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Review article

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Amended biochar in constructed wetlands: Roles, challenges, and future directions removing pharmaceuticals and personal care products

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ABSTRACT

Pharmaceuticals and personal care products (PPCPs) in wastewater pose significant threats to both human health and aquatic ecosystems. Wastewater discharge from various sources is the primary cause of these contaminants, and proper treatment is essential for protecting the environment. Traditional treatment technologies are often too expensive and ineffective in removing PPCPs. Constructed wetlands (CWs) offer a sustainable, cost-efficient alternative for wastewater treatment, though their capability to eliminate PPCPs can vary based on multiple aspects. Recent studies highlight biochar—a carbon-rich material resultant from biomass pyrolysis—as a promising amendment to improve CW performance. However, there is a deficiency of proper literature reviews on using biochar in CWs specifically for PPCP removal. This review focuses on biochar's role in CWs and its effectiveness in removing PPCPs and enhancing microbial activity and nutrient cycling. A bibliometric analysis using Vosviewer software was used to assess the current research trends in the biochar-amended CWs to attenuate PPCPs. While biochar shows potential in eliminating PPCPs, challenges, such as optimizing its application and addressing long-term operational concerns for treating emerging pollutants like PPCPs. Future research should enhance biochar production and low-cost techniques for diverse groups of PPCPs and perform field trials to validate laboratory results under actual conditions exploring microbial-biochar and plant-biochar interactions. Addressing these challenges is crucial to advancing biochar-amended CWs and enhancing wastewater treatment on a global scale.

1. Introduction

The propagation of pharmaceuticals and personal care products (PPCPs) in various environmental settings can pose a significant environmental concern with implications for both human health and the environment [1–3]. The PPCPs encompassing the antibiotics, hormones, and cosmetics ingredients are frequently detected in low concentrations in different surface, drinking, and groundwater sources due to continuous inputs primarily from domestic, hospital, and industrial sources [4,5]. Domestic inputs arise from the everyday use and discard of medications and personal care products, including improper practices such as flushing down unused pharmaceuticals in toilets. Industrial contributions include the pharmaceutical manufacturing processes and effluents from

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pharmaceutical industries. Whereas, agricultural activities also introduce PPCPs through veterinary drugs and fertilizers containing these compounds. When discharged into the environment through various pathways, PPCPs undergo various attenuating processes that dictate their persistence, transformation, and distribution [6,7]. In natural aquatic settings, PPCPs can persist over extended periods or undergo degradation via biotic and abiotic processes [8,9], transforming various byproducts. Such transformed products resulting from metabolic or chemical pathways may exhibit different properties and bioactivity than their parental compounds [10], potentially introducing novel risks to ecosystems and human health.

The environmental impacts of PPCPs spread to their effects on aquatic organisms and ecosystems. Studies have well-documented disruption to endocrine systems in fish and amphibians, interference with reproductive systems, and physiological changes even at low exposure concentrations [11,12]. Moreover, chronic exposure to PPCPs can change the behavior of aquatic organisms, growth, and survival rates, influencing their population dynamics and overall ecosystem stability [11]. In addition, the accumulation of PPCPs in soil and sediments and their bioaccumulation through food webs pose persistent exposure risks to higher trophic levels, including in humans [2,13]. However, there are concerns about human health, primarily around potential exposure to drinking water sources contaminated by wastewater effluent or agricultural runoff [14,15]. Even though the concentrations of PPCPs in drinking water are typically low, the cumulative effects of long-term exposure to mixtures of these compounds raise alarms about public health and the development of antibiotic resistance in microbial populations [16]. Such antibiotic-resistance genes have gained more attention due to their resistance to particular antibiotics during health treatment [16].

Similarly, PPCPs have garnered more attention as 'pseudo persistent' organic pollutants, promoting significant research efforts into their elimination from the environment [1,7]. However, traditional wastewater treatment plants (WWTPs) can partially remove PPCPs; their efficacy varies widely depending on the characteristics of PPCPs, climatic conditions, and treatment facilities [4]. Conventional treatment methods may reduce some PPCPs, but significant quantities can still enter surface waters through treated effluent discharge [7]. It has been reported that the overall elimination of emerging contaminants in conventional WWTPs varies significantly, with efficacies ranging from 12.5 % to 100 %, depending on compound characteristics and operational conditions [14]. Several PPCPs —such as atenolol, atrazine, diclofenac, carbamazepine, erythromycin, diazinon, mefenamic acid, and metoprolol —show a limited reduction in conventional WWTPs, with removal efficiencies falling below 40 % or even resulting in negative reductions [2,7,14]. Alternative technologies, such as advanced oxidation processes, can potentially reduce over 80 % of many PPCPs [17]. However, they encounter challenges related to high costs and logistical complexities, highlighting the need to investigate low-cost treatment alternatives [17].

Constructed wetlands (CWs) have emerged as a nature-based solution for wastewater treatment, utilizing natural wetland processes to remove contaminants in a minimal cost, efficient, and environmentally friendly manner with minimal operational requirements [18]. CWs showed good removal efficiency for organics, nutrients, and some microorganic pollutants, including PPCPs [18,19]. However, the efficiency of PPCP removal in CWs is influenced by various design and operational factors [20]. Substrate-based CWs utilize the substrates that directly adsorb PPCPs and support microbial activity for biodegradation [21,22]. While affordable, traditional substrates like sand and gravel often exhibit limited adsorption capacities for PPCPs [23,24]. Recent attention has turned to biochar, a carbon-rich material derived through biomass pyrolysis under controlled oxygen-limited conditions, as a promising amendment to enhance CW performance. Biochar's high surface area, porosity, and presence of functional groups prove it a versatile



Fig. 1. The count of pharmaceutical substances analyzed in sewage, influents, effluents, and sludge from wastewater treatment plants for each country. Reproduced from Refs. [26,34] with permission of Elsevier and [34], Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA.

adsorbent for diverse pollutants, including PPCPs [23,25]. Therefore, this review aims to explore amended biochar's role in CWs for PPCP removal, discussing mechanisms, performance outcomes, current challenges, and future research directions.

2. Presence of PPCPs in wastewater and treated effluents

PPCPs are often stated as "pseudo-persistent" emerging contaminants due to their continuous release into aquatic environments through multiple pathways [26]. Most countries lack the infrastructure for PPCP monitoring, and affordable advanced removal technologies for wastewater and treatment plants remain largely unavailable [27]. Previous studies have focused on detecting PPCPs in both the effluents and influents of WWTPs [28–32]. Discharges from WWTPs not only pose direct threats to ecosystems but can also lead to the formation of various byproducts. Duan et al. [33] reported that 149 out of 168 pharmaceuticals were scrutinized in wastewater samples from a WWTP in China. Notably, 76 compounds were present in all samples, including 12 metabolites of different PPCPs in 50 % of samples. The highest concentrations were identified for acetaminophen, caffeine, and their metabolites, while ambroxol, gliclazide, metoprolol acid, and ceftazidime were the predominant compounds [33]. It has been seen that PPCPs are widely detected in wastewater globally [Fig. 1], with higher concentrations found in densely populated regions and areas with advanced pharmaceutical industries, such as North America, Europe, and Asia [26,27]. Globally, approximately 559 pharmaceutical

