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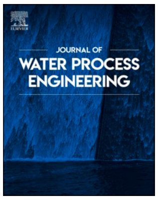

Biochar application in constructed wetlands for wastewater treatment: A critical review

Diksha Pandey [a], Shiv Vendra Singh [b,*], Nikhil Savio [a], Javed Khan Bhutto [c], R.K. Srivastava [a], Krishna Kumar Yadav [d,e], Rashmi Sharma [f], Tony Manoj K. Nandipamu [f], Binoy Sarkar [g,*]

[a] *College of Basic Sciences and Humanities, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar 263145, Uttarakhand, India*
[b] *Department of Agronomy, College of Agriculture, Rani Lakshmi Bai Central Agricultural University, Jhansi 284003, Uttar Pradesh, India*
[c] *Department of Electrical Engineering, College of Engineering, King Khalid University, Abha, Saudi Arabia*
[d] *Department of VLSI Microelectronics, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS), Saveetha University, Chennai 602105, Tamil Nadu, India*
[e] *Environmental and Atmospheric Sciences Research Group, Scientific Research Center, Al-Ayen University, Nasiriyah, Thi-Qar, Iraq*
[f] *College of Agriculture, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar 263145, Uttarakhand, India*
[g] *Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia*

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ABSTRACT

Constructed wetland (CW) is a cost-effective and ecologically sustainable technique for the restoration of polluted aqueous ecosystems through physical, chemical, and biological purification processes. The substrate of CWs is considered as the integral component that significantly influences the wastewater treatment efficacy and ecological associations. Biochar's high surface area and pore volume, suitable pore size distribution, high cation exchange capacity, surface functionality, fixed carbon, and stability along with low-cost availability enhance its potential application as an adsorbent besides ensuring microbiological diversity and stability in CWs. This review provides an overview of significant properties of biochar associated with bioremediation, biochar-plant-biological association and mechanisms involved in the efficient removal of organic and inorganic contaminants, emerging contaminants, and pathogens from wastewater under CWs. Biochar obtained from various feedstocks and pyrolysis conditions significantly influences the composition, functionality, porosity, surface properties, and stability of biochar, and hence its applicability and efficacy in CWs. Factors such as substrate properties, hydraulic retention, oxygenation, and redox condition also influence the pollutant removal efficiency in CWs. This review presents the feasibility and practicalities of biochar application in CWs and identifies the existing research gaps, uncertainties, and future research needs for large-scale wastewater treatment using biochar in CWs. Future research should evaluate biochar's long-term stability and performance in real-world CW settings. This includes modifying biochar properties for targeted pollutant removal and exploring synergies with technologies such as electrochemistry and advanced oxidation.

1. Introduction

Wetlands are sites where soil is regularly covered by water coming from surface or underground sources, to maintain saturated conditions [1]. They are transition zones with extensive stands of solvent-tolerant plants such as reeds, cattails, and bulrushes that are usually <0.6 m deep. Constructed wetlands (CWs) are an ecotechnology that relies on natural wetland dynamics for wastewater treatment [2]. These structures are widely used to purify a variety of wastewater, including decentralized domestic sewage, industrial wastewater, and refinery effluent. CWs have been shown to achieve not only conventional water quality indicators but also efficiency in the removal of emerging contaminants [3,4]. A wide range of wastewater, including raw sewage, effluent from sewage treatment plants, storm and agricultural runoff, polluted surface and underground waters, industrial and livestock wastewater, and acid mine drainage have been treated by CWs worldwide. Purified water can be reused for irrigation and landscaping, which can resolve the problem of water scarcity [5,6]. When wastewater circulates through CWs, pollutants can be microbially broken down, absorbed by adsorbents, immobilized in the matrix, and/or biodegraded

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* Corresponding authors.
E-mail addresses: shiv1992gbpuat@gmail.com (S.V. Singh), Binoy.Sarkar@unisa.edu.au (B. Sarkar).

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by aquatic macrophytes. Based on water flow, types of the CWs are Surface flow CW (SFCW) and Subsurface flow CW (SSFCW). Again, SSFCW can be divided into two wetland types, i.e., horizontal flow CW (HFCW) and vertical flow CW (VFCW). In SFCW, wastewater naturally flows over the top of the substrate layer. Along with improving water quality, it aids in flood prevention and shoreline erosion control. However, in SSFCW, the water flows below the substrate layer and remains in direct contact with the root zone. Moreover, the hybrid-built wetland is a system that uses both HFCW and VFCW as part of a multistage treatment process. In comparison to other types of CWs, the hybrid wetland poses higher removal efficiency for different wastewater contaminants [5,7]. Further, the rhizosphere of a plant with active oxygenic photosynthesis permits the transfer of oxygen to the rhizosphere zone where most of the reactions are taking place. Thus, each plant's root system is thought to be a miniature aerobic biological treatment system.

Microorganisms in CWs contribute to crucial activities including degradation and transformation of contaminants. Microorganisms remove pollutants from wastewater through biosorption, bioaccumulation, and speciation transformation even though these chemicals are often difficult to biodegrade [8]. Additionally, by boosting phytoremediation, microorganisms can increase the aquatic plants' tolerance to pollutants and enhance their removal effectiveness [9]. Essential to CWs is the substrate which provides reactive materials for pollutant breakdown, encourages plant growth, adsorbs pollutants, and acts as a surface for the production and attachment of biofilms. A short period is needed for gravel or sand packed CWs to efficiently eliminate nutritional contaminants from wastewater by encouraging the buildup of Ca, Fe, Al, and Mg with P. As a result, Ca, Fe, Al, and Mg dominant components are preferred for successful P removal and the system's life expectancy [10]. The selection of right substrates becomes essential for the efficient working of CWs. The performance of conventional substrate used in CWs is often unsatisfactory due to the poor pollutant entrapment capacity, and low microorganism attachment, suggesting the need to develop an alternative substrate.

Constructed wetlands (CWs) have traditionally relied on substrates such as gravel, sand, and soil to support plant growth and facilitate pollutant removal. However, these conventional materials often exhibit limitations in terms of pollutant adsorption capacity and overall treatment efficiency. For instance, studies have shown that gravel and sand substrates typically achieve only moderate removal rates for nutrients and heavy metals, often below 60 % [177]. This lower performance is attributed to their limited surface area and lack of chemical reactivity, which restricts their ability to adsorb and transform contaminants.

One significant research gap is the need for a deeper understanding of the interactions between traditional substrates and various pollutants under different environmental conditions. While some studies have explored these interactions, comprehensive data on the long-term stability and effectiveness of these substrates in diverse settings is lacking. Additionally, there is a need to investigate the potential for combining traditional substrates with innovative materials, such as biochar, to enhance CW performance. Biochar, produced via pyrolysis of organic materials, is increasingly recognized for its role in enhancing the efficiency of CWs for pollutant removal. The high surface area of biochar, often reaching 300 m^2/g, and its porosity provide extensive sites for the adsorption of contaminants, thereby improving the retention and treatment efficacy [11,141]. The cation exchange capacity (CEC) of biochar, reaching up to 150 cmol/kg, further elevates the adsorption and immobilization of contaminants [12,13]. Besides, biochar also facilitates microbial colonization in CWs, which is crucial for the biodegradation of organic pollutants [149]. Biochar being recyclable and cost-effective becomes an ideal substrate for CWs. Biochar helps to augment the performance of CWs because it serves as a carrier for microorganisms, provides large surface area and reactive sites for pollutants to adsorb [14], and can extend the life span of CWs. Recently, biochar has gained tremendous attention owing to its efficient bioremediation of both organic and inorganic contaminants from aqueous ecosystem [15–17]. Biochar has high adsorption potential due to huge surface area and porosity, pore size and pore distribution, high carbon content, mineral components, and diverse functional groups as compared to conventional adsorbents [18]. Biochar's influence extends to microbial activity, with studies indicating an increased microbial diversity and enzymatic activity in biochar-amended CWs, leading an efficient breakdown of complex compounds [19]. Furthermore, biochar influences the redox conditions in CWs, promoting the reduction and precipitation of certain metal(loid)s. This is particularly beneficial for treating metal(loid)-laden wastewater.

Numerous contemporary studies have reported the potential and mechanisms involved in biochar that led to eco-toxicant immobilization under the soil and aqueous ecosystems. However, documentation of knowledge on the multifunctional application of biochar in enhancing contaminants bioremediation under CWs is inadequate. Given the increasing curiosity and advantages associated with using biochar in CW treatment systems, it is imperative to get a comprehensive grasp of their functionality, associated processes, research findings and future application outlooks. The present compilation is among the first review papers of its kind promising to improve the existing knowledge base on the consolidated as well as interactive effects of biochar on contaminants immobilization through various interspecific reactions in CWs. This review encompasses the remediation of organic compounds, nutrients, heavy metals, pathogenic and emerging pollutants mediated by biochar-microorganism-plant interactions besides highlighting the significant environmental benefits. This paper also aims to explore the prospects and challenges and propose a future outline for using biochar coupled with other ingredients of CWs to attain the goals of effective remediation.

