochar management, ecotoxicological assessment, and data-driven optimization of biochar-assisted NBSs.

Keywords: biochar; nature-based solutions; pesticide bioremediation; urban water management; green infrastructure



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1. Introduction

Pesticide contamination of aquatic systems has emerged as one of the most pressing environmental challenges of the modern era, threatening ecosystem integrity, water security, and human health while directly hindering progress toward multiple United Nations Sustainable Development Goals (SDGs), particularly those focused on clean water, sustainable agriculture, and environmental protection [1]. The unprecedented intensification of agricultural production has driven extensive global pesticide use; however, the inefficiency of pesticide application results in up to 80–90% of applied chemicals failing to reach their intended targets, instead dispersing into surrounding ecosystems through runoff, leaching, spray drift, and subsurface transport [2]. Consequently, pesticides and their degradation products are now ubiquitously detected in surface waters, groundwater, and drinking water resources, frequently occurring as persistent and complex contaminant mixtures [3]. This issue is particularly critical in urban and peri-urban water systems, where pesticide residues originate from multiple diffuse sources, including landscaped public areas, parks, roadside vegetation, residential zones, golf courses, urban agriculture, and pest-control activities. These contaminants are rapidly mobilized through impervious surfaces, stormwater drains, retention basins, and urban streams, frequently appearing as short-duration pollutant pulses during rainfall events [4]. Urban runoff is further complicated by fluctuating hydraulic loading, recurrent low-level pesticide inputs, co-occurring nutrients, hydrocarbons, metals, suspended solids, and dissolved organic matter, and limited hydraulic residence time for contaminant attenuation [5]. Moreover, many pesticide transformation products may exhibit greater mobility, persistence, or toxicity than their parent compounds, thereby intensifying ecological disruption and long-term public health risks [6,7]. Although conventional remediation technologies have been employed for pesticide removal, their practical implementation remains constrained by high operational and energy costs, variable removal efficiency for complex contaminant mixtures, and the possible generation of secondary pollutants or toxic residues [8]. These limitations highlight the need for sustainable, cost-effective, and adaptable treatment strategies specifically designed for the dynamic conditions of urban water systems, where conventional batch adsorption studies and agricultural runoff models do not adequately represent stormwater variability, substrate aging, clogging potential, biochar–microbe interactions, contaminant transformation, and long-term field performance.

In this context, biochar has rapidly emerged as a highly promising and sustainable remediation material due to its low-cost production, renewable feedstock sources, and multifunctional pollutant removal capabilities [9]. Produced from biomass wastes via thermochemical conversion processes such as pyrolysis or hydrothermal carbonization, biochar possesses tunable physicochemical properties including high surface area, hierarchical porosity, mineral-rich matrices, and diverse surface functionalities that enable multiple remediation pathways such as adsorption, redox transformation, hydrogen bonding, electrostatic interactions, and microbial facilitation [10]. Beyond acting solely as an adsorbent, biochar increasingly represents a multifunctional environmental platform that integrates pollutant sequestration, catalytic degradation, carbon sequestration, and circular waste valorization. At the same time, biochar performance is not universally positive, as removal efficiency, ecological safety, and long-term stability depend strongly on feedstock origin, pyrolysis conditions, modification chemistry, particle size, environmental matrix, and post-application aging. Therefore, a balanced assessment must consider not only adsorption and degradation benefits, but also studies reporting contaminant release, phytotoxicity, microbial disturbance, particle mobility, and secondary pollution risks. Despite rapidly expanding research interest, current scientific understanding remains fragmented. Most existing reviews primarily focus on isolated aspects such as adsorption performance, feed-

stock comparisons, or modification strategies, while often neglecting critical integration of biochar design parameters, environmental performance variability, large-scale engineering challenges, techno-economic feasibility, and predictive optimization frameworks. Moreover, the transformative potential of advanced engineered biochars, hybrid remediation systems, and machine learning-assisted process optimization remains insufficiently explored, despite their capacity to revolutionize pesticide remediation strategies [11,12]. Machine learning tools, including random forests, support vector machines, and neural networks, offer unprecedented opportunities to model nonlinear interactions among biochar properties, environmental variables, and pesticide chemistry, thereby accelerating rational material design and reducing experimental burdens [13].

Addressing these critical research gaps, this review provides a comprehensive and strategically integrated framework for biochar-based pesticide remediation by systematically linking biochar production technologies, structural properties, adsorption and degradation mechanisms, modification approaches, environmental applications, and sustainability considerations. Unlike prior reviews, this work uniquely emphasizes the convergence of engineered biochar systems, techno-economic scalability, circular economy integration, and emerging data-driven optimization strategies. By bridging fundamental mechanistic insights with practical deployment challenges and future technological innovations, this review offers researchers a forward-looking roadmap for advancing biochar from a promising laboratory material into a scalable, high-performance, and globally relevant solution for sustainable pesticide remediation and long-term water security.

2. Biochar-Mediated Mechanisms for Pesticide Removal

Over the past decade, biochar has emerged as a promising tool in remediation of environmental pollutants. Biochar acts as a dynamic bridge between physical and biological processes and plays a dual role by adsorbing pollutants and simultaneously creating a conducive environment for the microorganisms to degrade it. To acknowledge this dual role of biochar, it is necessary to understand how biochar is produced, what its properties are, and how these properties affect the pesticide removing ability of biochar.

2.1. Adsorption Mechanisms and Surface Interactions

Adsorption is a process by which pesticide molecules accumulate at the surface of biochar, driven by a combination of physical and chemical forces. The adsorption of pesticides onto biochar occurs via multiple mechanisms rather than a single process, each contributing to different extents, depending on target pesticide and biochar properties. The dominant interactions that govern pesticide adsorption onto biochar include π - π electron donor-acceptor interactions, hydrogen bonding, hydrophobic partitioning, pore filling, electrostatic interactions, van der Waals forces, and Lewis's acid-base interaction. Each of these mechanisms is discussed further, in detail.

One of the dominant interactions observed in biochar and aromatic pesticides is π - π electron donor-acceptor interactions. The condensed aromatic rings in high-temperature biochar acts as π -electron donors, while the electron-deficient aromatic rings in many herbicides and insecticides serve as π -electron acceptors. Density functional theory (DFT) calculations have continuously reported that π - π stacking contributes significantly to the overall adsorption. This interaction is prominently strong in pesticides such as atrazine and imidacloprid. The strength of this interaction increases with increase in pyrolysis temperature and depends on the electron density of both pesticide and biochar. High temperature of pyrolysis results in highly condensed, more graphitic carbon structures with increased π -electron availability [14]. "Like dissolves like"-based mechanisms take place in the case of hydrophilic and hydrophobic pesticides. Hydrogen bonding plays a significant

role in binding to hydrophilic or polar pesticides. The oxygen-containing functional groups on biochar surface such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (-C=O) groups, can form hydrogen bonds with nitrogen- and-oxygen rich moieties on pesticide molecules. This mechanism is particularly essential for remediation of pesticides that contain amine, hydroxyl, or carboxyl groups, including triketone and neonicotinoids pesticides [15], whereas the mechanism involved in the remediation of the non-polar pesticide is hydrophobic partitioning. These pesticides partition into the lipophilic domains of biochar, which are found majorly in high-temperature biochars that have lost most of their oxygen-rich functional groups [16].

The pore-filling mechanism works on a size-exclusion principle in which pesticide molecules that are small enough to enter the micro and mesopores of biochar become physically trapped. This mechanism depends on the pore-size distribution of the pesticide and the molecular size of the pesticide molecule [17]. The pyrolysis temperature and biomass selection play a critical role in determining the pore size. Electrostatic interactions are involved when either the biochar or target pesticide carry net charge. This interaction is highly dependent on the pH of the matrix, as pH determines whether the pesticide will exist in its anionic, cationic or neutral form. Similarly, the surface charge of the biochar dictates the shifts in pH due to protonation and deprotonation of its functional groups. The interplay between these two charge states can either increase or decrease the adsorption, making pH a critical parameter in remediation strategies [18]. Additionally, van der Waals forces, which are the weak temporary interactions, contribute to the adsorption in almost all systems. Along with these mechanisms, Lewis's acid–base interaction can also support other mechanisms for adsorption of pesticides onto biochar surface [19]. This mechanism is governed by electron donor–acceptor reactions between electron-rich and electron-deficient sites present on the adsorbent and adsorbate. Biochar surfaces contain heterogeneous acidic and basic sites whose abundance and strength depend strongly on feedstock type and pyrolysis temperature. Acidic sites are commonly associated with oxygen-containing functional groups such as carboxyl, lactone, phenolic hydroxyl, quinone, and carbonyl groups, whereas basic sites may arise from pyrone- or chromene-like structures, cyclic ethers, nitrogen-containing groups, inorganic mineral phases, or delocalized π -electrons on carbon basal planes [20]. These basic sites can behave as Lewis bases by donating electron density toward electron-deficient regions of pesticide molecules, while mineral- or metal-associated sites on biochar may act as Lewis acids by accepting electron density from heteroatoms such as N, O, S, or halogen-containing groups in pesticides. Site-modeling studies have shown that biochar acid–base behavior is not controlled by a single surface property, but by the combined concentration and strength of coexisting acidic and basic sites. A three-site model consisting of two acidic sites and one basic site was sufficient to describe the acid–base behavior of biochars derived from *Spartina alterniflora* and water hyacinth. The study also showed that increasing pyrolysis temperature progressively increased the concentration of basic sites, while acidic sites initially decreased and then increased, indicating that thermal treatment reorganizes the electron-donating and electron-accepting character of the biochar surface [21].

