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Review

A critical review on using biochar as constructed wetland substrate: Characteristics, feedstock, design and pollutants removal mechanisms

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ABSTRACT

Constructed wetlands (CWs) are constructed systems that simulate natural wetlands and can be used to treat wastewater from several sources of pollution through physical, chemical and biological depuration processes. This work aims to critically review the updated literature on constructed wetlands (CWs) integrating biochar in the substrate. In detail, the study focuses on the characteristics of biochar that are generally integrated into this treatment ecotechnology and the processes used to prepare the materials, including conditions of thermal conversion and the kind of feedstock used (e.g., agricultural, food, and wood wastes, sewage sludge and algal marine feedstock). Based on the literature review, it is found that the feedstock must be rich in carbon and low in the mineral matter to produce good quality biochar, i.e. large pore volume and high specific surface area, thus allowing to effectively remove pollutants from wastewater. The biochar quality is affected by the conditions involved in preparing biochars (e.g., pyrolysis temperature, heating rate and carbonization time). The properties of biochar used for wastewater treatment, the effect of its implementation as CW substrate and its treatment efficiency have also been described. Several factors alter the removal efficiency of pollutants in CWs, such as substrate chemical and physical properties, hydraulic retention time, oxygenation, and redox conditions in the reed bed. In addition, the mode by which biochar is implemented in the filter and the choice of macrophyte are crucial for regulating the efficiency of the treatment system. *Phragmites australis* was the most used plant in the previous studies because of its large advantages. Different configurations of CWs integrating biochar into the wetland as a filling medium, were reported and compared. In vertical flow CWs (VF-CWs), which are the system mostly investigated, several studies have shown that the optimal position for the biochar substrate is the intermediate one between two layers of inert materials, to avoid clogging of the filtration system or biochar flotation.

1. Introduction

Constructed wetlands (CWs) are a kind of green technology that can be considered as sustainable nature based solution for wastewater treatment (Younas et al., 2022). In such systems, the plant and the substrate play an important role in the removal of pollutants (Addo-Bankas et al., 2021;Ohore et al., 2022). The substrate is an essential component of CWs since it can mediate and promote the implementation of mechanical, physical and biological mechanisms for reducing pollutants concentration in CW effluents, allowing for the direct removal of contaminants, making available reactive agents for transforming pollutants, promoting plant growth, and ensuring biofilm adhesion (Deng et al., 2021). Furthermore, plants uptake nutrients, directly increase biological activity in the substrate by supplying oxygen through their roots, and play an important role in the hydraulic conductivity within the filter. Hence, choosing the most appropriate plant species is important for obtaining the best performance; (Srivastava et al., 2008; Guittonny-philippe et al., 2015; Kataki et al., 2021; Karungamye, 2022).

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The CWs have been widely tested for urban wastewater treatment, while the purification of sewage from industrial or mixed urban-industrial origin has been investigated with lesser extent (Stefanakis, 2018; Kataki et al., 2021). CWs demonstrated high efficiency in removing conventional pollutants such as suspended solids, nutrients, biodegradable organic matter, and heavy metals (Huong et al., 2020; Zhuang et al., 2022). However, in most cases, CWs have shown a lower efficiency against various ecotoxic pollutants, such as detergents, heavy metals, plasticizers, disinfectants, pesticides, and pharmaceutical residues, which remain largely unremoved in CWs effluents (Gosset et al., 2020). To improve CWs efficiency, various materials, other than those conventionally used in CWs (i.e., gravel and sand) (Zhang et al., 2021; Fu et al., 2020), have been tested as substrates, namely pozzolan (El Ghadraoui et al., 2020), charcoal (Hamada et al., 2021), zeolite (Du et al., 2020), and biochar (Vymazal et al., 2021). Among them, biochar has recently gained an increasing interest (De Rozari et al., 2016) as a stable, porous, carbon-rich, and originated from inexpensive material obtained by thermochemical conversion of waste biomass through various thermochemical processes such as. hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), gasification, and pyrolysis (Deng et al., 2021). Slow pyrolysis (i.e., thermal conversion in the absence of oxygen and with contact time from minutes to hours) is commonly used as it is cheaper than other processes and/or gives rise to a higher yield of the solid fraction(i.e., biochar) with low syngas and bio-oil production (Enaime et al., 2020; Wang et al., 2020a). Various renewable and locally available waste biomaterials, such as compost, agricultural by-products, sludge, manure, and shellfish, have been used to produce biochar (Zhuang et al., 2022). In addition, biochar may also be produced from wetland plant straws and then reintroduced into wastewater treatment environments, thereby facilitating wetland plant management and sustainable exploitation of wastewater treatment systems (Wang et al., 2020a; Deng et al., 2021). Introducing biochar as a substrate in CWs can significantly increase the system's efficiency since it may have a high sorption capacity for organic and inorganic pollutants (Srivastava et al., 2008; Wang and Wang, 2019). However, the sorption capacity of biochar depends on the kind of feedstock used and its preparation conditions (Tan et al., 2015). The location of the biochar substrate in the filter can also affect the efficiency of the treatment system. Recently, several existing studies have investigated the effect of biochar used in CWs. Nevertheless, each study focused on one of the aforementioned aspects separately, while no review exists to date that critically evaluates all parameters involved in the treatment and how they might interact to improve the treatment efficacy of CWs (Wu and Wu, 2019; Wang et al., 2020a: Ambaye et al., 2021: Cui et al., 2022; Zhuang et al., 2022). and, no synthetic review exists until now discussing the optimal position of substrate biochar in the CW. We tried to collect all this aspects to enrich our synthetic review. In addition very few reviews have described the emergent pollutants removal capacities of constructed wetland integrating biochar CWB.