2. Bibliometric data collection, screening and analysis

In this study, Scopus database was used to access the articles, reviews, book chapters, and conference papers provided by publishers on the topic of "Biochar and Constructed Wetlands". The search queries on Scopus were: title – Biochar and Constructed Wetlands (250 documents); duration – 2000 to 2022 (198 documents); subject – Environmental Science, Chemical Engineering and Agriculture & Biological Sciences (189 documents); document type – article & review (180 documents); keywords – biochar, wetland, constructed wetlands, waste water treatment, charcoal (171 documents); language – English (151 documents). VOSviewer software (version 1.6.18.0) was used for analyzing and constructing bibliographic network of the obtained 151 scientific publications. Only two reviews were available on the topic "Biochar amended CWs/Biofilters". A keywords assessment showing a huge attention around the use of biochar in CWs for wastewater treatment is depicted in Fig. 1. Descriptive statistics, including mean and standard deviation, were carried out for determining the biochar mediated bioremediation efficiency of contaminants such as total N, NO_3^--N, NH_4^+-N, PO_4^{3-}, and heavy metals in CWs. Data were collected from relevant publications after a bibliometric analysis. Data were organized into categories, and a five-number summary (minimum, Q1, median, Q3, maximum) was obtained. Boxplots were generated using the Origin 2023 package with contaminant parameters on the X-axis and removal efficiency (%) on the Y-axis, highlighting the central tendency and variability.

3. Biochar-plant-microbe interaction under CWs

The interactive functions of different components such as biochar, microorganisms, and plants utilized in CWs can be further modified to increase their remediation efficacy and longevity. Phytoremediation alone is inhibited by the presence of high concentrations of pollutants in CWs. Most of the time, biochar does not remove organic contaminants by itself; instead, reduces their bioavailability through immobilization [20]. The presence of biochar helps to reduce the abiotic stresses

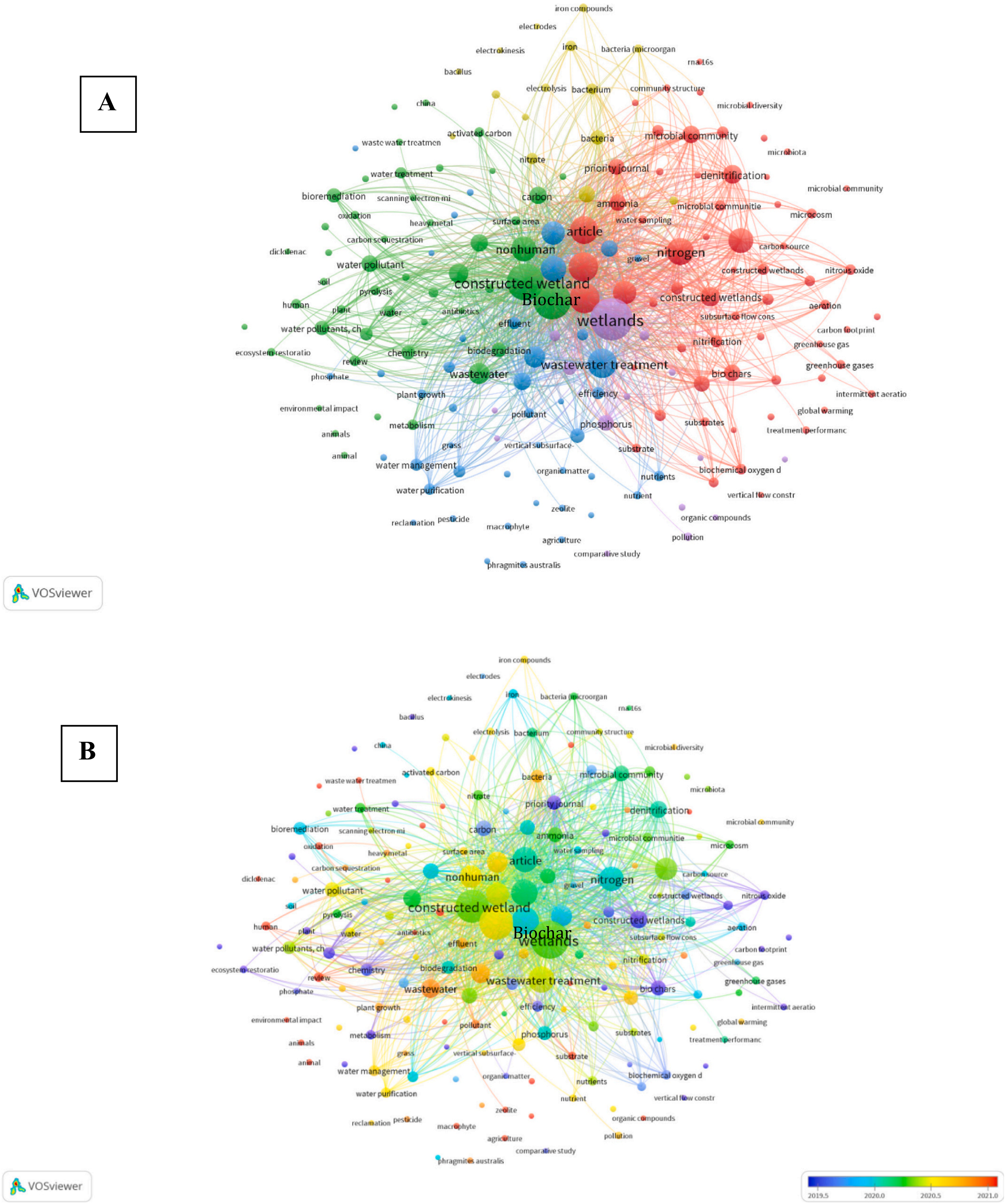

Fig. 1. Keyword analysis concerning the application of biochar for wastewater treatment: (a) co- occurrence network visualization, and (b) overlay visualization.

brought on by the contaminant, which significantly increases microbial survival, activity, and synergy of components (biochar–bacterium–plant) in the matrix [21]. Biochar provides a tenacious and instantly stable physical carbon framework to promote gas exchange and minimize pollution loads. Biochar offers several benefits, which have led to its use in wastewater treatment systems [22,23]. Because of the huge specific surface area and very porous structure, it provides reactive sites for microorganisms [24]. Other features of biochar include its ability to adsorb NH_4^+, NO_3^--N, and PO_4^{3-} from aqueous solutions, as well as remove suspended particles, metals, BOD, and coliforms from wetlands [25].

The organic pollutant removal pathways of plants, microbes, and biochar could contribute to 10, 28, and 34 % removal, respectively, within a vertical flow CW. The metabolic processes of microbes and macrophytes may be responsible for 38 % of the pollutant's removal. This may be owing to the important function of plants in the microcosm, i.e., providing surfaces, encouraging aeration and gas exchange in the root zone thereby promoting microbial activities. Additionally, the plant absorbs organic compounds and supplies carbon from the root secretions, improving the removal of organic matter. The contribution of chemical oxygen demand (COD) removal follows this trend: biochar > microbe > plant. In another research, Zhou et al. [26] found that sodium dodecyl sulfate (SDS) containing greywater was treated using lab-scale CWs that had been amended with a biochar substrate and run in tidal flow (TF) mode. Biochar-amended CWs considerably outperformed gravel-only CWs, particularly for NH_4^+-N. In addition to significantly enhancing the pollutant removal efficacy, TF also successfully reduced SDS stress in the CWs. The CWs achieved mean SDS removal rates of 75.3–79.3 %. In the CWs, the TF mode changed the metabolic rhythm and microbial community structure, and it increased the abundance of functional bacteria involved in N and P removal.

4. Mechanisms involved in biochar-led pollutant biodegradation

Plant species and microbes can increase the effectiveness of pollutant removal in CWs due to the synergistic interactions between biochar, plants, and microorganisms. Biochar-led treatment efficiency relies on three fundamental and interconnected processes, i.e., physical, chemical and biological pathways. The physical architecture of biochar establishes the foundational matrix, while biochar's surface properties drive chemical transformations of pollutants. The biocompatible nature of biochar supports diverse microbial communities in CWs. This multi-mechanism approach creates a dynamic treatment environment where pollutant removal occurs through concurrent pathways. By understanding how these mechanisms complement each other (Fig. 2), engineers and researchers can optimize biochar applications to achieve superior water treatment outcomes in CWs. Significant findings on various biochar-mediated inorganic, organic and emerging contaminants bioremediation and the mechanisms involved are reviewed in Table 1.