Van der Waals interactions represent an important non-specific physisorption mechanism in the adsorption of pesticides and other aromatic organic contaminants onto biochar- or biomass-derived adsorbents. These interactions arise from transient dipole-induced dipole attractions between the electron clouds of adsorbate molecules and carbon-rich surface domains of the adsorbent. Although individually weak, their collective contribution becomes significant when molecules are closely associated with pore walls, hydrophobic regions, and graphitized or lignocellulosic surface structures. This mechanism is particularly relevant for neutral, weakly polar, or hydrophobic compounds, where electrostatic

attraction is limited and adsorption is governed mainly by molecular contact, surface compatibility, and dispersive forces [22]. In a mechanistic study on naproxen adsorption using peanut shell-derived biosorbent, different operational and analytical approaches were applied to identify the dominant adsorption forces involved in interaction. The adsorption was only weakly affected by solution pH and ionic strength, indicating that electrostatic attraction was not the primary mechanism. In contrast, the adsorption capacity decreased from 55.1 mg/g at 25 °C to 45.6 mg/g at 40 °C and 35.9 mg/g at 55 °C, while thermodynamic parameters showed spontaneous and exothermic adsorption, with ΔG° values of approximately -21.1 to -21.7 kJ/mol and ΔH° of -14.9 kJ/mol. Desorption under alkaline water released 39.2% of adsorbed naproxen, further supporting the role of weak and partially reversible physical interactions. These findings indicate that van der Waals forces can serve as a major adsorption mechanism, particularly when charge-controlled interactions are limited. In biochar-assisted pesticide removal, such forces generally operate together with pore filling, hydrophobic partitioning, hydrogen bonding, and π -associated interactions to stabilize pesticide molecules at the solid–liquid interface [23].

2.2. Biochar Production and Key Physicochemical Properties

2.2.1. Production Strategies

Biochar is produced through the thermochemical conversion of biomass in an oxygen-limited environment, a process called pyrolysis (Figure 1). Any organic waste stream can serve as feedstock, and, by adjusting a few parameters, we can tune the final product to target specific applications. Feedstock selection is a fundamental decision in biochar production. Agricultural residues such as rice husks, corn straw, peanut shells, sugarcane bagasse, and forestry waste including wood chips, saw dust, pine needles, leaves, animal manure, and sewage sludge have been reported as promising feedstocks [24]. The characteristics of feedstock in terms of chemical composition, mineral content, and moisture dictate the biochar's quality, yield and how it interacts with pesticides and other pollutants. For instance, feedstock with high lignin content results in high biochar yield with better stability and porosity, due to lignin's thermal stability, which, in turn, produces complex, aromatic carbon structures that can persist in the environment for a prolonged duration and adsorb organic contaminants more efficiently [25]. On the other hand, cellulose and hemicellulose, being relatively less stable, can decompose at lower temperatures, producing substantial volatile gases that generate high porosity and surface area, although lower biochar yield. Biomass with high mineral content can generate biochar with a high ash content, which increases the nutrient value and pH of the biochar, and which can influence how it reacts with charged pesticide molecules. The elemental composition of biomass helps in the development of different functional groups on the surface of the biochar, which improves biochar's Cation Exchange Capacity (CEC) and its ability to bind various pollutants via chemical interactions [26]. The biomass is generally dried before conversion to biochar, as high initial moisture first needs to evaporate, which results in an unstable porous structure, thus reducing the biochar's affinity towards contaminants, as well as its stability in the environment.

One of the most influential parameters in shaping biochar's properties is pyrolysis temperature. At a temperature range between 300 and 400 °C, biochar retains oxygen-containing functional groups such as hydroxyl, carboxyl, and carbonyl groups, which become available for hydrogen bonding with polar pesticides. This biochar tends to have higher yields but low surface area [27]. With an increase in temperature, biochar undergoes an increase in carbonization. This is generally observed in biochar synthesized within temperature of 500–600 °C. With progressive carbonization, the surface area, along with the porosity, increases significantly, and the carbon matrix becomes more aromatic and

graphitic. These aromatic structure are important for π - π electron donor-acceptor interactions, which form the basis of the adsorbing mechanism for a wide range of pesticides. The H/C and O/C ratios drop significantly within this range, which imparts resistance to microbial degradation [28]. With a further increase in temperature, around $>700\text{ }^{\circ}\text{C}$, the density of oxygen functional groups starts to decline, which results in reduced chemical reactivity. However, the surface area can exceed $500\text{ m}^2/\text{g}$, enabling this biochar to trap large molecules. Higher temperatures typically result in biochar with higher ash content and alkaline pH, due to concentration of inorganic minerals [29]. Other than the pyrolysis temperature, heating rate, residence time and the choice of carrier gas influence the properties of biochar. Slow pyrolysis is defined by low heating rate ($<10\text{ }^{\circ}\text{C}/\text{min}$) and longer residence time, ranging from minutes to hours. During this process, biomass has ample time to develop a balanced internal structure, resulting in higher stability, increased aromaticity, and functional groups ideal for binding both polar (via hydrogen bonding) and non-polar (via π - π interactions) pesticides. Fast and flash pyrolysis use rapid heating rate, often exceeding $100\text{ }^{\circ}\text{C}/\text{min}$ and shorter residence time, ranging from seconds to a few minutes [30]. This method of biochar synthesis is optimized for bio-oil production and yields less biochar with different surface characteristics. Although small particle size results in better adsorption, such biochar has reduced structural integrity and is prone to pore blockage, due to dissolved organic matter, common in urban waste water [31]. Gasification takes place at temperatures of more than $700\text{ }^{\circ}\text{C}$ with limited oxygen. Gasification is often used for the production of syngas, in which biochar is a byproduct. This process results in highly activated biochar with extreme porosity and surface area. This type of biochar is highly efficient in the removal of non-polar pesticides through physical trapping in micropores [32]. Hydrothermal Carbonisation (HTC) is a process in which wet urban waste, such as sludge or food waste, is converted to biochar at $200\text{--}300\text{ }^{\circ}\text{C}$ under high pressure. It results in hydrochar which is found to be superior in removing polar pesticides and heavy metals via chemical complexation, using a dense layer of oxygen-rich functional groups. Hydrochar requires further activation via physical or chemical and/or microwave-assisted techniques to create its affinity towards non-polar organic contaminants [33].

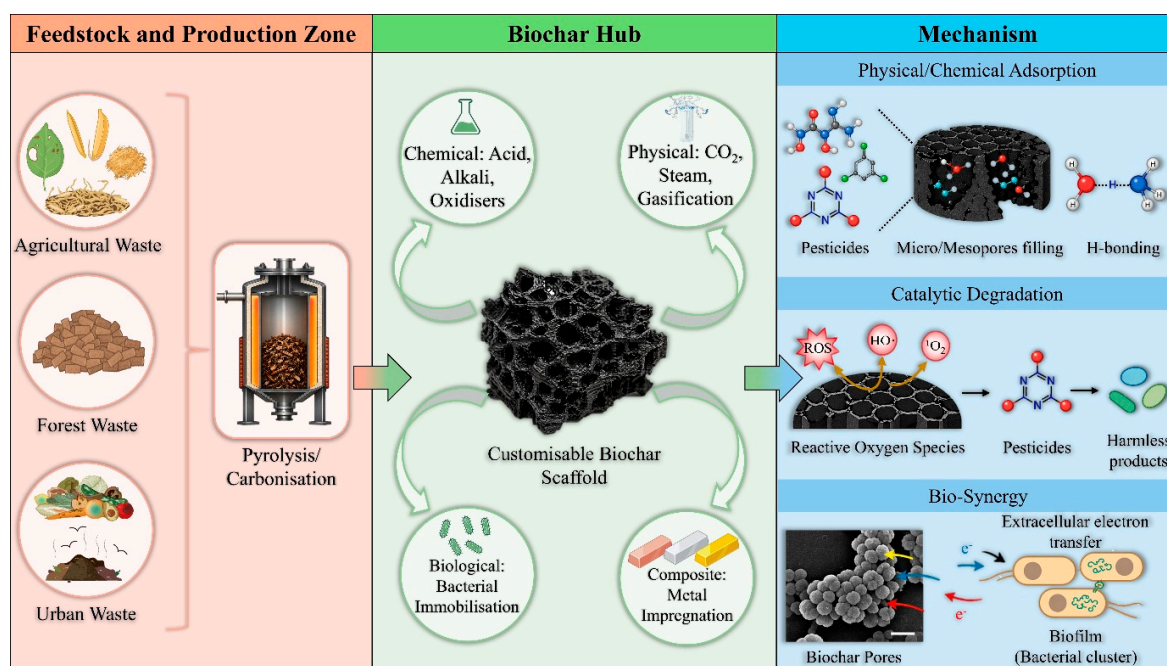


Figure 1. From Waste to Wealth—biochar production and its application in pesticide remediation. Figure prepared using bioRender premium account (<https://www.biorender.com/>).