Table 1

PPCPs detected in wastewater a	and treated	effluents across	different	global	regions.
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Region	Country	Group	Compound	Influent Concentration (ng/L	Effluent Concentration (ng/L	References
Africa	South Africa	Antibiotics	Sulfamethoxazole	1436.5-14811.0	1296.0-10897.9	[38]
		Stimulant	Caffeine	20358.9-43731.8	633.8–9731.10	
		Anticonvulsants	Carbamazepine	459.40-9100.5	465.5–3806.6	
	Kenya	Antibiotics	Sulfamethoxazole	10140-54830	2860-4090	[39]
		NSAIDs	Diclofenac	930-1510	30-61	
	Algeria	NSAIDs	Naproxen	1220-9585	ND - 334	[40]
		NSAIDs	Diclofenac	991–2319	1616–2711	
South Asia	India	Antibiotics	Ciprofloxacin	14.91–35.98	7.33–26.83	[41]
		Stimulant	Caffeine	102000	278	[42]
		Anticonvulsants	Carbamazepine	155	177	
	Pakistan	NSAIDs	Naproxen	1516-2100	NA	[28]
		NSAIDs	Acetaminophen	6780–18020	NA	
		PCPs	Methylparaben	142-228	NA	
Southeast	Indonesia	Anticonvulsants	Carbamazepine	12	23	[29]
Asia		Insect repellents	N, N – diethyl – m toluamide (DEET)	4968	82	
		Stimulant	Caffeine	12220	< LOQ	
	Vietnam	NSAIDs	Naproxen	110-170	ND	[31]
East Asia	China	Anticonvulsants	Carbamazepine	30–190	<loq -="" 50<="" td=""><td>[31]</td></loq>	[31]
		NSAIDs	Diclofenac	1.8-17.8	0.9–3.7	
		Insect repellents	DEET	9568.4	909.9	
Middle East	Greece	Antibiotics	Ciprofloxacin	104-390.1	<mdl -="" 17.2<="" td=""><td>[43]</td></mdl>	[43]
		Stimulant	Caffeine	45925.2-91690.40	15.2-4678.3	
North	USA	Antibiotics	Sulfamethoxazole	846–3905	ND - 1328	[44]
America		Anticonvulsants	Carbamazepine	66–348	66–270	
		Lipid regulator	Gemfibrozil	315–1757	6–207	
North	Canada	Antibiotics	Sulfamethoxazole	2950-8570	3160-4980	[45]
America		NSAIDs	Naproxen	4260-4710	31–7580	
Europe	Spain	Antibiotics	Ciprofloxacin	53,054	2194	[46]
		NSAIDs	Diclofenac	170	98	
		Anticonvulsants	Gabapentin	3208	1069	
	Germany	Anticonvulsants	Carbamazepine	7100	3700	[32]
		NSAIDs	Diclofenac	4300	3400	
		β-Blockers	Metoprolol	3300	990	
	Sweden	Antibiotics	Ciprofloxacin	320	94	[30]
		NSAIDs	Diclofenac	270	485	
		NSAIDs	Naproxen	4900	340	
		Estrogen	Estrone	14.5	70.0	
Eastern	Czech	Antibiotics	Clarithromycin	10-2500 10-550	_	[47]
Europe	Republic	Anticonvulsants	Gabapentin	32–54000	160-3700	
		NSAIDs	Ibuprofen	4200–64000	2400-11000	
		Antibacterial	Triclosan	14-2200	<20-310	
		agents				
		Beta blockers	Metoprolol	455–5350	30-2470	
Oceania	New Zealand	Anticonvulsants	Carbamazepine	435–725	595–793	[48]
		NSAIDs	Ibuprofen	3149–11165	<loq< td=""><td></td></loq<>	
		Beta blockers	Metoprolol	2636–7443	4305–3097	

Note: LOD: limit of detection, MDL: Method detection limit, ND: Not detected, NA: not applicable.

Table 2					
Various feedstock,	their surface	area, and	application	in removing	PPCPs.

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Source	Feedstock	Pyrolysis temperature (°C)/ residence time	Surface area/pore volume/ pore size	Point of zero charge (pHpzc	Composition	Application/Reduction
[60]	Wood dust	700/6h	488.60 m ² /g, 0.286 cm ³ /g	-	C (81.50 %), H (1.87 %), O (15.63 %)	Stormwater with Bisphenol-A (98.4 %)
[52,61]	Wetland plant-based biochar	450/2h	24.83 m ² /g /15.62 nm	-	C (33.56 %), H (1.946 %), O (7.048)	Synthetic wastewater Diclofenac (95 %)
[23]	Cow dung	350/4h	Porosity: 0.36 %	-	-	Synthetic wastewater: Amoxicillin (53.82 %), Caffeine (68.8 %) Ibuprofen (63.98 %)
[62]	Activated sludge	600	$133.4 \text{ cm}^2/\text{g}/0.159 \text{ cm}^3/\text{g}$	3.94	C (38.34 %), O (41.24 %)	Batch sorption (tetracycline)
[63]	Corn straw	300/2h	25.55 cm ² /g/0.030 cm ³ /g	7.20	C (37.53 %)	Batch sorption, (Sulfamethoxazole, acetaminophen)
[63]	Corn straw	600/2h	98.94 cm ² /g/0.065 cm ³ /g	9.80	C (69.08 %)	Batch sorption (Sulfamethoxazole, acetaminophen)
[64]	Walnut shell	450/1h	$686 \text{ m}^2/\text{g}/0.070 \text{ cm}^3/\text{g}$	2.00	C (45.03 %)	Batch sorption (Ibuprofen)
[50]	Pinewood	525/8 min	Pristine: $2 m^2/g/0.003 cm^3/g$, KOH treated: $24 m^2/g/0.05 cm^3/g$	-	-	Batch sorption (ciprofloxacin and carbamazepine)
[65]	Tea waste	700/2h	$576 \text{ m}^2/\text{g}/0.1091 \text{ cm}^1/\text{g}$	_	_	Batch sorption (caffeine)
[66]	Peanut shells	800/4h	596 m ² /g/0.343 cm3/g	9.15	_	Batch sorption (naproxen)
[67]	Banana peel	750/30 min	523.8 m ² /g/0.250 cm ³ /g	90.8	C(74.2 %)	Batch sorption (acetaminophen, ciprofloxacin)
[68]	Autoclaved aerated bloc	:k _	41.69 m ² /g/0.240 cm ³ /g	8.2	_	Batch sorption (Carbamazepine, diclofenac,
	Blast furnace slang	-	1.23 m ² /g/0.0053 cm ³ /g	6.5	_	ibuprofen
	Brickbats	-	0.026 m ² /g/0.0018 cm ³ /g	4	_	
	Natural zeolite	-	33.235 m²/g/0.0995 cm³/g	7.4	_	

compounds, such as influents and effluents, have been spotted in the wastewater matrixes [34]. Furthermore, Table 1 indicates the typical PPCPs found in WWTPs across different global regions. It includes the data by region and country, focusing on various compound groups, including antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), stimulants, and anticonvulsants. South Africa shows significant concentrations of sulfamethoxazole (1436.5–14811.0 ng/L) and caffeine (20358.9–43731.8 ng/L), while Kenya also reports high levels of antibiotics. In South Asia, India demonstrates significant pharmaceutical usage, with influent levels of ciprofloxacin ranging from 14.91 to 35.98 ng/L and caffeine reaching 102,000 ng/L. Meanwhile, Pakistan exhibits noteworthy concentrations of NSAIDs, particularly naproxen, which ranges from 1516 to 2100 ng/L. Southeast Asia presents variable contamination, with Indonesia detecting carbamazepine (12 ng/L) and caffeine (12220 ng/L), while Vietnam shows lower levels of naproxen (110-170 ng/L. In East Asia, China shows significant levels of carbamazepine (30-190 ng/L) and diclofenac (1.8-17.8 ng/L). North America reports sulfamethoxazole concentrations in the USA (846-3905 ng/L) and higher naproxen levels in Canada (4260-4710 ng/L). In Europe, Germany and Spain have elevated carbamazepine (7100 ng/L) and ciprofloxacin (53,054 ng/L) concentrations, respectively. Despite some removal during treatment, the persistence of PPCPs in effluents poses significant risks to aquatic ecosystems and public health. Furthermore, Fig. 1 shows the potential distribution and number of PPCPs detected in wastewater matrices across different countries. According to Aus del Beek et al. [34] and Hawash et al. [26], there is a noteworthy and close connection between surface waters and WWTP effluents, with utmost WWTP releasing effluents directly entering surface water bodies such as lakes and rivers. A national survey by the U.S. Geological Survey identified pharmaceuticals and chemicals near public wastewater discharges and livestock farming facilities. On a global scale, WWTP effluents contribute to the contamination of about 25 % of lakes and rivers [26]. Insufficient wastewater management in developing nations contributes to substantial PPCP presence in various water bodies [28,29, 35].