4.1. Physical mechanisms

The surface functionality of biochar in CWs is governed by its physicochemical architecture, which exhibits distinct characteristics based on pyrolysis conditions. Thermally induced structural

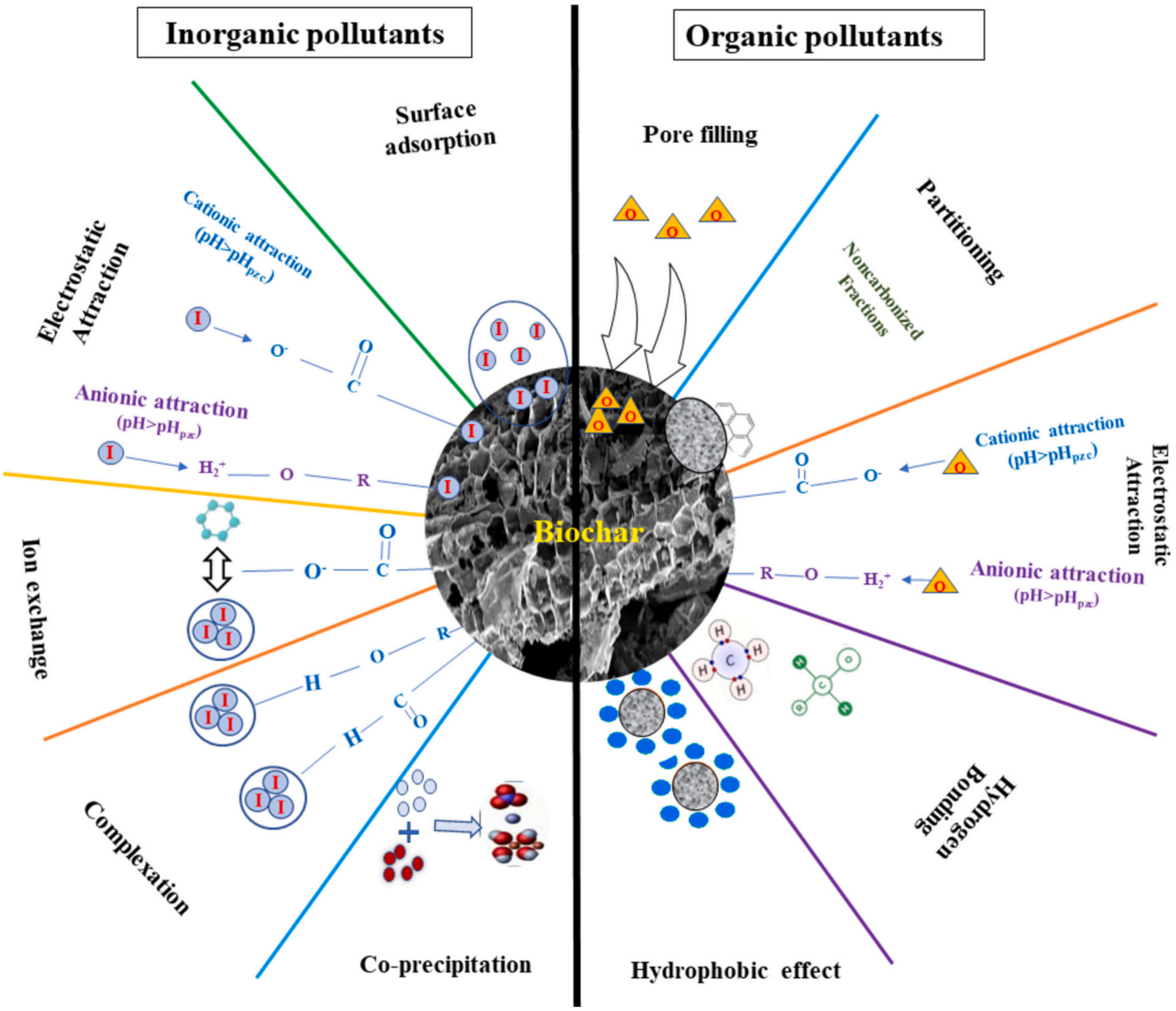

Fig. 2. Mechanisms involved in organic and inorganic pollutant bioremediation using biochar.

Table 1
Surface tailored biochar for pollutant removal and mechanisms involved.

Biochar		Modifications	Pollutants removed	Removal efficiency	Mechanism	References
Feedstocks	Pyrolysis temperature (°C)					
Rice straw	400 °C	Zero-valent iron	Cr(VI)	40.0 mg g^{-1}	Electrostatic attraction	[27]
Municipal sludge	900 °C	Pristine	Cr(IV)	7–20 mg g^{-1}	Surface sorption, ion exchange	[28]
Herb residue	400 °C	Iron oxide	Cr(VI)	23.9 mg g^{-1}	Precipitation	[29]
Pineapple peel	750 °C	Nickel and manganese oxyhydroxides	Cr(VI)	7.4 mg g^{-1}	Ion exchange	[30–33]
Eggshell	450 °C	Bamboo, hickory, and peanut hulls	Pb	103–261 mg g^{-1}	Electrostatic attraction	[34]
Celery biomass	350–500 °C	Pristine	Pb	288–304 mg g^{-1}	Ion exchange, complexation precipitation	[35]
Hickory wood	600 °C	$KMnO_4$	Cu(II)	34.2 mg g^{-1}	Surface sorption	[171]
Swine manure	800 °C	MnO_2	Cd(II)	45.8 mg g^{-1}	Ion exchange	[36]
Pomegranate-peel	600 °C	NaOH	Cr	16.2 mg g^{-1}	Surface adsorption	[37]
Rice straw	450 °C	Alkali-modified	Cd^{2+}	99.0 %	Chemisorption	[38]
Bamboo biochar	300–700	Pristine	*N*-nitrosodimethylamine	61.68 %	Hydrophobic interaction	[39]
Palm kernel shell	660 °C	Ferrous chloride and ferric chloride	4-Nitrotoluene	23.9–59.9 mg g^{-1}	Electrostatic interaction	[40]
Bamboo hydrochars	200 °C	Graphene oxide and graphite	Congo red	90.5 g g^{-1}	π–π interaction	[41]
Pine sawdust biochar	700 °C	Fe_3O_4	Sulfamethoxazole (SMX)	86.8 %	Hydrophobic interaction	[42])
Spent coffee grounds	500 °C	Magnesium	Phosphate	111.2 mg g^{-1}	Surface adsorption	[43]
Bamboo biochar	600 °C	Al-modified	Sulphamethoxazole and sulphapyridine	1200–2200 mg/kg	hydrophobic, π-π, and electrostatic interactions	[44]

modifications at high temperature (700–900 °C) generate extensive microporous networks with specific surface areas (SSA) reaching up to 300–500 m^2/g, whereas lower temperature pyrolysis (300–500 °C) produces materials with moderate SSA of 50–100 m^2/g [45]. The SSA of biochar is highly correlated with pollutant immobilization efficiency via providing increased reaction sites and microbial habitat provision. Low-temperature biochar may have a comparatively high mechanical strength, more polar and functional groups for pollutant adsorption. The elevated mechanical strength ensures structural integrity of CWs, allowing to withstand varying hydraulic loads and environmental conditions. Further, biochar facilitates the establishment of diverse microbial populations that contribute to the degradation and transformation of pollutants [6,46]. High-temperature biochar contains more p-p bonds, a higher carbon content, SSA and porosity [2,47]. To boost pollutant adsorption, biochar can be functionalized or activated physically, chemically, or biologically, which in turns elevates the SSA, porosity, pore volume and quantity of functional groups in biochar [48]. The pore architecture demonstrates a hierarchical distribution pattern where micropores (<2 nm, 40–60 %) facilitate the interaction at molecular level, mesopores (2–50 nm, 25–35 %) support microbial colonization, and macropores (>50 nm, 15–25 %) enhance the hydraulic dynamics [49]. The pore-filling process promotes pollutant adsorption at low solute concentrations [50]. The diffusion of adsorbate into the pores of biochar is the first stage in pollutant partitioning [50]. Biochar's multi-scale porosity network allows an efficient capture and immobilization of contaminants, thereby reducing the bioavailability and toxicity in the environment [45,49]. This also improves the microbial colonization potential [51]. Morphological surface roughness of biochar could enhance bacterial adhesion by 200–300 % compared to smooth surfaces, creating protected microenvironments for biofilm development [46,52]. Overall, biochar integration in CWs offers a multifaceted role in effective treatment and bioremediation of a wide range of pollutants in CWs by optimizing the adsorption capacity, structural stability, hydraulic performance, and microbial activity.