2.2.2. Modification Strategies

Depending upon the feedstock and pyrolysis conditions, biochar can suffer from a range of limitations. Its surface area may be modest, and its pore size may be too small or too large to effectively trap the specific pesticide molecule of interest. The desired functional groups might be present in small numbers or can be of the wrong type, resulting in slow, limited adsorption affecting the performance of biochar across different water chemistries. Modification strategies including physical and chemical methods, nanoparticle and metal impregnation and microbial functionalization address each of these shortcomings in different ways (Table 1). Modified biochar has consistently exhibited higher adsorption capacity, better stability, and enhanced adaptability compared to its original biochar, making it a promising option for large-scale treatments [34].

Table 1. Comparative summary of biochar feedstocks, modification strategies, targeted pesticides, experimental matrices, and removal efficiencies.

Biochar Feedstock	Modification Strategy	Target Pesticides	Matrix	Efficiency	References
Rice husk	Pristine	Mixture—atrazine, chlorpyrifos, chlorfenvinphos, cyprodinil, diazinon, dimethoate, diuron, ethion, malathion, profenofos	Aqueous solution (competitive system)	Removal: 61–97% (highest for diuron/chlorfenvinphos ~97.6%, lowest for atrazine/dimethoate ~61%)	[1]
Date pit	Pristine			Removal: 56–95.4% (highest for diuron/chlorpyrifos ~95.4%, lowest for atrazine/dimethoate ~56%)	
Sugarcane bagasse	Pristine			Removal: 60.8–90.8% (highest for chlorpyrifos/malathion ~90.8%, lowest for atrazine/dimethoate ~60.8%)	
Cotton straw	MgO modification + N-TiO ₂ doping	Glyphosate	Aqueous solution (photo-Fenton system)	Degradation: 95.17% (100 min), adsorption capacity for phosphate: 33.62 mg/g	[35]
Cashew nut shell	KOH activation	Chlorpyrifos	Aqueous solution	Removal: 94.2% (optimum conditions: pH 6, dose 0.5 g/L, 120 min); adsorption capacity: 31.34 mg/g	[36]
Rice straw	α -Fe ₂ O ₃ + MgO co-impregnation	N-phosphonomethyl iminodiacetic acid (NPA)	Aqueous solution (photocatalytic)	Degradation: 90.1% (80 min); phosphate recovery: 82.3%	[37]
Orange peels	Iron oxide co-precipitation (nano-magnetized)	Chlorpyrifos	Aqueous solution	Adsorption capacity: 100 mg/g	[38]
Pomegranate peels	H ₃ PO ₄ activation + ball milling	Chlorpyrifos	Aqueous solution and real wastewater	Batch removal: 89.94% (real wastewater); column removal: 84.74%; adsorption capacity: 100 mg/g	[39]
Coconut shells	Pristine	Profenofos	Aqueous solution	Removal: 88% (initial conc. 20 mg/L, dose 1 g/L, 20 min)	[40]

Table 1. Cont.

Biochar Feedstock	Modification Strategy	Target Pesticides	Matrix	Efficiency	References
Walnut shell	Boric acid activation	Tricyclazole, propiconazole, imidacloprid, thiamethoxam	Aqueous solution (pH 3–9)	Adsorption capacities: tricyclazole 171.67 mg/g, propiconazole 112.27 mg/g, imidacloprid 156.40 mg/g, thiamethoxam 137.46 mg/g; removal >70% for all at pH 3–9	[41]
Sludge from lignocellulosic fermentation	Combined with ZnO	Lambdacyhalothrin (LM), malathion (MA), oxamyl (OX)	Synthetic wastewater	Removal (ZnO/BC, 0.4 g/L ZnO + 1 g/L BC, 135 min): OX 55%, MA 70%, LM 46.9% (vs. pristine ZnO alone: OX 38%, MA 30%, LM 24%)	[42]
Sugarcane filter cake	Pristine	Thiamethoxam	Aqueous solution	Removal: ~70% (60 min); adsorption capacity: 10.17 mg/g	[43]
Date seeds	H ₃ PO ₄ activation	Carbendazim, linuron	Aqueous solution and real municipal wastewater	Removal: carbendazim 92.6%, linuron 89.4%; adsorption capacities: carbendazim 28.3 mg/g, linuron 25.7 mg/g	[44]
Corn stalk	H ₂ SO ₄ modification	Atrazine	Constructed wetland (wastewater)	Removal: increased from ~50% (no biochar) to ~70% (with biochar bags)	[45]
Coconut fiber	HCl washing	Paraquat	Aqueous solution	Adsorption capacity: 12.74 mg/g; Freundlich K _f = 11.39 (mg/g) (L/mg) ^{1/n}	[46]
Agricultural waste-derived biochar (commercial)	Physical mixing (biochar + <i>Chlorella vulgaris</i> + activated sludge)	Chlorpyrifos (CPF) and cypermethrin (CYP)	Synthetic wastewater	CPF removal: 87.2%; CYP removal: 93.4% (initial 0.5 mg/L each, 72 h); Langmuir Q _m : CPF 5.72 mg/g, CYP 6.32 mg/g	[47]
Coconut fiber	Biological (immobilization of <i>Pseudomonas putida</i> via adsorption method)	Paraquat	Aqueous solution	Removal: 94.49% (30 mg/L, 35 h); q _e (kinetic) = 15.81 mg/g	[48]
	Biological (immobilization of <i>P. putida</i> via covalent binding with glutaraldehyde)	Paraquat	Aqueous solution	Removal: 90.61% (30 mg/L, 35 h); q _e = 16.79 mg/g; bacterial retention 60.7%	
Corn straw	Biological (immobilization of <i>Bacillus cereus</i> MZ-1 by adsorption)	Imazethapyr	Aqueous solution	Removal: 79.85% (200 mg/L, 3 d); adsorption capacity of BC500 alone: 11.62%	[49]
<i>Phragmites australis</i> (common reed)	Biological (biochar-immobilized bacterial consortium CB2H)	Chlorpyrifos (CPF) and bispyribac-sodium (BIS)	Agricultural runoff water (lab-scale)	CPF removal: >99% (>9.9 mg/L); BIS removal: 84% (8.4 mg/L); pseudo-first-order k = 0.097 day ^{−1} (CPF)	[50]

One of the oldest methods of biochar activation is physical activation, in which biochar is exposed to an oxidizing gas such as steam or carbon dioxide, or air at high temperatures ranging from 600 °C to 900 °C. This gasification widens the existing pores and creates new pores throughout the process [51]. For herbicides such as atrazine and terbutylazine, activated biochar derived from agricultural waste like hazelnut shell and rice husks have demonstrated significant increase in adsorption capacity compared to non-activated counterpart [52]. Although no chemicals are involved in this process, making