According to a literature overview performed using the search engines SciFinder, Elsevier ScienceDirect, and Google Scholar, this paper critically reviewed data and information on (i) the characteristics and properties of biochars used in constructed wetlands (e.g. the conditions of thermal conversion and the type of feedstock used for the preparation of biochars, as well as the specific surface area (SSA) and environmental compatibility of the material), (ii) the methods of integrating the biochar within the CWs, and (iii) the results obtained in terms of removal of macro-parameters, as well as conventional and emerging micropollutants.

2. Biochar incorporated into CWs

2.1. Biochar feedstock

Biochar can be made from a wide variety of feedstocks (Gabhane et al., 2020; Berslin et al., 2022; Garcia et al., 2022; Zhuang et al., 2022). The composition of the feedstock and its availability are essential factors in the production of efficient and cost-effective biochar. Therefore, proper classification and characterization of feedstocks are required for their successful application.

Biochar feedstock used in the literature comes from various materials that can be classified into sewage sludge, agricultural waste and wood, food waste, and marine feedstock (Table 1).

Agricultural waste and wood-derived biochar have been recently employed for the application in CWs. Bamboo is widely used as a raw material for biochar production, due to its abundance and high carbon content (>50%), which gives a good quality of biochar (Zhou et al., 2017; Jia et al., 2020; Gao et al., 2018; Zhang et al., 2021; Xin et al., 2021). Furthermore, plants such as *Arundo donax* and cattail (*Typha latifolia*) can absorb phosphorus and nitrogen from wastewater through their roots and transport them to the shoot, which may then be harvested and converted into biochar that can be reused as functional substrates in CWs, thus thu achieving a virtuous circular approach in this fiels. (Guo et al., 2020a, 2020b; Li et al., 2018a, 2018b). Other vegetal materials have been transformed into biochar and used for wastewater treatment, such as cut residues of *Alnus* (Kasak et al., 2018), *Acacia auriculiformis* (Nguyen et al., 2020), Gliricidia (Athapattu et al., 2017), coconut shell (You et al., 2020), and various agricultural waste (Abedi and Mojiri, 2019), because of their wide availability and high productivity. However, terrestrial macroplants have so far been the primary source of biochar used in CWs(Aghoghovwia et al., 2020; Du et al., 2020). The biochar performance derived from sewage sludge or marine life (e.g. macroalgae) may differ from terrestrial plants (Zhuang et al., 2022). In addition, Deng et al. (2021) stated that the biochars used in the CW treatment systems are generally made from *Arundo donax* straw, corn/straw cobs, bamboo, shells, tree branches and wooden containers (Deng et al., 2021). Finally, the feedstock must be rich in carbon and low in the mineral matter to produce good quality biochar.