4.2. Chemical interactions and pollutant binding mechanisms

The chemical functionality of biochar in CWs operates through multiple simultaneous mechanisms (Fig. 2). Organic pollutant adsorption by biochar in CWs includes the interplay of many interactions, including complexation, precipitation, ion exchange, surface adsorption, electrostatic contact, hydrophobic interaction, pore filling, and partitioning interaction. Electrostatic interaction, ion exchange, surface complexation, intermolecular contacts, cation-p bonding, and p-p interaction are among the prominent pathways for metallic pollutant adsorption by biochar [18,53]. Electrostatic interaction is a crucial stage in the immobilization of ionic organic contaminants in aqueous ecosystem [51]. Ionic adsorbates are drawn to the adsorbent surface with opposite charges. The cationic sites in biochar attract anionic pollutants and vice-versa. Electrostatic repulsion between biochar and ionic contaminants could promote adsorption of pollutants via hydrogen bonding [54]. Surface adsorption, also known as physical adsorption, could occur via creating chemical bonds caused by metal ion migration into the adsorbent pores [52].

Surface charge characterization of biochar reveals pH-dependent zeta potential typically ranging from −35 mV to +15 mV, with point of zero charge (pHpzc) values between 6.5 and 8.2 [55]. This could facilitate electrostatic interactions of both cationic and anionic pollutants based on biochar characteristics. An analysis of functional group density demonstrates the dominance of carboxyl groups (0.5–2.0 mmol/g), hydroxyl groups (1.0–3.0 mmol/g), and phenolic groups (0.3–1.5 mmol/g) in biochar [56]. These surface functionalities participate in specific binding mechanisms, viz., complexation with heavy metals, π-π interactions with aromatic compounds, and hydrogen bonding with polar organic compounds [57–61]. Studies on biochar surface precipitation demonstrate the formation of metal phosphates, carbonates, and hydroxides, with nucleation rates 2–4 times higher than in conventional CW substrates [62–64]. Redox characterization reveals distinct zones within biochar-amended systems which enable simultaneous operation of multiple pollutant transformation pathways. Aerobic microsites in biochar facilitate nitrification and organic matter oxidation while anaerobic regions support denitrification and metal reduction [65,66].

Another process is ion exchange which involves the surface of the biochar being exposed to dissolved metals and exchanging cations and protons. The immobilization of inorganic pollutants on biochar may also lead to co-precipitation of metals. During the adsorption process, solids can develop either on the surface or in the solution. High Cd and Cu adsorption rates on N-doped biochar were found due to complexation and cation bonding mechanisms [67]. Ion exchange and surface complexation could make a significant contribution to the maximum adsorption capacity of biochar [68–70]. Biochar amendments could accelerate the breakdown of contaminants by forming reactive oxygen species (ROS) and reducing the bioavailability of pollutants by surface adsorption. As a substrate in CWs, biochar also serves for biofilm attachment and the performance markedly differs according to the porosity, SSA, and elemental composition of biochar [68–70].

4.3. Biochar-led biological dynamics and biodegradation pathways

The electrochemically active microbial phylum in CWs, such as Protobacteria, significantly contributes to removing organic materials, phosphate, and nitrogen. The surface charges of biochar enable the growth of microorganisms in the voids and the binding of microbial cells with wastewater chemicals [51,52,62–64,71]. The pores of biochar can give microorganisms a favorable habitat and speed up the elimination of pollutants [151]. By retaining nutrients and trace elements, the porous structure of biochar facilitates plant development and adhesion and reproduction of microorganisms in wetlands (Fig. 3). In addition to being an electron donor [165], iron tailored biochar potentially maintains the hypoxic conditions for denitrification, encouraging bacterial growth and phosphate precipitation [6]. To boost the electron transfer efficiency, negative electrode materials or microbial fuel cells could be incorporated into the CW system using the redox theory [65,66]. For example, the use of biochar with intermittent aeration significantly enhanced the nitrogen bioremediation by diversified nitrogen-removing microbes [6]. Biochar fostered a diverse microbial population that secreted macromolecular polymers and released tryptophan-like compounds, which improved the heavy metal removal ability in CWs [55].

The biological dynamics in biochar amended CWs represent a complex interplay of microbial and plant processes. Biochar embedded CWs demonstrated enhanced dehydrogenase (200–400 % increase), urease (150–300 % increase), and phosphatase (180–350 % increase) activity compared to non-biochar systems [72]. These are strongly correlated with improved removal efficiencies for nitrogen, phosphorus, and other organic pollutants by 40–80 % [73]. Root-biochar interaction studies demonstrate an enhanced colonization which reflects enhanced root length, density, and surface expansion (40–70 %) in biochar-amended systems [68–70]. Because the makeup of the microbial community has a direct bearing on the effectiveness and operational reliability of the wastewater treatment process, a mutual transformation of microorganisms within CWs is essential to their functioning and to the elimination of pollutants [163,167]. Actinomycetes, Proteobacteria, and Bacteroidetes have a significant role in the eradication of antibiotic resistance [56]. The inclusion of biochar has shown to increase the functional microorganisms (e.g., *Dechloromonas, Thiobacillus, Hydrophilia, Pseudomonas, Nitrospira, and Nitrosomonas*) that are involved in the breakdown of organic matter and the removal of nitrogen in CWs [55,74,143].

In artificial wetlands, charcoal was reported to promote antibiotic resistance genes (ARGs) abundance [75,140,148]. A negative correlation between ARGs buildup and sulfamethoxazole elimination, and reduced concentrations of *int* and *sul* genes was reported [75]. Wang et al. [76–79] observed that a higher abundance of the MC-degrading gene *mlrA* led to the mitigation of sulfonamide ARGs (*sul1, sul2,* and *intl1*) and a removal efficiency of microcystis using biochar (>96.47 %) in CWs. Fang et al. [73], reported a horizontal mobility of ARGs with biochar application, which inhibited the ecosystem-wide proliferation of ARGs. Biochar's high porosity and specific surface area provide a favorable environment for denitrifying bacteria, as evidenced by a rise in *nirS* and *nirK* gene abundance under CWs. The nitrite reductase genes (*nirS* and *nirk*) and nitrous oxide reductase genes (*norZ*) frequently serve as functional genes to perform denitrification. According to Zhang et al. [59–61], the combination of zeolite and iron carbon-based CWs resulted in a considerable rise in the *czcA* gene and substantial Cd recovery. By increasing the number of denitrification functional genes in wetlands, one may improve the denitrifying potential of wetlands. This allows transforming more nitrate into N_2, which reduce NO_3^- from wastewater by using bimetallic Fe-Cu/polyvinylpyrrolidone modified biochar [46].

4.4. Integration of electrolysis with biochar for enhancing effectivity

The bulk of N in CWs is removed via microbial catabolism, substrate adsorption, and nitrification and denitrification. Denitrification accounting for 60–95 % of NO_3^--N removal in CWs is a crucial mechanism for the removal of N [80,81]. However, due to poor adsorption capacity, the substrate can easily become saturated, reducing the effectiveness of both plants and microbes in remediation [82]. Microbial growth

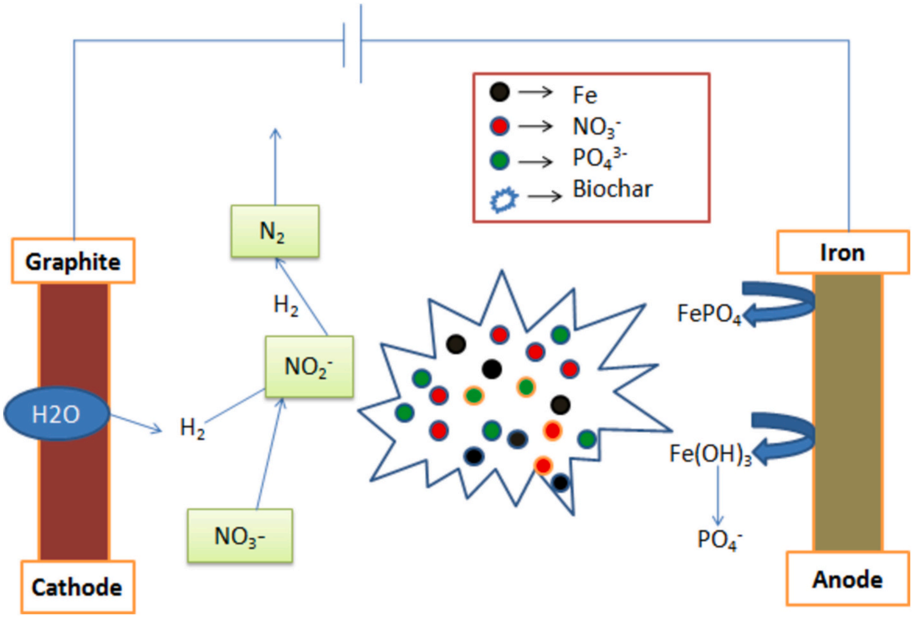

Fig. 3. Biochar led biological and genetic alterations elevate the performance of CWs for wastewater treatment by enhancing the microbial relative abundance and structural composition, modulating enzyme activities and gene expressions.

stabilization, plant absorption, and substrate adsorption are promising mechanisms for P elimination in CWs. If the substrate's capacity to adsorb P gets saturated, the rate of P removal will eventually slow down. This might result in a secondary discharge of P-containing water from the substrates of CWs [83]. Since these unfavorable characteristics continue to be significant barriers to CWs for N and P elimination from wastewater, CWs must be accustomed to mitigate this issue [84]. It was discovered that CWs might be coupled with photovoltaic energy for the best outcomes in removing N and P from wastewater [84].