it a clean process, it requires high temperatures and specialized equipment, increasing the cost. Chemically, biochar can be activated via pre-carbonization activation or post-synthesis activation using alkali, acids and oxidizing agents, leaving their own signature on biochar. Alkali activation is mostly performed using potassium hydroxide (KOH), as it results in ultra-high-surface-area carbons. KOH reacts with carbon at high temperatures, generating potassium carbonate, potassium oxide, and metallic potassium, all of which become intercalated into the carbon matrix and then are removed, leaving behind a highly porous structure [53]. For pesticide removal, sodium hydroxide activation of date-seed biochar enhanced the removal efficiency of 2,4-D herbicide from 33.6% to 89.3%, under optimized conditions [54]. Similarly, KOH activation of poplar-wood biochar (PBC) enhanced adsorption performance toward four neonicotinoid insecticides, namely imidacloprid, acetamiprid, clothianidin, and dinotefuran, as well as sulfoxaflor, a sulfoximine insecticide that also acts on insect nicotinic acetylcholine receptors (nAChRs), thereby demonstrating the broader applicability of alkali-activated biochar for structurally related systemic insecticides [55]. Agents such as phosphoric acid (H_3PO_4), hydrochloric acid (HCl), or nitric acid (HNO_3), are used in acid activation, in which oxygen-containing functional groups are introduced onto the biochar surface [56]. Pilot scale and field studies have demonstrated that H_3PO_4 -activated biochar significantly retains pesticides like atrazine and glyphosate, extending the lifespan and efficiency of constructed wetlands [57]. Similarly, treating wheat-straw-derived biochar with acid resulted in the removal of mineral matter, which made the biochar superabsorbent and capable of trapping organic pollutants with different levels of hydrophobicity [58]. The choice of method depends on the target pesticide, since acid activation increases the abundance of carboxyl groups, whereas alkali activation increases hydroxyl groups. Activation via oxidizing agents makes use of hydrogen peroxide (H_2O_2), potassium permanganate (KMnO_4), or ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$] to modify the biochar surface. It introduces oxygen-rich functional groups without increasing the porosity of the biochar [59]. H_2O_2 -modified biochar (HPBC-700) demonstrated a 46.3-fold increase in adsorption capacity for the herbicide tembotrione. Density functional-theory calculations showed that the carboxyl groups on the surface of modified biochar were involved in dual hydrogen bonds with the herbicide [60]. Another strategy to modify biochar is via impregnation of metal or metal-oxide nanoparticles into the biochar, which not only just adsorb pesticides but also catalyze its degradation via surface-mediated reactions or via activating oxidants. One of the most studied metals for biochar modification is iron, as it provides additional adsorption sites, can catalyze Fenton-like reactions, and can be recovered due to its magnetic property [61,62]. Iron-modified base-activated biochar (FeBBC) derived from sugarcane bagasse demonstrated 92% removal of imidacloprid from an aqueous solution, with adsorption happening through both physical and chemical mechanisms [63]. The properties of iron-modified biochar also depend on which state of iron—nanoparticles, magnetite, maghemite, or iron oxyhydroxides—is incorporated, each imparting different capabilities to biochar. Bimetallic modification takes advantage of synergistic effects between different metal species. X-ray photoelectron spectroscopy of Fe-Mn biochar derived from sugarcane bagasse revealed that 2,4-D removal occurred mainly via Fe^{3+} -carboxylate complexation, while adsorption of picloram involved weaker polar and van der Waals interactions. The composite was able to maintain constant removal efficiency across pH 2–10, showing remarkable robustness, as compared to unmodified biochar [64]. Copper oxide-modified biochar supported on reduced graphene oxide (Cu/MPBC/rGO) has shown promising results in the removal of neonicotinoid pesticide from water [65]. Boron-modified biochar was developed to remove imidacloprid with boron doping and optimized pore structure and surface functionality to mediate rapid pore filling and stronger electrostatic interactions. This biochar was found to be stable in extreme environmental conditions, ensuring

its long-term applicability [66]. Chitosan-modified graphitic biochar (NBC900) was able to adsorb 140.1 mg/g of imidacloprid, achieving 97.2% removal efficiency. Characterization studies revealed that nitrogen groups, specifically pyridinic nitrogen, act as electron donors involved in strong Lewis acid–base interaction with electron-accepting groups on the pesticide molecule. The biochar showed consistent performance across pH 2–11, even after multiple regeneration cycles, marking strong resistance to interference from common ions [67]. Biochar can act as a catalyst when modified appropriately, resulting in active conversion of harmful organic pollutants into harmless products. When biochar is added to the water containing persulfate, it can generate reactive oxygen species such as sulphate radicals ($\text{SO}_4^{\cdot-}$), hydroxyl radicals ($\text{HO}\cdot$), and singlet oxygen ($^1\text{O}_2$), which non-selectively attack and degrade organic pollutants. Under optimized conditions, hardwood biochar pyrolyzed at 700 °C was able to achieve over 90% removal of both pesticides, lindane and β -endosulfan, within 4 h. Singlet oxygen radicals and sulphate radicals, along with hydroxy radicals were responsible for degradation of lindane and β -endosulfan, respectively [68]. Unlike adsorption, catalytic degradation achieves true detoxification. Biochar-based catalyst are solid, recoverable and generally eco-friendly, unlike many homogenous catalyst that leach into water, causing secondary pollution.

2.3. Biochar–Microbe Interaction and Biofilm Formation

The porous structure of biochar provides a sheltered microenvironment where microorganisms can thrive, even under extreme conditions. The same pores that trap pesticide molecules also create refuge from predators, competition, and environmental stressors such as temperature extremes or pH fluctuations. Recent studies show that biochar-supported microbial systems can be transformative solutions for persistent organic pollutants, due to superior adsorption capacity with microbial degradation capabilities [69]. The extracellular polymeric substances (EPSs) released by bacteria play a significant role in the adhesion onto biochar via biofilm formation. This EPS enhances the microbial resistance to environmental stressors, facilitating pollutant degradation. The four fundamental mechanisms of microbial–EPS–biochar interactions are adhesion and interfacial processes, shelter and nutrient transfer, signaling and bioregulation, and microbial electron transfer with biochar. The synergistic effects of these interactions improve pollutant removal capacity and soil fertility [70]. These interactions can simultaneously improve both pollutant removal and soil fertility—at least under laboratory-controlled conditions. However, the scenario becomes complex when we take into consideration real urban water systems. Urban runoff brings unique challenges such as sudden changes in flow rate, fluctuating pH and dissolved oxygen, low temperatures in cold seasons, and mixtures of pesticides, heavy metals and organic matter [71]. Under these conditions, the standard mechanisms fail. For example, EPS production can be inhibited by low temperatures or high salinity, reducing biofilm formation, and thus microbial retention, on the biochar [72]. The type and concentration of EPSs vary widely among microbial species and even strains, and not all EPSs are equally efficient at promoting adhesion or resisting force exerted by flowing water.

The graphitic structures and redox-active quinone moieties in biochar can mediate extracellular electron transfer between microorganisms and pollutants. This shuttling function can bypass rate-limiting steps in microbial metabolism, accelerating biodegradation of redox-sensitive pesticides. Recent work on nano-magnetite-loaded biochar in anaerobic digestion has further shown that magnetic biochar can improve microbial activity, process stability, and functional microbial interactions, supporting the broader concept that mineral-modified biochars can act as conductive and microbially favorable interfaces in biological treatment systems [73]. In constructed wetlands amended with fungus-Fe/Mn biochar, the redox-active $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{2+}$ species additionally promote electron

transfer and rhizosphere iron plaque formation, improving pollutant sequestration and in situ degradation. Removal of imidacloprid (32.78%) was facilitated by both substrate adsorption and microbial degradation, with enhanced production of degradation metabolites in biochar-amended systems [74]. Metagenomic analysis revealed increased microbial diversity dominated by *Rhodococcus* and *Pseudomonas*, along with pesticide degradation genes such as p450 (cytochrome P450 monooxygenases) and mnp (manganese peroxidase) [75]. Recent studies comparing pellet-form and chip-form biochar revealed that the physical form of biochar influences bacterial immobilization efficiency and subsequent degradation efficiency. The residual ash content of biochar supplies essential macro- and micronutrients such as phosphorous, potassium, calcium, and magnesium, along with dissolved organic carbon, supporting initial microbial establishment before the system reaches steady state [76,77]. Over the last five years, many studies using biochar-immobilized bacteria have been conducted for the remediation of pesticides in soil, as well as the remediation of metals, dyes, and pharmaceutical waste in waste water. While biochar–microbe–EPS interactions hold real promise, the current understanding is still superficial when applied to urban water conditions. More critically, most studies lack direct comparisons between different biochar types under identical urban exposure scenarios. Without such comparative work, it is difficult to separate the effects of biochar properties from those of water chemistry and microbial community composition. Future research should explore pilot-scale urban stormwater studies with realistic mixtures of contaminants, variable temperatures, and natural microbial consortia.

3. Biochar-Integrated Nature-Based Systems

Urban water systems face mounting challenges from stormwater runoff, emerging contaminants, and the limitations of conventional grey infrastructure. Nature-based solutions (NBSs), including constructed wetlands, bio-retention systems, and biofilters, offer low-energy alternatives for urban water management (Figure 2). However, their performance often suffers from substrate saturation and incomplete contaminant retention [78]. Biochar integration addresses limitations. Its porous structure and abundant functional groups adsorb nutrients, heavy metals, and organic contaminants from water, improve water infiltration, sustain beneficial microorganisms that contribute to pollutant removal, and improve carbon sequestration [79]. Unlike activated carbon, biochar can be produced locally from municipal waste, supporting circular-economy goals [80]. When added to NBS substrates, biochar enhances filtration, supports microbial growth, and increases hydraulic conductivity. This section reviews biochar integration across four NBS platforms, namely, constructed wetlands, biochar–microbe-augmented bio-retention systems, and biochar-based biofilters and permeative reactive bio-barriers.