Upon entering the environment, PPCPs undergo various transformation processes through photodegradation, microbial degradation, sorption to sediments, and bioaccumulation in aquatic organisms, converting to different metabolites [36]. These metabolites might be more toxic than parent compounds [37]. Additionally, the recalcitrant nature, potential for bioaccumulation, and ability to induce antimicrobial gene modification and resistance raise significant concerns about long-term ecological and human health impacts [4,7]. These issues emphasize the urgent need for effective and efficient technologies to eliminate PPCPs and stricter regulations to address PPCP pollution and its detrimental effects. Addressing PPCP contamination demands by developing more competent wastewater technologies with biochar amended, CWs offer a promising low-cost alternative to such demands [23].

3. Biochar feedstock and production for PPCP removal in CWs

3.1. Biochar feedstock

Biochar derived from various feedstock has significant potential in treating PPCPs in different environmental settings. PPCPs, including antibiotics, analgesics, and cosmetics, are emerging pollutants detected globally in water bodies due to inadequate elimination by traditional WWTP units [25,49]. The effectiveness of biochar in adsorbing these contaminants largely depends on the feedstock used and pyrolysis conditions. Feedstocks such as agronomic waste, wood residues, organic wastes, and manure [Table 2] can produce biochar with specific properties tailored for PPCP adsorption [25,50]. Plant-based biochar results from biomass sources such as crop residues, wood chips, and forestry waste. Biochar from woody resources like oak, corn, and pine has a lower density



Fig. 2. The overall process of biochar production and amended in CWs.



Fig. 3. Probable mechanism for PPCPs and biochar interactions Reproduced from Ref. [74] with permission of Elsevier.

(0.10–0.26 g/cm³) compared to biochar from manure, paper waste, food waste, and poultry litter (0.12–0.65 g/cm³) [24]. Plant-based biochar typically has high carbon content and varying porosity levels depending on the feedstock and pyrolysis circumstances. For instance, Lei et al. [51] noted enhanced removal efficiencies in mesocosm CWs by utilizing combinations of bark and biochar to treat PPCP mixtures. Similarly, Wu et al. [52] employed plant-based biochar derived from wetland plants to enhance the removal of diclofenac, demonstrating the effectiveness of biochar in pharmaceutical removal. Moreover, biochar from high-lignin content feedstocks like wood tends to have a higher surface area and porosity, enhancing its adsorption capacity [53,54]. In CW applications, plant-based biochar effectively sorbs PPCPS due to its porous nature, providing ample surface area for molecules to adhere to, thus capturing PPCPs from wastewater as they pass through the CW system.

Animal-based biochar is developed from animal waste, such as manure and bones, as well as by-products from meat processing. It may contain higher levels of nutrients and minerals, reflecting the composition of the original animal waste [55,56]. In the CW systems, animal-based biochar can enhance microbial activity due to its nutrient-rich nature [23]. A homogenized mix of biochar (particle size 0.25–1 mm) derived from cow dung pats and river bed sand (6 cm) was used in a vertical flow constructed wetland (VFCW) setup to treat a mixture of caffeine, ibuprofen, and amoxicillin [23]. Microorganisms associated with such biochar may degrade or transform PPCPs through biotransformation processes. Additionally, the porous structure of animal-based biochar contributes to PPCP adsorption, similar to plant-based biochar [56]. Biochar from feedstocks rich in minerals can provide catalytic sites that improve the degradation of PPCPs [57,58].

Similarly, other waste-based biochars are derived from organic wastes such as municipal solid waste, activated sludge, and other industrial by-products [25,59]. These materials are processed through pyrolysis to produce biochar with unique chemical compositions. Waste-based biochar often contains a complex mixture of organic compounds and minerals [59], influencing its adsorption capacity and chemical interactions with PPCPs in CWs. Using waste-based biochar in CWs offers opportunities to recycle organic wastes while improving water quality through PPCP removal. Although biochar can be derived from a wide range of feedstocks, understanding the relationship between feedstock characteristics and biochar properties is essential for optimizing its use as a sustainable solution for removing pharmaceuticals and personal care products (PPCPs) from contaminated water systems.

3.2. Biochar production used in CWs in eliminating PPCPs

The preparation of biochar for use in constructed wetlands treating PPCPs typically involves pyrolysis [23,51,61], a thermochemical decomposition process where biomass is carbonized at different temperatures without oxygen. The overall process is shown in Fig. 2. Pyrolysis temperatures typically range from 250 °C to 1000 °C, with 300 °C–600 °C being the most frequently used [69]. The temperature is gradually increased at a fixed rate (e.g., 10 °C/min) during the pyrolysis process—whether it be slow pyrolysis, fast pyrolysis, or intermediate pyrolysis—until the predetermined set temperature (e.g., 500 °C) is reached. At this point, the temperature is normally maintained for a duration of 2–5 h [23,52,61]. These conditions determine biochar properties such as pH, carbon content, and porosity, subsequently affecting the wastewater treatment's performance [69]. Various studies have shown varying effects of pyrolysis temperature on biochar's adsorption capabilities. For instance, Biochar prepared from various herb residues at 250 °C showed a sorption capacity for sulfamethoxazole that was 2–7 times higher compared to biochar prepared at higher temperatures [70]. However, findings on the influence of pyrolysis temperature on pollutant adsorption are inconsistent across studies [61,69]. Apart from dry pyrolysis, other biochar production methods such as hydrothermal combustion and gasification exist, each potentially yielding biochar with different performance characteristics, although biochars derived from such techniques have not yet been applied in CWs [69] in eliminating PPCPs.

4. Role of biochar in eliminating PPCPs from CWs

4.1. Sorption of PPCPs

Biochar plays a crucial role in eliminating PPCPs from polluted water due to its unique properties and mechanisms [24], as shown in Fig. 3. Biochar's porous architectures and extensive specific surface area provide numerous sites for the adsorption of organic pollutants [71]. The effectiveness of adsorption hinges on the physical and chemical interactions between biochar and PPCPs [25]. The surface of biochar is rich in numerous functional groups, such as hydroxyl and carboxyl, which interact chemically with PPCPs through hydrogen bonding and other forces [72,73]. Furthermore, biochar can adsorb PPCPs through electrostatic interactions, and van der Waals forces effectively reduce the concentration of these contaminants in CWs [52]. The development of functional groups in biochar is contingent upon the pyrolysis circumstances and the type of feedstock used. During the pyrolysis process, the formation of biochars characterized by aromatic structures and reduced polarity allows for effective adsorption of non-polar PPCPs through hydrophobic interactions [74]. In contrast, polar PPCPs are preferentially adsorbed by biochar with a higher concentration of oxygen-containing functional groups formed at lower pyrolysis temperatures, facilitating adsorption via hydrogen bonding and electrostatic interactions [53,74]. For instance, the incorporation of biochar made from fruit stones into zeolite-based constructed wetlands (CWs) significantly improved the removal rates of antibiotics, such as ciprofloxacin and sulfamethazine, achieving removal rates of approximately 88 % and 56 %, respectively [75]. The primary reason for these enhancements is that the biochar facilitates the adsorption and biodegradation of targeted PPCPs [24,76]. The adsorption process for PPCP removal in substrates involves two primary steps [77]. The primary step is the separation of PPCPs from organic materials with identical chemical properties. The second step is the adsorption of these PPCPs onto the substrate surface, where their extractability, toxicity, and bioavailability decrease over time due to prolonged contact [22]. Additionally, biochar's negative surface charge [78] facilitates electrostatic interactions with positively charged PPCPs. Biochar can also form complexes with PPCPs [50,79] enhancing their removal. Ravichandran et al. [80] explored the removal of three pharmaceuticals (atenolol, carbamazepine, and diclofenac) using different substrates, including wood charcoal, in a Canna indica-supported wetland system. Their study estimated that sorption to the substrate accounts for 0.3-4.25 %, while plant accumulation as the parent compound is less than 0.1 %, indicating that sorption is the primary pathway compared to plant uptake. Similarly, Cheng et al. [81] investigated the effectiveness of Canna indica planted-constructed wetlands in eliminating 24 types of PPCPs, including antibiotics, steroid hormones, and biocides. They also reported a similar observation, noting that substrate adsorption was the primary contributor removal mechanism, accounting for 0.05 %-14.3 % of removal, whereas plant uptake contributed between 0.001 % and 0.44 %. Moreover, Wei et al. [52] demonstrated that the incorporation of plant-based biochar markedly enhanced the treatment efficiency, achieving 95 % removal of diclofenac (DCF) under optimal conditions, with a hydraulic retention time (HRT) of 7 days and a pH range of 6.5-7.5. Adsorption onto the substrate was identified as the primary mechanism for DCF reduction, with removal efficiency increasing proportionally with DCF concentration.