Aluminum (Al) and iron (Fe) can be used as anodes to electrocoagulate wastewater to remove P, which is proved to be highly effective treatment that takes up less space and costs [85] (Fig. 4). Electrolysis, in combination with biofilters and CWs, has already been utilized by some researchers to improve NO_3^--N and PO_4^{3-}-P removal [86]. Biochar adjusted CWs can be designed to solve the problem as biochar efficiently adsorbs Fe ions by electro-modification, which concurrently boosts the oxyanionic pollutants (NO_3^- and PO_4^{3-}) immobilization and reduces color of water. Fe ions are generated when Fe is used as an anode, which affects the color of water, odor and plant toxicity [87]. Gao et al. [88] found that the secondary wastewater treatment plant's N and P removal efficiency increased when HFCW was treated with biochar. To improve the elimination of NO_3^--N, NH_4^+-N, and PO_4^{3-}-P in HFCWs, photovoltaic energy was utilized for electrolysis alongside biochar. The NO_3^--N, NH_4^+-N, and PO_4^{3-}-P removal rates were 73.3 %, 53.1 %, and 67.6 %, respectively, when HFCW modified with biochar was combined with SFCW. Usage of Fe cathode for electrochemical reduction enhanced hydrogenotrophic microbes and the removal of NO_3^--N. Sacrificial Fe anodes released ferric ions that caused flocculation, physical adsorption, and chemical precipitation, all of which sped up the removal of PO_4^{3-}-P. Thus, biochar-amended HFCWs in conjunction with SFCWs could provide new insights for NO_3^--N, NH_4^+-N, and PO_4^{3-}-P removal in CWs. Zhong et al. [89] found that the N removal process might be affected by both electrochemistry and biochar properties. The biochar-electrochemistry system removed significantly ($p < 0.05$) higher level of TN (60–93 %) and NO_3^--N (83–100 %) than the control system. It was found that the inclusion of biochar could stimulate microbial activity, diversity, and richness. These findings provide a new and basic understanding of the biochar-amended CW system that is electrochemically coupled. These insights could provide a theoretical foundation for engineering applications of CWs in wastewater treatment plants for deep purification.

5. Biochar in constructed wetlands for targeted pollutants bioremediation

5.1. Nutrients removal

The application of biochar as an adsorbent under CWs plays a significant role in the efficient removal of nutrient contaminants from polluted wastewater. The bioremediation of nitrogenous compounds is influenced by multiple processes such as volatilization, nitrification, denitrification, nitrogen fixation, ammonification, nitrate-ammonification, anaerobic ammonia oxidation, fragmentation, plant and microbial uptake, adsorption, desorption, burial, and leaching. The effectiveness of biochar added CWs in treating wastewater is summarized in Table 2. Analysis of performance data indicates removal efficiencies spanning a broad spectrum, with values ranging between 63.1 and 100 %. Engineered and modified biochars exhibit particularly noteworthy results. For instance, the combination of bamboo and woodchips achieved complete phosphorus removal [93], while walnut shell-derived biochar demonstrated remarkable nitrogen species reduction exceeding 88 % within a brief 48-hour window [90]. The purification process encompasses multiple concurrent mechanisms. At the physical level, contaminants are captured through surface binding, void occupation, and water-repelling interactions. Chemical processes facilitate ion transfers, charge-based attractions, and surface-level molecular bonding. In extended treatment scenarios, biological pathways emerge through microbial activities and biofilm development [65,66,68–70]. Both agricultural residue-derived materials (from corn straw and cattle waste) and wood-sourced biochars (including oak and bamboo variants) consistently achieve removal rates exceeding 75 % [68–70]. This suggests the viability of utilizing regional biomass resources for water purification applications.

The source material characteristics and modification methods significantly influence the effectiveness of these mechanisms [182]. Metal-enhanced biochars, particularly those incorporating iron and manganese, exhibit superior performance through enhanced surface characteristics [76–79,93,99]. VFCWs efficiently remove ammonia-N (NH_3-N), although denitrification is quite limited in these systems [68–70,100]. While horizontal flow-built wetlands provide favorable

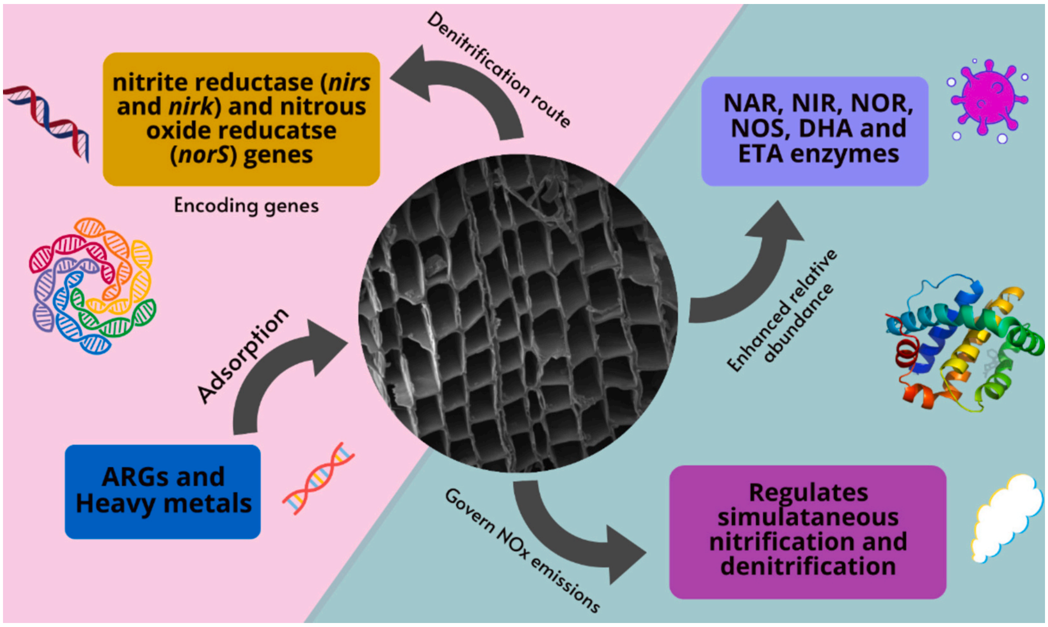

Fig. 4. Mechanisms involved in nitrate and phosphate removal in biochar-amended CWs using electrolysis process.

Table 2
Effective removal of nutrient pollutants from biochar integrated CWs with plants.

Pyrolyzed biomass	Pyrolysis temperature	Plant species	Experiment duration	Targeted pollutant	Removal efficiency	Potential mechanism and key features	References
Cyperus alternifolius	500 °C	*Cyperus alternifolius*	12 months	TN	75 %	Plant uptake and microbial processes; elevated plant-biochar synergy	[90]
Oak tree	–	*Canna* seedlings	2 months	NH_4^+-N NO_3-N	58.3 % 92.1 %	Physical adsorption and precipitation: Multi-pollutant removal capability	[91]
Alder	–	*Typha latifolia*	4 months	TN TP	20 % 22.5 %	Microbial attachment and biodegradation: High surface area and porosity support microbial colonization support	[92]
Bamboo	500 °C	*Javanica* species	3 days	TN	63.1 %	Physical adsorption and electrostatic interaction	[68–70]
Bamboo and wood chips	–	*Phragmites australis*	12 weeks	TN	95.7 %	Surface Adsorption, ion exchange, microbial transformation	[93]
Cattle dung	–	*Colocasia esculenta*	40 days	NH_4^+-N NO_3-N	97 % 81 %	Surface adsorption and ion exchange reported nigh nitrogen affinity	[94,95]
Coconut shells	300 °C	*Pennisetum sinese*	–	TN NH_4^+-N	80 % 99.6 %	Chemical precipitation and physical adsorption with rapid removal and long-term stability	[66]; [65]
Bamboo and woodchips	–	*Javanica* species	3 days	TP	100 %	Surface Adsorption, ion exchange, microbial transformation	[93]
Branches of tree	–	*Lythrum salicaria*	7 months	TP	76.2 %	Surface complexation and precipitation with long-term stability	[182]
Oak tree	600 °C	*Canna* seedlings	2 months	TP PO_4^{3-}	79.5 % 67.7 %	Physical adsorption and precipitation: Multi-pollutant removal capability	[91]
Coconut shell	–	*Typha latifolia*	6 months	TP	81.2 %	Pore filling and surface complexation: High surface area and porosity	[66]; [65]
Corn straw	–	*Acorus calamus*	2 months	TP TN NH_4^+ NO_3^-	52 % 82 % 84 % 89 %	Electrostatic interaction and surface adsorption: High removal efficiency for multiple pollutants	[76–79]
Iron modified biochar	–	*Canna indica*	11 months	NH_4^+ TN TP	89.1 % 88.1 % 75.9 %	Chemical precipitation and π–π interaction: Enhanced phosphate binding through iron modification	[96]
Fruit stone	–	*Phragmites communis*	4 months	TN NH_4^+ NO_3^-	62.98 % 93.93 % 93.28 %	–	[97]
Sewage sludge and cattail litter	600 °C	*Typha latifolia*	72 h	NO_3^- NH_4^+ TN TP	99.50 % 99.59 % 90.94 % 51.59 %	Combined adsorption and biodegradation: Synergistic effect of dual metal modification	[83]
Walnut shells	450 °C	*Salicaria* seedling	>3 months	NH_4 TP	92.1 % 74.7 %	Physical adsorption, surface complexation, electrostatic attraction and pore filling: Rapid removal for multiple nitrogen with high surface area (>500 m^2/g), microporous structure	[98]