3.1. Biochar-Amended Constructed Wetlands

Constructed wetlands (CWs) are engineered systems that mimic natural wetland processes to treat wastewater [81]. They are recognized as a cost-effective, efficient, and sustainable solution for pollution control, particularly in developing countries where treatment costs are a major constraint [82]. A CW functions through the complex, synergistic interactions among its substrate, vegetation, and the associated microbial community. The traditional and emerging substrates play a foundational role by supporting plant growth and providing a surface for biofilm formation, which is critical for pollutant degradation [83]. However, traditional substrates (sand, soil, and gravel) often have a limited capacity to adsorb specific contaminants, and their performance can be inconsistent [84]. Integrating biochar as a substrate amendment has become a key strategy to enhance CW performance [85,86]. Similar studies reported that biochar exhibits high

adsorption capacity for fipronil ($K_d > 500$ L/kg), and the adsorbed pesticide could be partially desorbed, indicating potential for regeneration and reuse of the spent biochar [87]. A comparative study found that subsurface-flow CWs containing biochar removed 90–99% of chlorantraniliprole (CAP) mass from agricultural runoff, whereas planted systems without biochar achieved less than 13% removal, underscoring the critical role of biochar specific surface area ($400 \text{ m}^2/\text{g}$) and hydrophobic interactions with CAP. Biochar also increased the hydraulic retention time and promoted the growth of CAP-degrading bacteria, such as *Sphingomonas* and *Rhodococcus* [88]. Other studies have also reviewed the application of modified biochars in CWs for the simultaneous removal of pesticides and antibiotics from wastewater. The studies reported that NaOH-modified corn-straw biochar integrated into vertical-flow constructed wetlands achieved sulfamethoxazole (SMX) removal efficiencies of (98.16–99.55%) [89]. Furthermore, H_3PO_4 -modified corn-straw biochar achieved a maximum atrazine removal efficiency of 96%, whereas physically modified *Merremia vitifolia* biochar exhibited a maximum (2,4-D) removal efficiency of 80%. The enhanced removal performance was attributed to the synergistic effects of adsorption and microbial degradation [90].

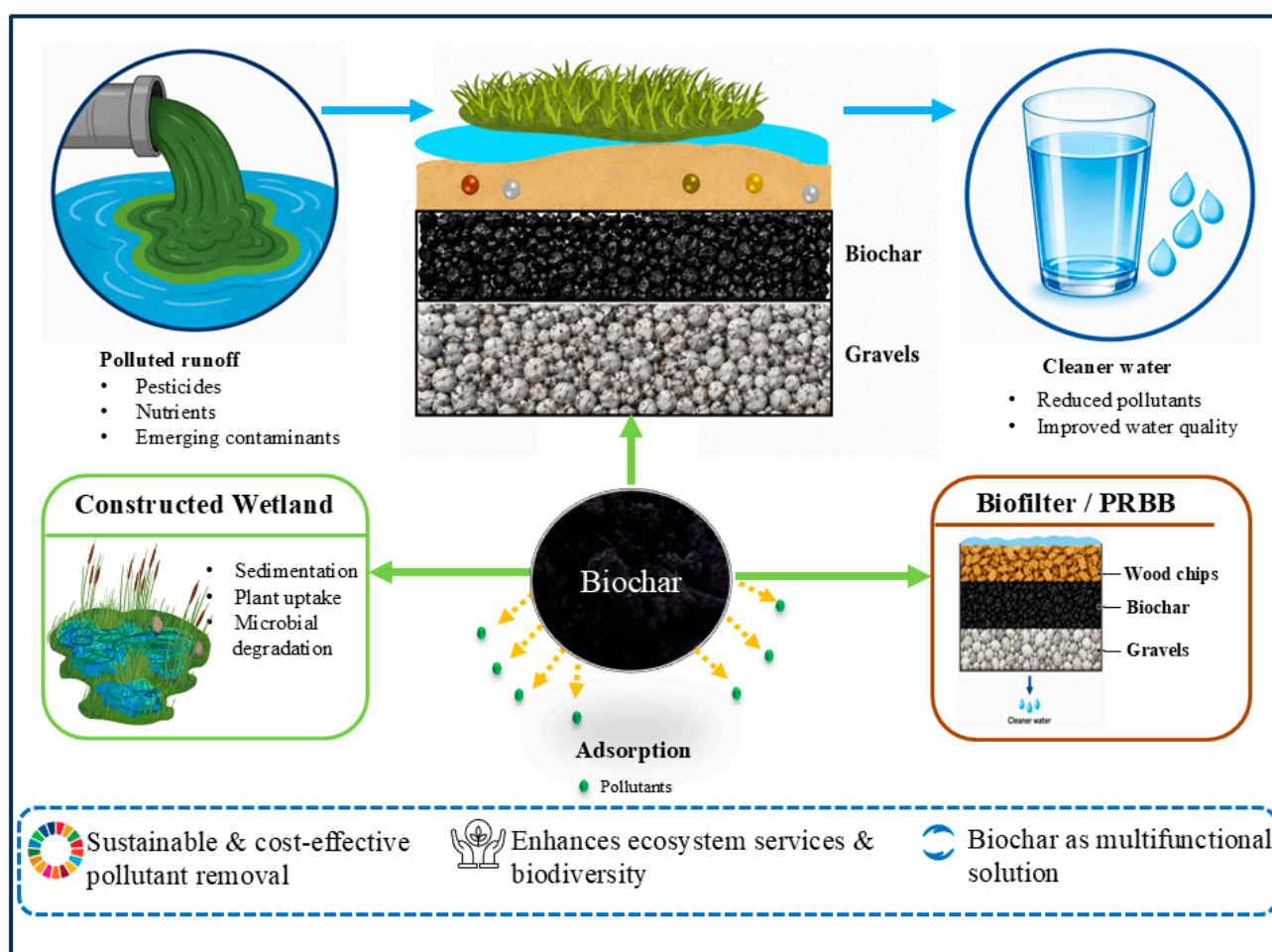


Figure 2. Conceptual framework of biochar-integrated nature-based systems for pollutant removal. Figure prepared using bioRender premium account (<https://www.biorender.com/>).

3.2. Biochar–Microbe-Augmented Bioretention Systems

Agricultural runoff delivers fertilizers, pesticides, and other agrochemicals into surface and groundwater systems, posing a significant source of diffuse pollution. Bioretention systems—vegetated, engineered facilities that treat stormwater and runoff through filtra-

tion, adsorption, and biological processes—offer an effective nature-based solution for mitigating these contaminants. However, conventional bioretention systems face inherent limitations, including variable contaminant-removal efficiency and the challenge of maintaining active microbial populations capable of degrading persistent organic pollutants [69]. The integration of biochar with specific pollutant-degrading microorganisms creates a synergistic dual-mechanism system. When combined with specific pollutant-degrading microorganisms, biochar acts as both a protective carrier and an adsorbent, allowing microbes to persist and perform biodegradation while the biochar simultaneously traps contaminants. This biochar–microbe synergy, often termed biochar-immobilized microbe (BIM) technology, enhances remediation efficiency by integrating physical adsorption with biological transformation. In addition to improving degradation pathways, biochar–microbe systems also influence the hydraulic performance of bio-retention units [91]. The presence of biochar enhances water retention and increases residence time, thereby improving contact between pesticides, microbial communities, and reactive surfaces. For organophosphate insecticide chlorpyrifos, *Aeromonas veronii* immobilized on rice-husk biochar achieved 96.25% removal in contaminated water within 24 h, and 92.4% removal in soil within 42 days, through synergistic adsorption and microbial degradation [92]. Studies investigated the removal of triclocarban (TCC) from agricultural runoff using a pilot-scale bioretention ditch amended with rice husk-biochar. Among three configurations which tested biochar only, biochar with free microbial cells (enriched with *Comamonas* and *Alcaligenes*), and biochar with pre-immobilized cells, the free-cell system achieved the highest removal (35%), followed by the immobilized-cell system (33%), whereas biochar alone removed only 20% under continuous flow, with a hydraulic retention time of 12 h, and influent TCC 500 µg/L [93]. Similar studies for imazethapyr, a long residual herbicide with high solubility, low soil-adsorption coefficient, and an average half-life of 90 days, used corn-straw biochar produced at 500 °C as a carrier for degrading strain *Bacillus cereus* MZ-1. The prepared immobilized system achieved a maximum imazethapyr removal efficiency of 79.85%, with enhanced detoxification efficacy against herbicide-induced harm in sensitive oilseed rape crops, surpassing the effects of using MZ-1 or biochar alone [49].

3.3. Biochar-Based Biofilters and Permeable Reactive Bio-Barriers

Adsorption using biofilters has emerged as a promising and cost-effective approach for pesticide removal, complementing conventional treatment methods by integrating physical adsorption with microbial degradation [94]. Biochar-based biofilters are engineered systems using biochar combined with sorbents like vermiculite and wood chips, offering high surface area, functional groups, and strong sorption capacity for pesticide removal. These systems are valued for their simplicity, operational efficiency, and use of sustainable, low-cost adsorbents derived from agricultural by-products [95]. These systems consist of stacked containers filled with a substrate containing microbial biomass capable of degrading active organic components present in wastewater. These biofilters remove pesticides through a synergistic combination of physicochemical adsorption and microbial biodegradation. Studies demonstrated this mechanism over six years in South Tyrol, where a stacked box biofilter achieved 98–99% pesticide reduction [96]. Degradation occurred primarily in the uppermost box via adsorption and microbial activity, through persistent compounds exceeded regulatory limits, indicating the need for further optimization. Studies demonstrated that a field-scale biofilter (biochar:vermiculite:wood chips, 1:1:1) achieved up to 99.98% glyphosate removal and >96% removal of other pesticides, with enhanced performance in vegetated systems, due to synergistic adsorption and rhizosphere-driven degradation [97].