4.2. Microbial activity enhancement

Biochar can also enhance microbial activity within CWs. Its porous nature provides a suitable habitat for microbial communities, promoting biofilm formation and microbial colonization. It acts as an excellent carrier for biofilms, indirectly enhancing the degradation of contaminants like bisphenol [60]. These biofilms can degrade PPCPs through metabolic processes, enhancing the biodegradation efficiency of the wetland system. Ravichandran et al. [82] assessed the effectiveness of CWs in removing 14 PPCPs. They reported that microbial degradation played a major role, accounting for 74.9 %-93.8 % of removal, compared to direct contribution by sorption (0.54 %-12.56 %) and plant uptake (<1 %). Cheng et al. [81] also reported microbial degradation as the predominant contributor to PPCP removal, exceeding 85 %, in constructed wetlands. The presence of biochar can enhance microbial diversity and activity, leading to the more effective breakdown of complex organic compounds such as PPCPs. In certain conditions, biochar may catalyze redox reactions that contribute to the breakdown of PPCPs through biodegradation [69,81]. While the impact of biochar addition on microbial diversity and richness in CWs remains variable across studies, recent research indicates that biochar substrates in CWs support an increased abundance of functional microorganisms [75,83]. Biochar's heterogeneous surface, characterized by a large specific area and abundant pores, effectively traps nutrients and organic compounds, promoting microbial proliferation and metabolic activity [69]. This enhancement strengthens microbial processes involved in PPCP degradation, transformation, and elimination [23]. Actinobacteria, Proteobacteria, Bacteroidetes, and Planctomycetes are the dominant phyla in CWs supplemented with wood biochar, suggesting their potential adaptation to pharmaceutical compounds exposure in CWs [80]. The amended top layers with bark and charcoal exhibited a high dominance of Rhizobium, Pseudomonas, and Acinetobacter [84]. It has been found that biochar-amended CWs were dominated by microbial phyla such as Bacteroidota and Proteobacteria, with over 88 % of sequences from key phyla [52]. Citrifermentans and Symbiobacterium were abundant in CWs, including control CW units, while Paenibacillus and Polycyclovorans increased significantly in DCF-treated units [52]. The presence of DCF significantly influences the composition of microbial communities, with the effects varying across different microbial groups, indicating the high potential for microbial community medication due to the presence of PPCPs. This finding indicates the microbial diversity in CWs supplemented with biochar-dealing PPCPs. Although DCF exposure transiently inhibited nitrifying and denitrifying bacteria growth, the microbial community rapidly adapted, restoring functional stability [52]. However, only a few studies have investigated microbial diversity in biochar-amended systems, highlighting the need for further exploration.

4.3. Nutrient cycling and plant growth

In addition to adsorption and microbial enhancement, biochar can improve nutrient availability and retention in CWs, supporting plant growth. In biochar-amended CWs, nutrient recycling is enhanced by the addition of biochar, a highly porous material that improves the wetland's efficiency in removing and cycling critical nutrients like nitrogen, phosphorus, and carbon [69,85]. Studies show biochar addition increases nitrogen content in plant biomass in CWs, potentially aiding nitrogen removal through plant harvesting, although moderately [83], contributing to nutrient retention. Biochar increases the adsorption capacity of the wetland, trapping nutrients and pollutants while providing a stable habitat for microbial communities that drive nitrification, denitrification, and other biochemical processes [24]. It also enhances phosphorus retention by binding it to its surface, preventing it from leaching and making it available for plant uptake [86,87]. Moreover, adding biochar influenced the physicochemical conditions in CWs, such as hydraulic conductivity, dissolved oxygen and pH, thereby enhancing nutrient absorption by plant roots [88]. Biochar, along with microbes at the plant rhizosphere, can support the functionality of plant roots. Additionally, biochar may directly release substances that promote plant growth. As a consequence of these interactions, the nitrogen amount in Phragmites australis significantly increased from 1.40 mg/g to 1.95 mg/g with the addition of wood biochar [89]. The uptake of phosphorus also improved in biochar-amended CWs, where enhancements in nitrogen and phosphorus removal by plants were 15.4 % and 14.2 %, respectively, compared to only 8.00 % and 8.30 % in CWs without biochar [90]. These findings indicate that biochar can improve soil porosity, increase nutrient holding, and enhance water-retention capacity, creating a more favorable environment for plant growth [22,69]. This, in turn, such plant growth can enhance the overall removal efficiency of PPCPs in CWs through different mechanisms such as plant uptake and rhizospheric bacteria degradation. Plants also play a crucial role directly or indirectly in the uptake and degradation of PPCPs through processes such as plant uptake, phytodegradation, and phytovolatilization and facilitating rhizospheric bacteria degradation [91,92]. Plants CWs also function as indicators and contributors to their treatment efficiency. They play essential roles in removing pollutants, including PPCPs, primarily through assimilation and rhizofiltration [92]. Plants also support microbial communities by releasing oxygen through roots and secreting exudates [19]. Macrophytes in CWs influence hydrodynamic conditions [93] and provide multiple ecosystem services, enhancing aesthetic value and making CWs popular for water remediation and conservation. Optimal plant growth during the initial stages is crucial for CW establishment and function. Adding biochar in CWs significantly enhances plant growth, increasing aboveground and belowground biomass compared to biochar-free systems [83,94,95]. This improvement is further attributed to the release of nutrients such as Ca, K, Mg, P, and N from biochar and wastewater after desorption, as well as the enhancement of media porosity, which increases oxygen availability and supports plant growth [85,96]. Biochar substrates in CWs enhance nutrient utilization by supporting diverse microorganisms and adsorb plant growth inhibitors such as PPCPs, thereby reducing phytotoxicity [83,85]. They also promote root aerenchyma tissues and macrophyte porosity [97], which increase root oxygen loss, root exudates, and aerobic microbial activities like organic degradation of PPCPs [23,76,83,98].