circumstances for denitrification, their ability to nitrify ammonia is limited [92,101]. As a result, several types of artificial wetlands can be mixed to make use of the distinct features of each system (Table 2). Zheng et al. [83] suggested that a sustainable approach to improve the nitrogen removal efficiency of carbon-waste systems might involve the use of biochar.

Biochar addition improved total N and NO_3-N removal efficiency in wastewater by up to 93.03 % and 100 %, respectively [102–104]. Better microclimatic conditions for microorganisms in the substrate and the complementary effects of biochar on heterotrophic and autotrophic denitrifies in CWs may be the causes of this. Zhou et al. [105] found a significantly greater decrease of NH_4^+-N and TN (94.9 % and 99.1 %, respectively) in an aerated VFCW system with the incorporation of biochar as a substrate. Jia et al. [106] observed that an influent C/N ratio of 0.5 resulted in an optimal expulsion of NH_4^+-N, and total nitrogen by 99 % and 96 %, respectively, in VFCWs with agricultural biomass and intermittent aeration. Li et al. [107] investigated the wetland macrophytes, i.e., *Arundo donax* derived biochar integration into surface flow constructed wetlands (SFCWs) to improve organic matter and nitrogen removal. They also reported a significant release of dissolved organic matter (6.0 to 125.7 mgL^{-1}) which showed a positive correlation with microbial nitrogen removal efficiency. The SFCWs with 20 % biochar had better removal efficiency of NO_3-N (81.2 %) and total nitrogen (85.6 %), than SFCWs without biochar (36.2 and 57.9 %). The biochar inclusion also enhanced plant growth and development under SFCWs which may further improve phytoremediation abilities [108,109].

Along with nitrogenous compounds, biochar has shown tremendous effectivity in phosphorous removal. Phosphorous (P) removal in CWs primarily happens through oxidation, microbial breakdown, plant uptake, and physical-chemical reactions with substrates (precipitation, adsorption, ion exchange, mineralization) [3,4]. Biochar improves biotic P removal processes by encouraging plant growth and the growth of organisms that accumulate polyphosphate, in addition to its adsorbent properties [10,106]. Because biochar has a higher surface area and a porous structure, it may be used to remove total phosphorus (TP) with excellent results [59–61,110]. Anionic phosphate-P (PO_4-P) removal is significantly influenced by the chemical properties of biochar and effluent, especially by the surface charge of the biochar [111]. The P (TP and PO_4-P) removal effectiveness with sand medium can be further elevated by mixing biochar from sewage effluent in CWs. The inclusion of biochar with sand at 0 to 25 % rates showed removal efficiency of 43 to 92 % and 35 to 85 % for TP and PO_4-P, respectively. Later phases of the TP removal efficiency differed from the first stages, suggesting that the ion exchange capacity, microorganisms, and substrates (biochar and gravel) had limited adsorption capacity. Kasak et al. [92] planted *Typha latifolia* in experimental horizontal subsurface flow filters and filled them with charcoal and lightweight expanded clay aggregates (LECA) to filter the pretreated municipal wastewater. Plants, LECA, and 10 % biochar all worked together to improve the physicochemical accumulation of P by adsorption, precipitation, and accumulation in the substrate layers. Apart from that, microorganisms that lived in the porous structure of biochar were responsible for converting the available P into microbial biomass. The dissolved organic materials may be stored in the mesoporous biochar as a nourishment for these microorganisms, which may help increase P bio stabilization.

Addition of biochar into gravel-filled CWs did not always boost P removal and biochar-sand mixtures were even less effective at removing P than pure sand [112]. This might be attributed to the poor affinity of negatively charged biochar surface to PO_4-P anions and competition for exchange sites with other anionic substances in the ecosystem. The reinforcing effect for P immobilization was significantly smaller than N species [112]. The application of surface-tailored biochar using pre-treatments, physical, chemical, biological modification, physical mixing, magnetic exposure, etc. may enhance the P removal capacity [10,113]. Enhanced P removal efficiency has been reported by Bolton et al. [114] using enriched hemp charcoal substrate compared to gravel based CWs. With an average input P content of 15.5 mg/L, the wetlands containing an enriched biochar consistently reduced PO_4-P concentration to <2 mg/L. Moving forward, research priorities should address optimization of enhancement techniques and long-term performance stability of biochar (Ji et al., 2020). Critical areas include investigating efficiency-duration relationships, particularly for rapid treatment systems. Economic feasibility assessments of various biochar sources and modification approaches are essential for scaling up to commercial applications.

5.2. *Heavy metal removal*

Heavy metals constitute persistent and non-biodegradable pollutants in aquatic systems, presenting significant environmental challenges in sediments, storm runoff, mining wastewater, and industrial effluent. These elements pose severe ecotoxicological risks through bioaccumulation. Experimental investigations demonstrate biochar's efficacy as a high-capacity adsorbent of heavy metals, functioning through multiple physicochemical mechanisms including electrostatic attraction, ion exchange, precipitation, complexation, and π-binding interactions (Table 3). Additionally, by changing the oxidation states of metals (such as Cr(VI) and Hg(II) to Cr(III) and Hg(II)), biochar functions as a redox reactive electron transferer and shuttle, hence lowering the toxicity of metals [59–61,117,118]. The microbial conjunction with biochar further accelerates sulfide and hydroxide precipitation. Quantitative analyses reveal that agricultural waste-derived and bamboo biochars achieve exceptional removal efficiencies, particularly for Pb(II) and Cr(VI), reaching 99.9 % and 97 %, respectively, through ion exchange mechanisms [106,116]. Coconut shell biochar demonstrates 50 % arsenic removal via co-precipitation [115], while walnut shell biochar achieves 37.4–57.5 % removal for Cd(II) and 51.3–52.7 % for Zn(II) through electrostatic attraction and precipitation [117].

Surface engineering of biochar through acids, bases, heteroatoms and moieties (OH, HSO_3, S_2) further enhances the metal adsorption from aqueous ecosystems [113]. Inorganic composition of biochar makes the adsorbent alkaline which elevates the pH of acid mining wastewater and impairs the solubility, enhancing metal hydroxide precipitation [47]. Z. Z. Guo et al. [66] and F. Guo et al. [65] examined the efficacy of biochar, zeolite, and their combinations with biosorbents including compound microbial agents and chlorella. They observed ~80 % removal efficiency for As, Zn, and Cu. Chang et al. [98] reported that granular biochar packed into intermittently aerated wetland microcosms showed significant Hg(II) removal from containing wastewater over 100 days as compared to gravel systems. Here, biochar facilitated chemical and microbiological reduction, volatilization and phyto-assimilation of Hg (II). In the gravel CWs, however, substrate binding in an oxidizable fraction was the main mechanism for Hg elimination. According to Irshad et al. [121], arsenic (As) tainted water may be successfully bioremediated using a BCXZM composite (*Bacillus* XZM immobilized on rice husk charcoal) in a modified hybrid vertical subsurface flow-built wetland (VSSF-CW). The modified and planted (As + P + B) VSSF-CW scavenged 64 % of the total As with a removal efficacy of 95 %. This work is the first to show that As phytoextraction and biosorption may occur simultaneously in a hybrid VSSF-CW. It suggests that BCXZM can be used in CWs to efficiently treat As-contaminated water on a broad

Table 3
Summary of heavy metal and emerging contaminants removal efficiency of biochar-substrate under wastewater inflowed CWs.