Permeable reactive bio-barriers (PRBBs) are advanced in situ groundwater remediation systems that combine physicochemical processes with microbial activity to enhance contaminant removal [98]. Unlike conventional permeable reactive barriers (PRBs), which rely mainly on adsorption and precipitation, PRBBs incorporate materials that support microbial proliferation via bioaugmentation or biostimulation, enabling contaminant removal under both aerobic and anaerobic conditions [99].

4. Artificial Intelligence and Machine Learning

The increasing complexity of pesticide contamination in urban water systems, characterized by simultaneous exposure to pollutants, and fluctuating hydraulic conditions, poses substantial challenges for conventional empirical and mechanistic modeling approaches. Artificial intelligence (AI) and machine learning (ML) have emerged as effective complementary frameworks for capturing the nonlinear, multi-variable interactions that govern pollutant removal in biochar-integrated NBSs (Table 2). This section offers a critical assessment of four interrelated AI/ML approaches as applied to biochar-mediated pesticide remediation: artificial neural networks (Section 4.1), tree-based ensemble methods and support vector machines (Section 4.2), hybrid mechanistic–ML frameworks (Section 4.3), and digital twin systems that enable real-time monitoring and adaptive control (Section 4.4).

Table 2. Performance metrics of ANN and related ML models for biochar-based pollutant adsorption. All R^2 and MSE values are directly taken from the cited primary studies.

Target Pollutant/System	Model(s)	n	Best Model	Best R^2	Key Input Variables	References
Tetracycline on biochar	RF, ANN, GBDT, XGBoost	295	RF	0.9625	SBET, pore vol., O/C, H/C, T, pHsol, C_0 ratio	[100]
Tetracycline on biochar	ANN	295	ANN	0.941	Same as above	[100]
Biochar-AC from waste wood (iodine no.)	ANN, RF, XGBoost, SVM	108	ANN	0.96 (MSE 0.004017)	Activation time, temp., agent type/ratio	[101]
Organophosphorus pesticides on biochar	XGBoost, RF, ensemble	Lab-based	XGBoost	0.981 (test)	Pyrolysis T, pH, SBET, pore volume, pesticide conc.	[102]
Biochar yield and composition (pyrolysis)	MLP-NN vs. ANFIS	Multi-feedstock DB	MLP-NN	Up to 12.7% better than ANFIS, RF/XGBoost	Pyrolysis T, volatile matter, N content	[103]

Notes: RF = Random Forest; ANN = Artificial Neural Network; GBDT = Gradient Boosting Decision Tree; MLP = Multi-Layer Perceptron; ANFIS = Adaptive Neuro-Fuzzy Inference System; SBET = BET-specific surface area; AC = Activated Carbon; T = Temperature; C_0 = initial molar concentration ratio; n = Data size.

4.1. Artificial Neural Networks (ANNs) for Prediction

Artificial neural networks (ANNs) are computational frameworks inspired by biological systems that replicate the information-processing capabilities of the human nervous system through layers of interconnected processing nodes [104]. Among the earliest and most widely utilized AI models for adsorption systems, ANNs, especially multilayer perceptrons, are recognized for their capacity to approximate complex nonlinear relationships without relying on predefined equations. In biochar systems, ANNs can effectively incorporate a variety of variables such as surface area, pore volume, elemental ratios, pyrolysis temperature, solution pH, dosage, and contaminant concentration, making them particularly useful in situations where adsorption is affected by multiple interacting factors [103,105]. Several studies have reported impressive results from ANN models. For example, ANN frameworks have successfully predicted iodine number, adsorption capacity, and the qual-

ity of activated biochar sourced from waste biomass. These ANN techniques have also been applied upstream to biochar production, leveraging feedstock composition and pyrolysis parameters to estimate yield, carbon content, and physicochemical properties [101].

4.2. Machine Learning Models (Random Forest, SVM) for Optimization

Random Forest (RF), gradient boosting techniques, XGBoost, and Support Vector Machines (SVM) have emerged as the leading ML techniques for biochar water-treatment applications. These algorithms generally outperform ANNs, particularly when datasets are small-to-moderate, noisy, or heterogeneous [106]. Tree-based models offer significant benefits, since they automatically assess feature importance, enabling researchers to pinpoint the variables that crucially influence removal performance [102,107]. Across multiple studies, both RF and boosting models have consistently achieved excellent prediction accuracy for the adsorption of metals, antibiotics, and pesticides onto biochar. In tetracycline adsorption systems, RF and XGBoost performed slightly better than ANNs, suggesting that these models can capture complex adsorption behavior more effectively, while lowering the chances of overfitting [100]. Additionally, for the adsorption of organophosphorus pesticides, XGBoost achieved nearly perfect predictive accuracy, highlighting its strong applicability for pesticide-specific datasets [102].

One significant advancement provided by these models is the mechanistic insight gained through the feature ranking [101]. Consistent key factors that emerge include surface area, pore volume, pore diameter, cation-exchange capacity, oxygen-containing functional groups, pyrolysis temperature, pH, and influent concentration [108]. This repeated evidence across a variety of pollutants indicates that the primary goal for pesticide-focused nature-based solutions (NBSs) should be engineering biochar with an emphasis on high surface area, optimized porosity, and reactive surface chemistry [107,109–111]. Moreover, ML techniques have been utilized beyond batch adsorption. In vertical-flow constructed wetlands containing biochar, RF, and support vector machine (SVM) models have successfully predicted effluent quality and nutrient removal. Systems utilizing biochar media often showed more stable and predictable treatment performance than conventional mineral media. This is highly relevant to urban stormwater treatment, where variability in hydraulic conditions demands resilient and intelligent substrate design [109].

4.3. Hybrid (Mechanistic–ML) Modeling

Although ML models are strong at making predictions, they do not inherently respect physical principles such as mass conservation, transport dynamics, or sorption thermodynamics [112]. In contrast, purely mechanistic models provide interpretability but oversimplify real systems and require challenging parameter calibration. Hybrid mechanistic–ML models effectively combine the strengths of both methodologies, and are being increasingly acknowledged as the future framework for modeling environmental processes [113]. In biochar pesticide treatment, the mechanistic aspect usually includes advection, dispersion, and adsorption kinetics, while the ML aspect addresses residual effects resulting from surface heterogeneity, biofilm activity, competitive sorption, or aging processes. This integrated approach improves the reliability of extrapolating results under varying field conditions [114,115]. Physics-informed neural networks (PINNs) are among the most sophisticated techniques for modeling. These models incorporate governing partial differential equations directly into the training process, ensuring that predictions adhere to transport and adsorption laws while learning from limited data. PINNs have demonstrated considerable potential for modeling concentration breakthrough curves, estimating unknown kinetic constants, and reducing the reliance on extensive experimental

data. Such functionality is particularly beneficial for stormwater biofilters and constructed wetlands, where monitoring data is often scarce [114,115].

Hybrid frameworks have been improved with the addition of explainable AI tools such as SHapley Additive exPlanations (SHAP). These approaches elucidate the influence of individual variables on predictions and consistently demonstrate that factors such as surface area, pore volume, pH, dosage, and contaminant loading dominate treatment efficiency. Thus, hybrid models not only boost accuracy, but also provide interpretable insights for biochar design and process control [116].

4.4. Digital Twins and Real-Time Monitoring

Digital twins (DTs) represent the highest level of AI integration in biochar-based NBSs. A digital twin acts as a constantly updated virtual replica of a physical treatment system that receives real-time sensor data, forecasts future conditions, and recommends, or automatically implements, operational actions. For pesticide remediation, DTs could transform passive treatment systems into intelligent infrastructure [117,118]. A digital twin for biochar wetlands or biofilters would integrate data regarding hydraulic flow, residence time, adsorption capacity, microbial breakdown, and influent contamination patterns into a unified dynamic platform. Real-time data streams from sensors tracking flow, turbidity, conductivity, pH, dissolved oxygen, and weather conditions can continuously update the virtual model [109]. With the limited availability of affordable online pesticide sensors, developing soft sensors utilizing ML becomes crucial. These models estimate pesticide concentrations indirectly, relying on surrogate variables and algorithms such as Long Short-Term Memory (LSTM), RF, or XGBoost. This approach enables nearly continuous estimation of contaminants without the need for expensive chromatographic systems [119].