5. Factors influencing biochar effectiveness in PPCP removal

5.1. Pyrolysis temperature, feedstock characteristics, and surface modifications

The physicochemical properties of biochar, such as surface area, pore size distribution, and presence of various functional groups such as hydroxyl, carboxyl, and phenolic groups, determine its adsorption capacity and affinity for different PPCPs. These possessions brand biochar as an excellent candidate for environmental applications, predominantly for the adsorption of organic and inorganic contaminants from polluted water [54]. The variability in biochar properties due to different production conditions emphasizes the need to optimize factors like pyrolysis temperature for specific applications such as CWs. The pyrolysis temperature used in biochar production influences its PPCP adsorption mechanisms by changing the properties of biochar [99,100]. The pyrolysis of biomass at temperatures between 300 °C and 800 °C significantly affects the physicochemical properties of biochar, which are essential for eliminating PPCPs from aqueous environments [53]. At lower pyrolysis temperatures (250-450 °C), biochar surfaces have more organic functional groups and noncarbonized organic residues, which enhance PPCP removal through increased partitioning [24]. In contrast, higher pyrolysis temperatures (400-800 °C) yield biochar with greater aromaticity and larger surface areas, enhancing adsorption capacity [24]. Furthermore, the thermal degradation of hemicellulose, cellulose, and lignin during pyrolysis contributes to the adsorption capabilities of biochar. Specifically, hemicellulose and cellulose, which decompose at lower temperatures, yield oxygenated compounds and oxygen-containing functional groups that enhance interactions with polar PPCPs [53]. Meanwhile, lignin's relatively straightforward decomposition pathway increases the aromaticity of biochar, improving its efficacy in the adsorption of non-polar PPCPs. For example, Li et al. [72] explored that biochar produced at lower temperatures (300 °C and 600 °C) exhibited charge-assisted hydrogen bonding with covalent bond characteristics when the $|\Delta pKa|$ was less than 5.0. This led to almost double the adsorption capacities (Q) and affinities (K) of biochar produced at 300 °C (Q \geq 195 μ mol/g, K \geq 1.9956) compared to BCs-600 (Qs \leq 92 μ mol/g, Kf \leq 0.5192) for PPCPs (clofibric acid, sulfamerazine, and acetaminophen), compared to biochar produced at 600 °C. Similarly, Xu et al. [101] explained that biochar produced from wetland plants at 600 °C is less effective in the adsorption of diclofenac than that produced at 450 °C due to the loss of hydrophobicity caused by the degradation of aliphatic compounds at higher temperatures. Conversely, the sorption affinities of cow manure biochars produced at temperatures ranging from 300 °C to 700 °C for oxytetracycline and carbaryl were observed to upsurge with higher pyrolysis temperatures [102]. Moreover, biochar produced at lower temperatures typically encompasses more oxygen-governing functional groups, enhancing its ability to adsorb polar compounds and potentially providing greater mechanical strength for applications in CWs. In contrast, biochar produced at higher temperatures demonstrates increased porosity, surface area, aromaticity, carbon content, and hydrophobicity [59,69].

Therefore, the physicochemical properties of biochar, including pore distribution, surface functional groups, alkalinity, and specific surface area, are significantly influenced by the feedstock and pyrolysis conditions, which in turn affect its adsorption capacity and biofilm adhesion [69,100]. Moreover, the net surface charge of biochar is dependent on surface functional groups and ash content, which are essential for explaining its adsorption behavior towards ionized or ionizable compounds [69,103]. Typically, biochar exhibits alkaline pH values ranging from 7.9 to 9.8 when used in CW, reflecting its potential for effective pollutant removal [69]. Further, the carbon content of biochar is a key indicator of its quality and varies significantly with the feedstock [104]. For example, biochar derived from cow and pig manure contains approximately 43 % carbon, whereas wood-based biochar can achieve more than 80 % carbon content, underscoring the significant influence of feedstock on biochar characteristics [105,106]. Moreover, biochar exhibits substantial variability in specific surface area, influenced by production methods and feedstock variability [106].

Chemical, physical, and biological modifications can further enhance biochar's properties and adsorption capacities for pollutants [59]. The adsorption capacity of biochar can be enhanced through surface modifications, including acid/alkali treatment to increase oxygenated functional groups and impregnation with nanomaterials such as Cu and Fe. For instance, KOH treatment significantly increased the ciprofloxacin adsorption capacity, achieving an enhanced adsorption capacity of 9.8 mg/g compared to pristine biochar's 3.8 mg/g [50]. The increased adsorption capacity is attributed to the significantly higher specific surface area (>11 times) and the greater abundance of functional groups present in the modified biochar compared to the pristine form [50]. Nanomaterial-impregnated biochar composites also exhibit enhanced PPCP removal capacities. For example, the CuO/Cu₂O/Cu-biochar composite exhibited a more specific surface area and total pore volume compared to fresh biochar, attributed to Cu²⁺ acting as a pore-developing mediator during fusion [79]. Adsorption experiments demonstrated that the composite could remove 88.96 % of diclofenac and 93.02 % of carbamazepine, which was nearly double the removal efficiency compared to raw biochar [79]. Similarly, the iron-containing biochar displayed maximum monolayer adsorption capacities of 39.08 mg/g for CIP and 6.77 mg/g for DCF [78]. Additionally, combining alkaline treatment with nanoparticle impregnation [24] has yielded even more outstanding results. It has been observed that treating biochar with NaOH and Fe²⁺/Fe³⁺ ion solution through co-precipitation developed magnetic chitosan biochar, which eliminated 98.8 % of ibuprofen, 96.4 % of diclofenac, and 95.2 % of naproxen in batch adsorption [24,107].

In conclusion, understanding how biochar properties, modified through pyrolysis and other techniques, influence its performance in CWs is crucial for optimizing its application in pollutant removal systems. Further systematic research is necessary to investigate the specific impacts of biochar characteristics under diverse environmental conditions and with various target pollutants. To date, there has been no research on using surface-modified biochar in CWs to attenuate PPCPs and elucidate the real scenario.

PPCPs	Biochar	Removal efficiency (%)		
		Biochar amended CWs	Un-amended CWs	
Mixture of 12 PPCPs	Bark biochar	Carbamazepine & irbesartan (>80 %), trimethoprim (100 %)	Irbesartan (45 %) carbamazepine (34 %), Trimethoprim (95 %)	[127]
Triclosan (TCS)	Cow dung biochar	71.83 % (VFCW), 98.41 % (TFCW)	64.25 % (VFCW), 82.41 % (TFCW)	[76]
Amoxicillin (AMX), Caffeine (CF), Ibuprofen (IBU)	Cow dung pats	75.51 % (AMX), 87.53 % (CF), 79.93 % (IBU)	53.82 % (AMX), 68.8 % (CF), 63.98 % (IBU)	[23]
Diclofenac	Constructed Wetland Plants based biochar (BC)	>90 % (at initial DFC 0.75–1 mg/L, pH 6.5–7.5, HRT 7 days)	-	[52]
Hydrochlorothiazide, chloramphenicol, furosemide, gemfibrozil, triclocarban, and triclosan	Biochar (unknown)	>99.99 % reduction of all PPCPs	Hydrochlorothiazide(57.7 %), chloramphenicol(83.7 %), furosemide (68.6 %), gemfibrozil(64.1 %), triclosan (99.8 %), and triclocarban(99.5 %)	[128]
sulfamethoxazole (SMZ), trimethoprim (TMP), diclofenac (DFC), carbamazepine (CBZ), benzotriazole (BTA), furosemide (FRS), caffeine (CAF), metoprolol (MET), and propranolol (PRO).	Bark + Biochar	>80 % for all	CBZ (34 %) and IBT (45 %)	[51]
Ciprofloxacin (CIP), sulfamethoxazole (SMX)	Fruit stone biochar	CIP (88.05 %) and SMX (56.57 %)	-	[75]

Table 3

Types of biochar amended in improving the removal of various PPCPs from CWs.

ND: not detected, LOQ: Limit of quantification, MDL: method detection level, NA: not applicable.

5.2. Environmental pH

The pH of a solution critically regulates the sorption process by affecting the ionization and charge of the PPCPs, as well as the surface charge and speciation of the biochar [49,108,109]. The pH effect on the PPCP sorption ability of biochar is influenced by the pKa of the targeted PPCP, solution pH and the pHpzc of the biochar surface [67,110]. Maximum sorption is attained when the repulsion of PPCPs and the biochar surface is minimized (pKa of the PPCP < pH of solution < pHpzc of biochar) [24,69,100]. At pH levels above the point of zero charge, competition between protons and cationic pollutants diminishes, leading to a negative charge on the adsorbent surface due to the deprotonation of phenolic and carboxylic groups [69]. Conversely, basic functional groups like amines are protonated and positively charged at lower pH, enhancing the adsorption of anions [69]. Thus, acidic pH conditions enhance various PPCP removal because the surface of biochar remains protonated at low pH, reducing repulsion [111]. For instance, the sorption of triclosan and ibuprofen by biochar can reach up to 500 mg/g at low pH (4–7), compared to just 4 mg/g at higher pH levels (>10) [112]. Similarly, sulfonamide and sulfamethazine sorption on biochar was high at low pH (3–4.5) [113]. It has also been observed that the removal of PPCPs decreases significantly at pH levels above 8 [111], resulting in notable reductions in effectiveness. Therefore, biochar that exhibits high efficacy in removing PPCPs across the pH range commonly found in wastewater will likely enhance performance in wastewater treatment applications.