Pyrolyzed biomass	Pyrolysis temperature	Pollutant	Removal efficiency	Mechanism involved	References
A. **Bioremediation of heavy metals**					
Coconut shells	–	As	50 %	Co-precipitation	[115]
Agricultural wastes	500 °C	Pb	99.9 %	Ion exchange	[116]
Biogas slurry in pig farms	–	As	35.4–83.9 %	Electrostatic precipitation	[65]
		Zn	8.2–23.7 %		
		Cu	33–90 %		
Bamboo	–	Cr	75 %	Ion exchange	[106]
		Pb	97 %		
Walnut shell	450 °C	Cd	37.4–57.5 %	Electrostatic precipitation	[117]
		Zn	51.3–52.7 %		
–	–	Cr	95.0 %	–	[118]
Agricultural wastes		Pb	75–99 %	Ion exchange	[116]
B. **Bioremediation of emerging contaminants**					
Pine sawdust biochar	700 °C	Sulfamethoxazole (SMX)	86.8 %	Hydrophobic interaction	[42])
Fruit stone	–	Ciprofloxacin hydrochloride	93 %	Adsorption	[55]
Biochar-zeolite		Phenols	99.9 %	Adsorption	[116]
Cow dung	–	Triclosan	98.41 %	Hydrophobic interaction	[72]
Agricultural biomass	570 °C	Hexachlorocyclohexane	96 %	Microbial degradation	[173]
Corn stalk	–	Atrazine	50–70 %	Hydrophobic interaction	[20]
–	–	Amoxicillin,	75.51 %	–	[102,103]
		Caffeine,	87.53 %,		
		Ibuprofen	79.93 %		
Cornstalk	–	Reactive Yellow 145	95 %	Hydrophobic, electrostatic interactions	[119]
Bamboo	700 °C	Sulfamethoxazole	36.8 ± 6.2 %	Electrostatic interaction	[75]
Iron-modified biochar	500 °C	Benzofluoranthrene	20.4 %	π–π interaction	[120]
Bamboo	700 °C	Sulfamethoxazole	98 %	Hydrophobic interaction	[75]
Fe/Mn modified biochar	–	Imidacloprid, and acetamiprid	–	adsorption and biodegradation	[174]
Bark	–	Benzotriazole,	40 %	Adsorption, biodegradation and photodegradation	[175]
		Hydrochlorothiazide	60 %		
Straw	–	Sulfonamide antibiotics	94 %	Electrostatic interaction	[176]

scale. These findings underscore biochar's versatility in treating diverse aqueous pollutants. The variations in removal efficiencies across contaminants and biochar types emphasize the importance of optimizing physicochemical properties for specific applications. Future research should focus on enhancing removal efficiencies through surface modification strategies and investigating synergistic effects with complementary materials. Additionally, techno-economic analyses and environmental impact assessments are crucial for sustainable implementation in large-scale wastewater treatment systems.

5.3. Organic pollutant removal

The function of aerobic and anaerobic degradation under CW systems may effectively lower the biological oxygen demand (BOD) and chemical oxygen demand (COD) indices in wastewater, according to Cheng et al. [122]. Organic matter can be extracted from wastewater using a variety of techniques, including adsorption, separation/filtration, oxidation and reduction, hydrolysis, biological degradation, etc. [102,103]. The primary mechanism for removing organic debris in CWs is bacterial decomposition in conjunction with substrates [123]. Adding biochar significantly increased COD elimination in CWs (Table 3). This is explained by the fact that biochar can adsorb organic matter and offers a heterogeneous surface with numerous pores that may be occupied by a variety of bacteria that break down organic matter and fill it with oxygen [124]. Hazardous and emerging organic contaminants are found in industrial effluents, livestock wastes, storm water and wastewater, including dyes, pesticides, herbicides, and antibiotics [139,142,144,147,150,160,161]. Even at trace amounts, these contaminants can cause serious hazards to public health and ecosystem functions [26,125]. The main mechanisms of biochar-mediated bioremediation of such contaminants from the aqueous ecosystem are hydrogen bonding, pore-filling processes, aromatic p-donor and cationic p-acceptor conjugation, hydrophobic effects, and electrostatic attraction [13,16,17,75]. In addition to encouraging plant development, biochar increases the amount of oxygen available in the CW matrix for aerobic breakdown of contaminants. Using biochar as a substrate may encourage the establishment and reproduction of bacterial populations that help to break down organic contaminants [126]. However, there hasn't been much research done on the bioaugmentation activity of biochar under CW conditions [127,128].

The main processes involved in contaminant remediation in CWs are determined by the characteristics of the pollutants and biochar, as well as the operating circumstances [178]. In comparison to the control group that did not receive biochar (64–99 %), Tang et al. [90] reported that the addition of biochar made by processing *Cyperus alternifolius* with $Fe(NO_3)_3$ to CWs resulted high removal efficiencies (>99 %) for pesticides from wastewater. Kim et al. [129] claimed that biochar in CWs encouraged microbial breakdown and adsorption of pesticides. Adding biochar to zeolite-based CWs increased antibiotic removal rates and suppressed the development of quinolone and sulfonamide resistance genes because biochar facilitated antibiotic adsorption and biodegradation [97].

5.4. Emerging contaminants removal

The remediation of emerging contaminants (ECs) through biochar applications represents a significant advancement in water treatment technologies. Surface adsorption and co-precipitation, which are governed by biochar surface charge, functional groups and pore structure, are the primary mechanisms for antibiotic removal form aqueous ecosystem [161,168,169]. Emerging contaminants, encompassing pharmaceuticals, personal care products (PPCPs) and endocrine-disrupting compounds (EDCs), present unique challenges due to their molecular complexity and environmental persistence [26,132]. Biochar's effectiveness in removing these compounds stems from its distinctive physicochemical properties developed through controlled pyrolysis of diverse biomass feedstocks under specific temperature regimes. Several studies highlight ECs removal in CWs through various mechanisms of biochar (Table 3). Biochar's complex structure significantly enhances POPs removal, with studies reporting removal efficiencies of up to 99 % for certain compounds [130] due to high SSA providing numerous adsorption sites and fostering microbial degradation. In CWs, biochar amendment has been observed to reduce antibiotic concentrations in effluent by up to 92 % accompanied by a decrease of antibiotic resistance gene abundances by 2–3 orders of magnitude [131]. The surface chemistry and pore structure of biochar can be tailored to target specific EDCs and augment a hydrophobic interaction, pore-filling support, and activity of microbes capable of metabolizing these compounds [132,133]. For example, Fe-modified biochar as a CW substrate significantly reduced benzofluoranthrene (BbF) by 40.6 % and NH_4^+–N by 25.6 % [120]. Iron oxides acted as an electron acceptor in oxidizing NH_4^+–N, and increased the DOC content, which was beneficial for PAHs degrading microbes [120]. Biochar substrates enhanced bacterial growth and acted as a biofilm carrier in removing sulfamethoxazole (SMX), and ARGs were simultaneously adsorbed on biochar and broken down by persistent free radicals through direct electron transfer and reactive oxygen species (ROS) [75]. The accumulation of ARGs was reported to be associated with SMX removal efficiency, with reduced concentrations of *int* and *sul* genes in biochar added CWs. Microbial community analysis revealed a greater abundance of functional consortia capable of metabolizing SMX (*Arthrobacter, Ramlibacter* and *Flavobacterium*) in biochar amended CWs [75]. A recent investigation on biochar embedded tidal flow CW demonstrated a substantial removal efficiency (52.91 %) of triclosan, which was attributed to enhanced redox reactions, increased microbial activity, and the combined effects of biochar adsorption, photo-transformation, and biodegradation within CWs [72]. A NaOH-modified corn straw biochar in CWs showed ~94 % removal of eight sulfonamide antibiotics by influencing the ecosystem and dissolved oxygen level [176]. Chand et al. [102,103] reported an efficient removal of pharmaceuticals such as amoxicillin, caffeine, and ibuprofen in biochar and plants based VFCWs. The VFCWs recorded substantial removal of ciprofloxacin hydrochloride and sulfamethazine along with nitrogen by modulating the degrading microbial composition and diversity [97].

Surface modification of biochar with certain compounds could augment the electron exchange, redox reaction and photo-transformation processes, and microbial abundance and activity in CWs [72,102,103[176]. The integration of various substrates and operational conditions could significantly enhance the treatment efficiency. Research findings establish biochar as a versatile substrate for ECs remediation. The integration of these insights with process optimization will be crucial for developing more effective water treatment solutions. This comprehensive understanding provides a foundation for advancing biochar technology in water treatment applications, combining high removal efficiency with environmental sustainability. The continued exploration of modification strategies and mechanism elucidation will further enhance biochar's role in addressing emerging water quality challenges.

5.5. Pathogens removal

The inherent properties of biochar derived from diverse feedstock make CWs suitable for microbial decontamination of wastewater pathogens as compared to sand and/or gravel substrate. Surface adsorption, biofiltration, straining, predation, inactivation and oxidation in response to chemical stressors are necessary steps in the effective elimination of pathogens. However, there hasn't been much focus on pathogen removal in CWs treated with biochar to date. In contrast to CWs that were filled with sand or original rice husk, the CWs packed with rice husk biochar achieved significant elimination of fecal bacteria and bacteriophages from municipal sewage [120]. Biochar as a substrate in CWs for disinfecting wastewater has been highlighted by Lau et al.