The operational benefits of digital twins include predictive control during storm events, establishing early warning systems for detecting breakthroughs, optimizing flow routing, scheduling media replacements, and implementing energy-efficient pumping strategies. Examples from the water sector have shown that DTs can reduce overflow volumes, improve anomaly detection, and enhance overall plant management. These successes strongly advocate for the future application of DTs in biochar-based pesticide treatment systems [120]. However, several obstacles persist, including the lack of pesticide-sensing technologies, the high computational costs associated with real-time hybrid simulations, the absence of standardized data architectures, and the uncertainties associated with long-term biochar aging. Addressing these challenges will require concerted advancements in IoT sensing technologies, interoperable databases, and adaptable modeling frameworks [121]. The transition from ANN models to ANN models to multi-model learning, hybrid physics-informed systems, and digital twins highlights an increasing sophistication in the deployment of AI for environmental remediation. ANN models initially demonstrated their predictive capabilities. Subsequently, ANN models for multi-model learning improved both the robustness and interpretability. Hybrid models effectively merged statistical learning with physical realism, while DTs now offer the potential for autonomous and adaptive treatment systems [120,122]. For pesticide removal using biochar-integrated NBSs, the most promising future strategy lies in an integrated intelligence approach, rather than relying on a single approach. This would involve explainable multi-model learning models for material design, PINNs for process simulation, and DTs for field-scale operations. Such integration could facilitate predictive maintenance and rapid optimization under varying inflow conditions, and support evidence-based regulatory compliance.

5. Sustainability Assessment

5.1. Techno-Economic Evaluation (TEA)

The biochar-integrated nature-based systems discussed in Section 3 demonstrate significant potential for pesticide removal; however, their large-scale implementation is governed by both treatment efficiency and economic feasibility. Techno-economic assessment (TEA) is therefore essential to establish quantitative relationships between system performance, cost, and operational parameters, enabling systematic evaluation of the feasibility of biochar-based technologies for urban water treatment (Figure 3) [123].

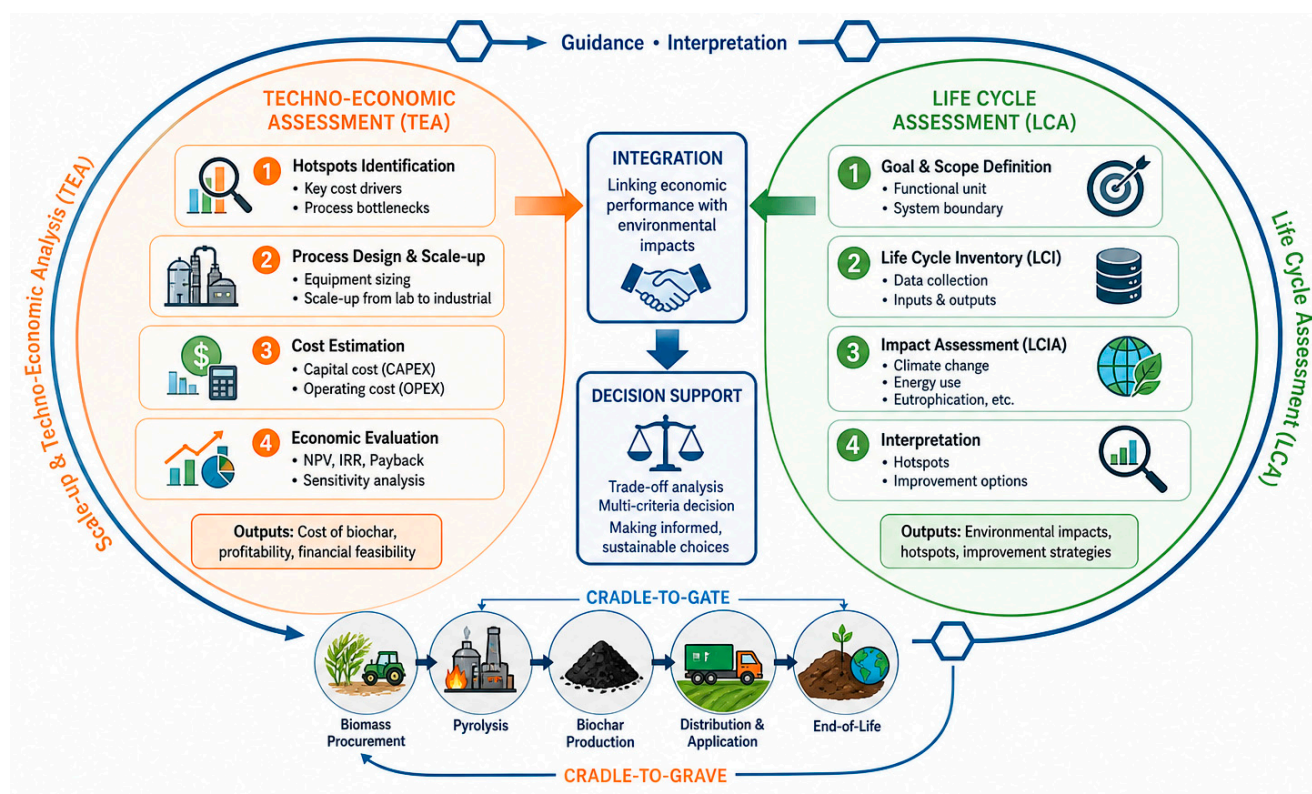


Figure 3. Integrated techno economic analysis (TEA) and life cycle assessment (LCA) for sustainable biochar system. Figure prepared using bioRender premium account (<https://www.biorender.com/>).

Recent TEA studies on biochar production highlight key economic drivers influencing overall system viability. Continuous pyrolysis systems with processing capacities of ~10 tons/h typically require capital investments (CAPEX) in the range of 15–25 million USD, while operating expenditures (OPEX) are dominated by labor, maintenance, and energy inputs [124]. The minimum selling price of biochar is generally reported within ~400–1000 USD/ton, with biochar sales contributing ~85–95% of total revenue, whereas energy co-products provide comparatively minor economic returns [125]. Sensitivity analyses indicate that feedstock cost (30–100 USD/ton) and biochar yield are critical parameters influencing net present value. From a treatment perspective, biochar exhibits high efficiency at relatively low dosages. Typical application rates of ~1 g/L achieve 70–90% removal of pesticides within 20–60 min, depending on feedstock and surface characteristics. Surface modification markedly improves the removal performance of biochar. In a recent comparative analysis, pristine biochars showed adsorption capacities ranging from 0.56 to 80.3 mg/g, whereas modified biochars achieved much higher capacities, ranging from 10.92 to 1723 mg/g [126]. This large improvement indicates that engineered surface features, such as increased active sites, altered surface charge, enhanced functional groups, and improved pore accessibility, play a critical role in strengthening biochar–pollutant

interactions and overall removal efficiency [127]. In integrated systems such as biochar-amended constructed wetlands and biofilters, removal efficiencies improve from ~50% to ~70%, while coupling with microbial processes further enhances removal by ~30–50%, due to synergistic adsorption–biodegradation mechanisms [128]. Field-scale evaluations further support the economic viability of biochar systems. For example, biochar–microbe integrated systems enhance process efficiency, achieving >90% removal of pesticides such as paraquat and chlorpyrifos, with performance improvements of 31–48%, compared to standalone adsorption or biodegradation processes. These enhanced removal rates translate into reduced hydraulic retention time and improved treatment throughput, which are critical factors in TEA [97]. Economically, the use of low-cost biomass feedstocks and relatively low dosage requirements (~1 kg/m³ of treated water) support cost competitiveness compared to conventional adsorbents such as activated carbon [129]. Additionally, the potential for regeneration and reuse of biochar across multiple cycles can further reduce operational costs. However, overall feasibility remains sensitive to modification costs, variability in wastewater composition, and long-term material stability. These factors underscore the need for optimized system design, standardized production, and large-scale validation to ensure reliable and economically sustainable implementation of biochar-based pesticide-removal technologies.

5.2. Life Cycle Assessment (LCA)

Life cycle assessment (LCA) is a standardized analytical framework used to quantify the environmental impacts associated with a product, process, or system, across its entire life cycle (Figure 3). It is based on a systematic accounting of material and energy flows, enabling evaluation from resource extraction and material production to operation and final outputs. The methodology follows four interconnected stages: (i) definition of the study objective and system boundaries, (ii) compilation of an inventory of inputs and outputs, (iii) quantification of environmental impacts across selected categories, and (iv) interpretation of results to identify key contributing processes and improvement opportunities [130]. This structured approach ensures consistency, transparency, and comparability across different systems. In wastewater treatment applications, LCA is commonly applied using a functional unit such as 1 m³ of treated water or per unit mass of contaminant removed, allowing direct comparison of treatment efficiencies. The inventory phase includes inputs such as feedstock, chemicals, and energy, along with outputs such as treated effluent, emissions, and recovered products [131]. Impact assessment then translates these flows into indicators such as global warming potential, eutrophication, toxicity, and resource depletion [132]. For pesticide-contaminated wastewater, which is typically characterized by elevated chemical oxygen demand (COD) and persistent organic compounds, LCA provides a means to relate treatment performance with environmental implications. In biochar-based systems, this is particularly important as the process combines material production (biochar synthesis and modification) with treatment functions such as pesticide adsorption, COD reduction, and potential energy recovery. The analysis allows identification of dominant contributors, often highlighting the influence of biochar production and operational energy demand on overall environmental performance [133].