5.3. Influent wastewater characteristics

The composition of wastewater, including influent PPCP concentrations, pH, and organic matter content, influences biochar's performance in PPCP removal. Higher concentrations of PPCPs with other competitive pollutants may require higher biochar dosage or longer contact times for effective removal [22,23,114]. The multifaceted characteristics of wastewater can pointedly impact the elimination process of PPCPs by biochar, primarily due to competition for available adsorption sites [24,83]. For instance, in actual conditions, PPCPs often coexist with organic matter such as humic acid, which can negatively impact the removal efficiency of PPCPs due to competitive adsorption [115]. However, the humic acid adsorbed onto adsorbents contains amino groups that form hydrogen bonds by hydroxyl groups in ciprofloxacin, thus increasing the removal of ciprofloxacin [116]. Further, it has been observed that the maximum adsorption capacity of biochar for metronidazole decreases significantly in the presence of nitrate and phosphate, which is attributed to the limited availability of active adsorption sites [117]. Increased phosphate levels in wastewater may diminish triclosan sorption onto biochar due to competition for adsorption sites, given that triclosan and phosphate are in anionic forms [118]. In contrast, the adsorption of heavy metals has been observed to elevate the positive charge on the biochar surface, thereby enhancing sulfamethoxazole sorption onto biochar [119]. Salts in wastewater environments can influence the removal of PPCPs in biochar-enhanced CWs. Elevated salt concentrations typically enhance sorption via the salting-out effect [21]. However, the practical applicability of these findings may be constrained by the higher ion concentrations typically used in batch adsorption studies compared to those found in natural water settings [21]. Similarly, it has been reported that elevated levels of carbonates negatively affect PPCP sorption due to competition for active adsorption sites [21,120].



Fig. 4. Mechanism of PPCP removal in biochar amended CWs.

Similarly, wastewater temperature also influences the effectiveness of biochar in constructed wetlands (CWs). The interactions between sorbates (PPCPs) and sorbents (biochar) involve energy exchange characterized by either endothermic or exothermic sorption [66]. Temperature plays a dual role: it affects the solubility of PPCPs in water and modifies the physical properties of biochar processes [21]. It is widely recognized that lower temperatures can impede pollutant removal efficiency. For instance, Cheng et al. [121] demonstrated that low temperatures significantly decreased the removal of TCS and DCF due to inhibiting microbial biochemical reactions in CWs. Conversely, higher temperatures accelerated enzyme activities, enhancing both phytoremediation and biodegradation of PPCPs while increasing sediment adsorption and bioavailability [122]. Therefore, these factors collectively influence the sorption dynamics of PPCPs onto biochar enhanced in CWs, necessitating thorough investigation under natural climatic conditions and the need to correlate with the considerations for hydraulic loadings of CWs.

5.4. Biochar dose

The amount of biochar added to CWs affects its ability to adsorb PPCPs. Optimal biochar dosage ensures sufficient adsorption capacity without causing hydraulic or operational issues in the CW system. Deng et al. [123] conducted an experiment using different quantities of biochar mixed with gravel (0 %, 10 %, 20 %, and 30 %) to investigate the effects of increased biochar depth on metabolite profiles and microbial communities. They observed that higher biochar doses in the gravel medium improved the removal efficacy of contaminants in CWs. Conversely, the total content of Extracellular Polymeric Substances (EPS) diminished with higher biochar percentages. Moreover, the increased biochar dosage in CW substrates improved EPS biodegradation and enriched microbial communities, thereby facilitating the removal of organic compounds [123]. Moreover, increased biochar dosage in CW substrates enriched microbial communities, potentially optimizing pollutant degradation pathways and overall treatment effectiveness.

5.5. CWs system design

The configuration and design of CW systems play a pivotal role in determining the efficacy of biochar in treating pharmaceuticals and personal care products. Factors such as flow rates, hydraulic retention time, and the spatial arrangement of biochar within the CW matrix directly influence the contact time between biochar and pollutants [24,124], thereby affecting treatment efficiency. These parameters are related to the CW's issues, such as clogging, affecting the overall pollutant reduction performance of CWs. In horizontal-flow wetlands, 'preferential clogging' occurs at the inlet and within the top layers of the substrates due to the nature of wastewater loading, leading to sludge accumulation that reduces subsurface permeability and promotes overland flow. In vertical flow wetlands, the influent is distributed through perforated pipes, with the first media layer of coarse gravel facilitating percolation; however, clogging is prevalent in the top layer due to high biological activity, and insufficient dosing intervals can hinder oxygen transfer and mineralization, exacerbating clogging [125]. Using biochar with coarser grain sizes enhances constructed wetlands by improving hydraulic conductivity, increasing surface area for microbial colonization, promoting better aeration, and reducing organic accumulation, ultimately mitigating clogging and enhancing treatment efficiency [126]. Biochar with 1–3 cm diameters is commonly used to mitigate clogging, as it reduces the accumulation of 'microbial extracellular polymeric substances in wastewater [125]. By enhancing the metabolic activity of heterotrophic bacteria, biochar promotes the conversion of heavy molecular weight EPS into lower molecular weight compounds, facilitating organic decomposition and reducing clogging. In vertical flow CWs, biochar is typically placed between two layers of inert material to prevent clogging [126]. Furthermore, using larger grain sizes (2–30 mm) at the filtration system's top also helps avoid clogging [69]. Moreover, clogging phenomena in constructed wetlands can be minimized by implementing pretreatment processes that reduce the organic load contributing to biological clogging to biochar-amended CWs. Strategies such as decreasing the organic loading rate, lowering the hydraulic loading rate, and enhancing aeration can effectively mitigate clogging issues [125,126]. Thus, the optimal design ensures that the residence time of wastewater in contact with biochar/substrate is sufficient for effective adsorption and subsequent degradation of PPCPs. Additionally, the strategic placement of biochar within the CW system enhances its interaction with pollutants, maximizing the overall removal efficiency of PPCPs from wastewater streams. This integrated approach underscores the importance of CW configuration in harnessing biochar's potential for sustainable water remediation practices.

6. Performance of biochar-amended constructed wetlands

Recent studies highlight biochar's role in enhancing micropollutant removal efficiency in CWs, with significant improvements observed for PPCP attenuation. Table 3 summarizes the performance of various biochar-amended CWs in attenuating PPCPs. Lei et al. [127] observed that replacing sand with bark and biochar in constructed wetlands noteworthily improved the elimination of various micropollutants, including irbesartan, carbamazepine, hydrochlorothiazide, and benzotriazole, with median removal rates exceeding 40 %. The bark-biochar CW demonstrated higher elimination efficacies for irbesartan, carbamazepine, and hydrochlorothiazide, ranging from 40 % to 90 %, compared to less than 40 % in the sand CW. This enhanced removal efficiency is ascribed to the higher adsorption capacity of bark-biochar compared to sand. Adsorption is a critical removal mechanism for irbesartan in CWs, as highlighted by this study. Carbamazepine, known for its resistance to biodegradation, primarily relies on adsorption for its removal. However, there were no significant changes in removing trimethoprim and clarithromycin. The bark-biochar CW displayed similar elimination efficacies for clarithromycin as the sand CW, both achieving close to 100 % removal during the study periods. This indicates that using bark-biochar had no supplementary value for clarithromycin removal, indicating the roles of other mechanisms such as photodegradation. Similarly, Wu et al. [52] observed that adding constructed wetland plants-based biochar to