[134] and Mohanty et al. [135]. It was shown that biochar with less volatile materials and polarity was efficient in eliminating *E. coli*. This is because biochar may produce antimicrobials and exploit hydrophobic interactions to absorb bacteria and viruses [135]. Lau et al. [134] reported that H_2SO_4 treatment of biochar increased the surface area, which increased the removal of *E. coli* with negligible remobilization during intermittent flow and drainage. Biochar remains an appealing filler in CW systems for pathogen removal because it can be made cheaply and easily from commonly available bio-waste. The levels of fecal indicator bacteria (FIB) in CW effluents are higher than most of the reuse regulation levels, so further improvement of FIB removal in CWs is needed [180].

6. Conclusions and perspectives

Biochar has considerable potential in imparting effective wastewater purification through several mechanisms directly as well as in association with other components of CWs. Effective organic matter purification requires improved high molecular weight chemicals breakdown into low molecular weight molecules. The contaminant adsorption efficiency is elevated by biochar in CWs besides providing the carbon source for microorganisms. Biochar-amended CWs improve several water quality parameters such as BOD, COD, nitrates, phosphates, and heavy metals (Fig. 5). Findings indicate that biochar-enhanced CWs are highly effective in removing pollutants, achieving nitrogen removal rates between 50 and 95 %, with some reporting TN removal up to 98 %. Phosphorus removal efficiencies generally range from 60 % to 90 %, with certain systems reaching up to 99 % removal. Heavy metal removal efficiency under biochar-enriched CWs consistently show high efficiencies, with removal ranging 80–99 %, 70–95 %, 75–98 %, and 85–99 % for Pb, Cu, Zn and Cd, respectively. Additionally, these systems demonstrate significant reduction in organic pollutants, with chemical oxygen demand (COD) reduced by 70–95 % and biological oxygen demand (BOD) by 80–98 %. The removal of specific organic contaminants, such as pharmaceuticals and personal care products (PPCPs), ranges from 60 % to 99 %, depending on the compound. Although less studied, initial research suggests that biochar-enhanced CWs can achieve total coliform removal rates of 90–99 %. The synergistic interactions between biochar, microorganisms, and plants in these systems contribute to their enhanced performance, with biochar shown to increase microbial biomass by 50–100 % compared to conventional CW substrates, leading to improved pollutant degradation rates.

The pollutant removal potential of biochar-enhanced CWs is highly dependent on biochar production processes and conditions including temperature, heating rate, resident time, and nature and composition of the feedstock. The optimum pyrolysis temperature (400–600 °C) produces biochar with high surface area, porosity, functionality, and stability. The porous structure of biochar provides favorable habitat to microorganisms as well plants in CWs which encourage the fixation/usage of nutrients and trace elements. In addition, biochar being a conductive material can increase the electron transmission, which further upscales the effective bioremediation potential. Biochar-enhanced CWs represent a promising advancement in wastewater treatment technology, offering a sustainable and efficient solution to address water pollution.

Biochar-enhanced CWs are poised to safeguard water resources and environmental sustainability but there are associated technological and scaling challenges, such as:

- The high cost associated with biochar production necessitates a careful consideration of viability for large-scale application in CWs.
- The pyrolysis process used in biochar production can release 3–12 % of the initial feedstock carbon as CO_2, which needs to be balanced for estimating the environmental footprint of biochar in water purification [30–33].
- The adsorption capacity of biochar may saturate over time, potentially leading to a substantial reduction in pollutant removal efficiency. This saturation effect highlights the need for research into biochar regeneration methods and long-term performance testing in CWs [14,136].

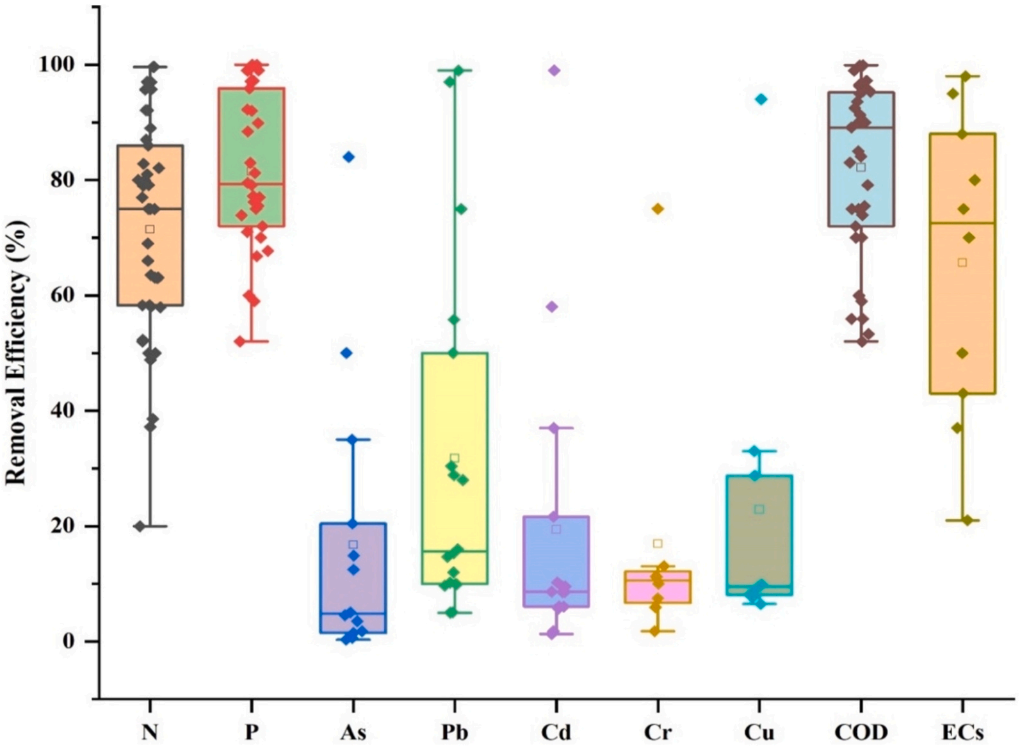

Fig. 5. Removal efficiency of contaminants and improvement of water quality parameters by biochar-amended CWs.

- The stability and effectiveness of biochar in CWs over long periods (5–10 years) remain uncertain, with potential degradation of biochar's structural and functional properties over time [14,11].
- Biochar's performance in CWs can vary significantly based on feedstock and production conditions, with widely varying SSA and cation exchange capacities, which requires a standardization for biochar application at industry scale [12,137].
- Long-term effects of biochar on CW ecosystems, including impacts on native microbial communities and potential leaching of contaminants need clear understanding.
- Transitioning from laboratory-scale studies to full-scale applications presents challenges in maintaining consistent performance, economic viability and real-world success [138].

These challenges emphasize the necessity for ongoing research and innovation to refine biochar production processes, improve performance reliability, and ensure environmental compatibility. Future research should concentrate on the use of biochar-modified CWs on a pilot and full-scale basis, considering the following aspects:

- Long term experiments are required to better understand the connections between biochar properties, biochar's stability in the system, and performance in pollutant removal [181].
- The configuration of biochar mediated CWs for performance intensification and potential innovation, such as interactive effects of biochar and electrochemistry, need to be explored [75].
- It is crucial to approach biochar use in CWs with a site-specific perspective, considering the unique conditions of each location for effective and sustainable implementation [5,6].
- Applying biochar as an interlayer between two inert layers may be investigated as the best configuration for CW to prevent biochar float or blockage of the filtering system.
- More research is needed to understand the biochar production process optimization, optimal application rates to maximize efficacy, and potential ecological consequences, if any [55].
- Many studies to date presented laboratory-based results treating artificial wastewater for a relatively short period of time. Scaling up the biochar-amended CW methods to practical applications over longer time spans is critical for providing realistic results [74].
- Before biochar is applied widely, in-situ tests should be carried out to evaluate its efficacy with genuine effluents and to investigate the true impact of biochar on the environment [74].
- It is important to research the stability of biochar over several cycles of usage in CWs as well as methods for recycling the spent biochar [71].
- Extent of microbiological compositions and ARG expression mechanisms need to be well explored for enhanced performance and sustainability of biochar amended CWs in a long run.

CRediT authorship contribution statement

Diksha Pandey: Writing – original draft, Visualization, Conceptualization. **Shiv Vendra Singh:** Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Nikhil Savio:** Writing – review & editing, Conceptualization. **Javed Khan Bhutto:** Writing – review & editing, Conceptualization. **R.K. Srivastava:** Writing – review & editing. **Krishna Kumar Yadav:** Writing – review & editing. **Rashmi Sharma:** Writing – review & editing. **Tony Manoj K. Nandipamu:** Writing – review & editing. **Binoy Sarkar:** Writing – review & editing, Visualization, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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