Life cycle-based evaluation of a biochar-integrated system for pesticide-contaminated wastewater highlights improvements in pollutant removal and energy recovery. For a treatment volume of 1 m³, the addition of ferromagnetic biochar (~0.2 g/L) enhanced pesticide degradation and significantly improved COD removal, leading to better overall treatment efficiency compared to the control system. This was accompanied by a ~74.7% increase in methane production and an energy recovery of 6.18 kWh/m³, indicating effective conversion of organic pollutants into biogas. The improved COD removal

contributed directly to a higher carbon-reduction potential (~52.8% versus ~21.4% without biochar). However, biochar production can contribute to environmental impacts. Pyrolysis-related emissions have been documented to be approximately 86.9 kg CO₂ eq/tonne of dry biochar, mainly from electricity use, methane emissions, and LPG used for reactor preheating [134]. This highlights the need to optimize energy use, feedstock logistics, and process efficiency in a biochar-based treatment system. Biochar production contributed over 50% of total impact, while reducing the dosage of lowered emissions to ~1.16 kg CO₂ eq/m³ [135].

6. Challenges and Future Perspectives

6.1. Challenges

Despite substantial progress in biochar-based remediation technologies, several critical limitations continue to restrict their practical deployment for pesticide-contaminated water and environmental restoration. A major technical challenge is the heterogeneity of biochar physicochemical properties arising from variations in biomass feedstock, pyrolysis temperature, heating rate, residence time, and activation or modification methods [136]. These factors significantly alter pore architecture, aromaticity, mineral composition, surface functional groups, cation exchange capacity, and redox behavior, ultimately affecting adsorption capacity, selectivity, catalytic performance, and microbial interactions [137]. Such inconsistencies hinder reproducibility, process optimization, and the development of universally applicable remediation systems.

Modified biochars, including metal-oxide-doped, nanocomposite, and chemically activated variants, often demonstrate enhanced adsorption and catalytic degradation efficiencies; however, these modifications may also introduce environmental risks [82]. Potential leaching of metals, toxic by-products, persistent free radicals, or residual chemical reagents can generate secondary contamination risks, particularly under variable environmental conditions such as fluctuating pH, ionic strength and dissolved organic matter [138]. These concerns are not limited to modified biochars. Although biochar has considerable potential as a sustainable amendment for pesticide remediation, its application may introduce environmental risks when feedstock selection, production conditions, application dose, and post-treatment are not properly controlled. Biochars produced from contaminated biomass or under suboptimal thermochemical conditions may retain or generate hazardous constituents, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), dioxins, perfluorochemicals, volatile organic compounds, and environmentally persistent free radicals. These components may subsequently be released through leaching, runoff, wind-driven transport, abrasion, or environmental weathering, thereby enabling the transfer of biochar-associated contaminants across soil, water, and atmospheric compartments [139].

Recent risk-oriented assessments further distinguish between endogenous and exogenous risks of biochar application. Endogenous risks arise from pollutants inherited from the parent feedstock or formed during pyrolysis, whereas exogenous risks emerge after environmental application through pollutant adsorption–desorption, aging-induced surface transformation, colloidal transport, and nanobiochar formation. These processes may alter contaminant mobility and bioavailability and may adversely affect plants, soil and aquatic organisms, microbial communities, and, potentially, human health [140]. Biochar performance is also highly context-dependent: unsuitable biochar formulations, excessive application rates, high soluble-salt content, unstable mineral phases, residual phytotoxic compounds, or poor matching between biochar properties and site-specific conditions may suppress seed germination, impair early root development, modify microbial community structure, or reduce overall remediation efficiency [141]. Therefore, biochar-integrated nature-based solutions should not be considered universally risk-free. Their safe de-

ployment in pesticide-contaminated urban water systems requires systematic feedstock screening, optimization of pyrolysis temperature and residence time, contaminant leaching assessment, particle-size control, phytotoxicity and ecotoxicity testing, monitoring of aged or spent biochar, and integration of life-cycle assessment with regulatory quality standards.

These safety considerations are closely linked with the unresolved challenges of long-term performance and post-application management. Long-term aging processes, structural degradation, fouling, and contaminant desorption remain poorly understood, raising concerns regarding operational stability, regeneration efficiency, and disposal of spent biochar materials. Although biochar is frequently considered a lower-cost alternative to activated carbon, large-scale implementation may be constrained by energy-intensive pyrolysis processes, feedstock logistics, modification expenses, reactor design limitations, and maintenance requirements. In field systems such as constructed wetlands or filtration units, challenges including hydraulic clogging, reduced permeability, mechanical instability, and biochar recovery further complicate operational sustainability [142]. Additionally, insufficient field-scale demonstrations, limited techno-economic analyses, and lack of international regulatory standards for production, characterization, and application continue to impede commercialization. Addressing these challenges requires robust environmental impact assessments, life-cycle analyses, and regulatory frameworks, to ensure both technical feasibility and environmental safety [143].

In addition to material and field-scale constraints, the application of AI-based tools for predictive optimization of biochar-assisted pesticide remediation also presents methodological challenges. Although AI models can support material screening, performance prediction, and process optimization, hybrid systems require dependable governing equations, substantial computational resources, and high-quality calibration data gathered under realistic operational conditions. Their future effectiveness depends on pilot-scale datasets that reflect seasonal loading fluctuations, media aging, and microbial succession. These limitations are particularly evident for ANN-based models, which have been widely used for nonlinear prediction but remain constrained by data quality, model interpretability, and transferability across environmental conditions. Despite their predictive advantages, ANN models generally require relatively large and well-structured datasets and may be prone to overfitting when data are scarce, imbalanced, or unevenly distributed. Furthermore, these models provide limited mechanistic interpretability, as the learned weights lack direct physical significance. Their reliability may also decline when applied outside the range of the training data. In pesticide remediation, where experimental datasets are often scattered across different contaminant classes, biochar types, water chemistries, and operating conditions, these challenges have encouraged a shift toward more robust and interpretable ML methods [107].

6.2. Future Perspectives

Future research should prioritize the rational design of biochar materials with highly controlled physicochemical properties through standardized feedstock selection, optimized thermochemical conversion, and precision surface engineering. Tailoring biochar to specific pesticide classes and contaminant mixtures will require deeper mechanistic understanding of adsorption, electron transfer, surface complexation, and microbially mediated degradation pathways [144]. Advanced analytical tools such as synchrotron spectroscopy, molecular dynamics simulations, and density functional theory can significantly improve molecular-level insights into pollutant–biochar interactions, thereby guiding the development of next-generation functionalized biochar.

The integration of biochar into hybrid remediation platforms represents a critical advancement for overcoming limitations associated with standalone adsorption systems.

Combining biochar with photocatalysis, persulfate activation, advanced oxidation processes, membrane separation, electrochemical systems, and bioaugmentation strategies may create multifunctional treatment systems capable of simultaneous adsorption, catalytic transformation, and biological mineralization of pesticides and co-contaminants [124]. In particular, biochar-mediated electron shuttling and microbial habitat support can be strategically exploited to enhance biodegradation and redox-driven pollutant transformation [145]. Recent developments have also focused on multi-contaminant removal and integration with technologies such as electro kinetics to improve efficiency [146]. Despite their advantage, PRBB performance is influenced by complex biological, chemical, and hydraulic interactions, with challenges such as clogging, variable field conditions, and long-term stability limiting their widespread application. Most biofilter studies are limited to pilot or field-scale units, without standardized design. Future research should optimize multi-media configurations, integrate real-time monitoring, and validate performance under realistic environmental conditions and pesticide mixtures.

Emerging technologies such as artificial intelligence, machine learning, and process automation are expected to significantly accelerate optimization of biochar synthesis, predictive performance modeling, and large-scale operational management. AI-assisted process modeling can facilitate feedstock selection, performance prediction under variable environmental matrices, and adaptive treatment optimization for site-specific applications. To support commercialization, future studies must emphasize pilot-scale validation, regeneration technologies, circular-economy integration, and comprehensive sustainability assessments encompassing carbon sequestration potential, greenhouse gas emissions, economic viability, and resource efficiency [147]. The development of internationally accepted certification systems and regulatory guidelines will be essential for ensuring product consistency, environmental protection, and stakeholder confidence. Ultimately, biochar is expected to transition from a passive sorbent to an engineered multifunctional platform for integrated environmental remediation, climate mitigation, and sustainable-resource recovery.

7. Conclusions

Biochar has evolved from a conventional adsorbent into a multifunctional remediation platform capable of simultaneously immobilizing pesticides and enhancing their degradation through physicochemical and biological pathways. Its tunable structure, sustainability, and compatibility with advanced treatment systems position biochar as a powerful solution for pesticide-contaminated environments. However, realizing its full-scale potential requires overcoming challenges related to material standardization, environmental safety, long-term stability, and economic scalability. Future advances in engineered biochar design, green modification strategies, and hybrid remediation technologies will be pivotal in transforming biochar into a next-generation tool for sustainable pesticide remediation, environmental restoration, and circular resource management.

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