vertical subsurface flow-constructed wetlands significantly enhanced the elimination of DCF, achieving over 90 % removal at an initial DCF concentration of 0.75–1 mg/L, pH of 6.5–7.5, and a hydraulic retention time of 7 days. The study also found that DCF concentration significantly reshaped the microbial community assembly, highlighting its role in elimination. Hu et al. [128] investigated how substrates (sand, perlite, vermiculite, and biochar) in constructed wetlands affected arbuscular mycorrhizal fungi (AMF) colonization in Glyceria maxima roots and their role in PPCP removal. Results showed that perlite, vermiculite, and biochar enhanced AMF colonization, influencing PPCP uptake and translocation differently across substrates. This study highlights substrate-dependent effects on the symbiotic relationship between AMF and plant roots in PPCP removal within CWs. Chand et al. [23] examined the elimination efficiency of amoxicillin (AMX), caffeine (CF), and ibuprofen (IBU) in VFCWs, comparing setups: SB (substrate matrix + biochar), SBP (substrate matrix + biochar + plant), and SP (substrate matrix + plant). SBP effectively removed 75.51 % (AMX), 87.53 % (CF), and 79.93 % (IBU) at an influent load of 1 mg/L, surpassing SB and SP significantly (p < 0.00). The study underscored the potential of biochar-enhanced planted VFCWs for pharmaceutical removal from wastewater, suggesting future research on the impact of pharmaceutical load on plant toxicity in these systems. Suthar et al. [76] evaluated triclosan removal in VFCWs with three setups: B-VFCW (biochar), PB-VFCW (plant and biochar), and C-VFCW (plant only), operating in normal flow and tidal-flow modes (B-TFCW, PB-TFCW, C-TFCW). PB-TFCW exhibited the highest TC reduction efficiency (98.41 %), followed by C-TFCW (82.41 %) and B-TFCW (77.51 %), surpassing VFCWs (PB-VFCW 71.83 %, C-VFCW 64.25 %, B-VFCW 52.19 %) significantly (p < 0.001), highlighting biochar and tidal flow as effective strategies for TC elimination. Yuan et al. [75] employed a VFCW employing various substrates—zeolite (CW-Z), manganese ore (CW-M), and biochar (CW-C)-to treat antibiotics in wastewater. CW-M exhibited notable efficacy in removing ciprofloxacin hydrochloride (93 %) and sulfamethazine (69 %). High abundances of amoA, nirK, and nirS genes were observed in CW-M and CW-C, whereas CW-C suppressed quinolone resistance genes. The study highlighted substrate-dependent impacts on microbial diversity and revealed that Mn ore promoted nitrogen-related phyla abundance, underscoring its potential for dual antibiotic and nitrogen removal in VFCWs. Overall, biochar addition in constructed wetlands enhances the removal of PPCPs either through direct sorption mechanisms or indirectly by promoting microbial activity and facilitating pollutant degradation processes. However, factors such as organic loading rates, environmental conditions, biochar substrate configuration, dosage, and specific characteristics of biochar can significantly influence the efficacy of PPCP elimination in CWs.

7. PPCP removal mechanism in biochar amended constructed wetland

The removal of PPCPs in biochar-amended CWs involves the synergistic actions of plants, microorganisms, and biochar-substrate [76], as shown in Fig. 4. In brief, plants promote oxygen transfer through their roots, creating aerobic zones that enhance microbial activity and provide surfaces for biofilms to degrade pollutants [129]. While plants can directly absorb and break down PPCPs, their indirect effects—stimulating microbial activity in the rhizosphere and forming supramolecular complexes with humic acids from decaying plant material—are more impactful, boosting the removal efficiency of PPCPs [92]. Various plants such as Vetiver, *Colocasia*, and *Canna* have been proven to remove different PPCPs [91]. Moreover, Microorganisms, especially bacteria, are crucial in breaking down complex PPCPs into simpler compounds through biodegradation. These microbes thrive in both aerobic and anaerobic zones of the CW, facilitated by the oxygen released by plant roots and biochar's ability to improve the redox conditions. The key microorganism like *Proteobacteria, Firmicutes, Chloroflexi*, and *Actinobacteria* degrade PPCPs [130,131]. Cyanobacteria further enhance degradation by producing oxygen and serving as electron acceptors, particularly improving the breakdown of pharmaceuticals like ciprofloxacin and sulfamethazine [130]. Biochar amended with other substrates in CWs enhances the adsorption of PPCPs due to its porous structure, reducing the mobility of pollutants and allowing microorganisms more time to degrade them [74,83]. It also provides a habitat for microbial communities, supporting their growth and enhancing biodegradation processes. Together, these elements—plants, microorganisms, and amended biochar with other substrates —work in a coordinated manner to maximize the removal of PPCPs in constructed wetlands.

8. Challenges and considerations

8.1. Biochar quality and consistency

The variability in biochar properties, influenced by diverse feedstocks and production conditions, can significantly impact its performance. Biochar's physical and chemical characteristics, including surface area, porosity, pH, and nutrient content, are intrinsically linked to the type of biomass used and the specific pyrolysis parameters, such as temperature, heating rate, and residence time [59]. These variations are critical as they can affect biochar's efficacy in applications like PPCP removal in constructed wetlands. To ensure consistent and reliable performance of biochar in various applications, it is imperative to standardize biochar production processes. Establishing clear guidelines for feedstock selection and pyrolysis conditions can help generate biochar with predictable and desirable properties. Additionally, comprehensive characterization of biochar, including proximate and ultimate analysis, surface morphology, and identification of functional groups, are essential to understand its behavior and optimize its use in specific applications [132]. Implementing standardized testing protocols and quality control, measures will facilitate the comparison of results across different studies and enhance the credibility and adoption of biochar in CWs and other environmental applications. Addressing these variability issues through standardization and thorough characterization will enable researchers and practitioners to maximize the benefits of biochar and promote its sustainable utilization.

8.2. Long-term stability and reusability

The long-term stability and effectiveness of biochar in constructed wetlands treating pollutants like PPCPs require comprehensive investigation to ensure its sustainable application. It is crucial to understand the degradation processes that biochar may undergo over extended periods and to explore potential regeneration methods to restore its functional properties [72]. Assessing the reusability of biochar [111] is also essential to determine whether it can be effectively recycled within CW systems. Additionally, studies focusing on the long-term impacts of biochar on CW performance are necessary to evaluate its efficacy in pollutant removal and overall system



Fig. 5. (a) Co-occurrence network of keywords, (b) Overlay visualization map of Keywords occurrence networks and (c) keywords occurrence density mapping.





efficiency over time. Another critical aspect is investigating the potential for biochar to release previously adsorbed contaminants back into the environment, which could pose risks to both human health and ecological systems. Therefore, extensive research is needed to elucidate these aspects, enabling the safe, efficient, and sustainable use of biochar in CW applications at field scale.

8.3. Economic and environmental implications

The cost-effectiveness and environmental impact of large-scale biochar production and application are critical factors that need thorough assessment. Conducting life cycle analysis (LCA) and economic feasibility studies [56] is essential to comprehensively evaluate the overall benefits and drawbacks of using biochar in constructed wetlands. LCA can provide insights into the environmental footprint of biochar production, including metrics such as greenhouse gas emissions, energy consumption, and resource use [133]. This analysis will help determine whether the environmental benefits of biochar application, such as improved water quality and carbon sequestration, outweigh the associated production costs and environmental impacts. Economic feasibility studies are equally important to assess the financial viability of integrating biochar into CWs on a large scale, considering factors like production costs, operational savings, and potential revenue from enhanced ecosystem services [134]. Additionally, understanding the environmental impact of biochar production is crucial for ensuring that the process aligns with sustainability goals. This includes evaluating the emissions from pyrolysis, potential land use changes, and any adverse effects on local ecosystems. By rigorously analyzing these aspects, researchers and policymakers can make informed decisions about the practicality and sustainability of biochar use in CWs, ensuring that its implementation delivers net positive outcomes for both the environment and society.

9. Future perspectives and research direction

Future research should focus on optimizing biochar production and dosage for specific PPCP removal in CWs, understanding the interactions between biochar, microorganisms, and plants, and scaling from laboratory to field applications. Optimizing biochar production is a multifaceted challenge that necessitates a detailed understanding of the interactions between feedstocks and pyrolysis conditions to enhance adsorption capacities for diverse groups of pharmaceuticals and personal care products [120]. The pyrolysis temperature and residence time are key parameters along with feedstock-producing biochar with a desirable surface area and pore volume balance, contributing to its pollutant removal efficiency [53,74]. The choice of feedstock is vital; carbon-rich materials with low mineral content generally yield higher-quality biochar. Research should delve into how different pyrolysis temperatures, heating rates, and residence times impact biochar's physical and chemical properties to improve the adsorption efficiency of various contaminants in CWs. Moreover, several batch adsorption studies are viable for modified biochar using physical and chemical treatments; however, the examination of their performance in CWs in real scenarios is understated and needs further exploration.

Understanding the interactions between biochar and microbial communities in CWs is equally crucial. Biochar can significantly influence microbial activity and biofilm formation, which are critical for the biodegradation of PPCPs. Studies should investigate how biochar prepared from different feedstock amendments affects microbial diversity and richness, potentially enhancing the breakdown of contaminants. For example, biochar's porous structure can provide habitats for microbial colonization and facilitate electron transfer processes, which are essential for microbial metabolism [83]. To date, very few researchers explored the interactions of microbial diversity and richness with biochar-amended CWs in removing PPCPs. Gaining insights into these interactions can help optimize CW designs, making them more effective at removing PPCPs through both adsorption and microbial degradation. In the context of CWs, biochar has shown promise for enhancing pollutant removal. However, factors such as substrate properties, hydraulic retention time, oxygenation, and redox conditions significantly impact the removal efficiency [53,126]. An optimal configuration for biochar in CWs involves placing it as an interlayer between inert materials like sand or gravel [125,135]. This design helps prevent issues like clogging or biochar flotation, which can compromise the system's performance. These issues arise during the operation and maintenance of biochar-amended CWs, causing waterlogging and impacting the beneficial microorganism, which needs further in-depth study to explore the proper use of biochar in CWs treating PPCPs and other pollutants. Despite its potential, the application of biochar in CWs is still relatively underexplored, especially for removing emerging pollutants. There is limited research on its ability to remove emerging organic pollutants and pathogens. Therefore, the mechanisms involved in these processes require further investigation with biochar from different feedstock. Although biochar's effectiveness has been demonstrated in laboratory settings for a few PPCPs, more in situ studies are needed to understand its performance in real wastewater treatment scenarios.

While laboratory-scale studies have demonstrated the efficacy of biochar in CWs, translating these findings to field-scale applications is essential. Large-scale studies are needed to address practical challenges such as the optimal placement of biochar within CWs, maintenance requirements, and long-term performance. Field-scale validations can also help identify unforeseen issues that may arise in real-world settings, where environmental conditions are more variable and complex. This step is crucial for ensuring that biocharamended CWs are effective but also feasible and sustainable in practical applications. Additionally, investigating the potential for using biochar in different types of CWs, such as vertical flow, horizontal flow, and hybrid systems, can provide insights into the most effective configurations for PPCP removal.

Integrating biochar-amended CWs with other advanced treatment technologies holds significant potential for enhancing PPCP removal efficiency. Combining biochar-amended CWs with advanced oxidation processes such as membrane filtration and nano-technology could exploit synergistic effects, improving overall treatment performance [136,137]. For example, advanced oxidation processes can break down PPCPs into smaller, more adsorbable molecules, which biochar can remove effectively [138,139]. However, such integrations are needed for in-depth studies. Additionally, comprehensive life cycle assessments and economic analyses are vital to evaluating biochar production and application sustainability. These assessments should consider factors such as greenhouse gas emissions, energy consumption, and overall costs [83], ensuring that biochar use provides net environmental and economic benefits. It has been observed that in biochar-amended CWs, the average fluxes of N₂O and CO₂ were significantly lower, while CH₄ fluxes were elevated compared to non-biochar CWs. The incorporation of biochar reduced the global warming potential (GWP) of N₂O and CH₄ by 18.5 %–24.0 %. Additionally, as COD/N ratios increased, N₂O fluxes and GWP decreased, whereas CH₄ and CO₂ fluxes increased [140]. Thus, balancing these trade-offs will be vital to developing sustainable and effective CW systems that address the growing concern of PPCP contamination in wastewater. Key strategies include optimizing biochar properties, adjusting operational parameters, and enhancing microbial diversity to improve pollutant removal [88,115].

Further, to identify research gaps in the use of biochar in CWs for treating persistent pharmaceutical compounds, a bibliometric analysis was conducted via VOSviewer (version 1.6.20), using Scopus as a search engine. This analysis resulted in network visualizations of keywords and their co-occurrence, as shown in Fig. 5 (a) - (c). The layout of these networks illustrates the relationships and interactions between various research themes, while the density visualization highlights the concentration of research efforts in specific areas [141]. Fig. 5(a) displays the keywords network co-occurrence, revealing clusters of frequently co-occurring terms and indicating established research domains and potential areas for further investigation. The red cluster contains the largest group of keywords, focusing significantly on terms such as 'hydrophobicity,' 'carbamazepine,' and 'caffeine.' The blue and yellow clusters primarily emphasize the use of constructed wetlands (CWs) and water quality, particularly in relation to health and ecosystems. VOSviewer analysis further highlights the temporal distribution of keyword co-occurrence in recent years, as depicted in Fig. 5(b), indicating nodes that appear yellow represent keywords in their early stages of development. Since 2022, research has predominantly concentrated on ecosystem and human health risks, PPCPs, and bioremediation. Fig. 5 (c) shows the density of these keywords, with denser regions representing higher concentrations of research activity [141,142]. This bibliometric approach revealed clusters of frequently co-occurring terms, indicating established research domains and potential areas for further investigation. The analysis underscores the need for more comprehensive studies on the long-term efficacy and mechanisms of biochar in CWs, the standardization of evaluation methodologies, and the environmental impacts of biochar application. By providing a systematic overview of the current research landscape, this bibliometric analysis facilitates the identification of critical gaps and guides future studies aimed at enhancing the application of biochar in CWs for the treatment of PPCPs.

10. Conclusion

The presence of PPCPs in wastewater poses significant challenges to environmental and human health. CWs have emerged as a viable and sustainable solution for mitigating these contaminants, yet their efficiency can vary due to diverse operational factors. Recent studies have highlighted biochar, derived from biomass pyrolysis, as a promising amendment to enhance CW performance in PPCP removal. Biochar's efficacy in CWs stems from its multifaceted mechanisms, including adsorption capabilities, enhancement of

microbial activities, and facilitation of nutrient cycling processes. These attributes underscore biochar's potential to significantly improve the treatment effectiveness of CW systems. However, the performance of biochar amended in CWs can vary significantly based on the characteristics of the feedstock and the pyrolysis circumstances, which alter the physicochemical properties of biochar. Biochar enhances the removal of contaminants in CWs through its high specific surface area, porous structure, and numerous functional groups that facilitate adsorption and microbial activity. Additionally, biochar can improve nutrient retention and promote plant growth, contributing to the overall ecological health of the system. Despite these benefits, there are limitations to the use of biochar in CWs. The effectiveness of biochar can be influenced by factors such as the type of pollutants targeted, the age of the biochar, and environmental circumstances, which can impact its sorption ability. Integrating biochar into CWs requires overcoming challenges such as optimizing deployment strategies and addressing long-term operational and maintenance considerations. Further research should focus on refining biochar production techniques to tailor its properties for effective PPCP removal. Comprehensive field trials are also needed to validate laboratory findings, ascertain biochar's performance under real-world conditions, and assess clogging/waterlogging issues. Moreover, further studies are needed to explore the microbial, plant, and biochar interactions and their synergistic roles in treating PPCPs and other pollutants in CWs. Such endeavors are essential to advancing biochar's application in CWs, ensuring its sustainable implementation, and contributing to enhanced wastewater treatment practices globally. In conclusion, biochar-enhanced CWs hold promise as a crucial component in mitigating the environmental impact of PPCPs, safeguarding water quality, and promoting sustainable wastewater treatment solutions in the future.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author (s) used OpenAI (ChatGPT and Grammarly) to improve readability and language. After using this tool, the author(s) reviewed and edited the content as needed and took full responsibility for the content of the publication.

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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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