2.2. Biochar production conditions

Pyrolysis is commonly performed to prepare biochar used in CWs because of its advantages generally consisiting in higher yields of biochar and lower content of bio-oil and syngas (Enaime et al., 2020; Abdelhafez et al., 2021; Pereira and Astruc, 2021; Zhuang et al., 2022). The temperature range between 400 and 600 °C were the most commonly adopted to prepare the biochar used in the filters (Table 1) (Abedi and Mojiri, 2019; Chand et al., 2021; Zheng et al., 2022). The time and the temperature of pyrolysis are determining factors of the biochar characteristics (e.g., density, carbon content, pH, porosity) (Gong et al., 2019; Xiao et al., 2020) and, consequently, the performance of wastewater treatment (Alsewaileh et al., 2019; Hsu et al., 2019). Even though the kind of feedstock used for biochar preparation affects the characteristics of the material, it has been demonstrated that the increase in temperature generally produces higher percentages of ash, which is regulated by the EN 12915–1 standard (Comite Europeen de Normalisation (CEN), 2009) in materials intended for water filtration, since a high ash content in filtering media is expected to reduce adsorption activity (Castiglioni et al., 2022). Also the presence of polyciclyc aromatic hydrocarbons (PAHs), themselves regulated by the EN 12915–1, depends on the conversion temperature adopted, which plays a main role in PAH formation up to about 500 °C, but also in their degradation beyond this value (Castiglioni et al., 2022). The conversion temperature is also crucial in determining the SSA of the biochar and its microposorosity/mesoporosity distribution, being the highest SSA values obtained at the highest temperatures, due to the increase of both pore size classes (Del Bubba et al., 2020). This result is also related to the progressive loss of the functional groups present in the material as the temperature increases (Del Bubba et al., 2020). However, the yield of fabricated biochar decreases with the rise of pyrolysis temperature (Apolin and Conceptualization, 2020).

Based on the above considerations, the adsorption performance of

Table 1
Feedstocks used for the production of biochars intended to be used in CWs, preparation conditions and characteristics of the material obtained.

Feedstock	Pyrolysis temperature	Surface characteristics (SA, PV,PS) and pH	Composition	Reference
Bamboo	500 °C	SA(335 m^2/g)	C (68%)	(Zhang et al., 2021)
Bamboo	tubular furnace 500 °C - 10 °C/min - 2 h	SA(116.24 m^2/g)	C (74.56%); H (1.12%); O (6.28%); N (1.06%)	(Xin et al., 2021)
Bamboo	600 °C	SA (2.5 × 108 m^2/m^3)	C (59.44%); H (2.06%); O (15.89%); N (0.40%); P (0.34%)	(Jia et al., 2020)
Bamboo chips	500 °C - 2 h - N_2	PS(10 μm)	C (56.4%); O (6.3%)	(Feng et al., 2021a)
Bamboo	700 °C - 10 °C/min - 6 h	SA(228.26 m^2/g); PV(0.086 cm^3/g)pH(9.5)	–	(Ajibade et al., 2020)
Arundo donax	600 °C- 1 h	SA(281.15 m^2/g)	C (63.18%); H (1.80%); N (1.13%)	(Li et al., 2018b)
Arundo donax	Muffle furnace 500 °C - 10 °C.min^{-1} - 1 h - N2	SA(1272.67 m^2/g); PV(1.021 cm^3/g)	C(79.9%);N (2.27%); O (17.84%)	(Shen et al., 2020)
Agricultural waste	500° C	SA(809 m^2/g); PV(0.22 cm^3/g)	–	(Abedi and Mojiri, 2019)
Lodgepole Pine Wood	1000 °C	SA(152 m^2/g); PS(1–40 μm) pH(9.66)	–	(Huggins et al., 2016)
Oak woody (*Quercus Sp*)	600 °C - 10 h −10 °C/min	PS(1–10 μm)	O (8%); C (90%); P (0.54%); K (0.38%); S (0.1%); Ca (0.38%)	(Gupta et al., 2016)
Wood	600 °C - 10 °C/min - 10 h	SA(147 m^2/g); PV(0.176 cm^3/g); PS(5.3 nm) pH(9.8)	C (90%); H (1.5%); O (8.3%); N (0.5%); S (0.3%)	(Kizito et al., 2017)
Wood dust	700 °C	SA(488.60 m^2/g); PV(0.286 cm^3/g)	C (81.50%); H (1.87%); O (15.63%); N (0.07%)	(Lun and Chen, 2018)
Cattail (*Typha latifolia*)	600 °C - 2 h - 10 °C/min	SA(6.14 m^2/g); PV(0.02 cm^3/g) pH(8.9)	–	(Zheng et al., 2022)
Tree branches	550 °C - 2 h - N_2	SA(32.09 m^2/g); PV(2.31 mm^3g^{-1})	–	(Ji et al., 2020)
Softwoods	700 °C – (gasification)	SA(485 m^2/g) pH(7.8)	C (89.2%); H (1.6%); O (1.9%); N (1%); S (0.04%); P (4.3%)	(Kaetzl et al., 2018)
Corn on the cob	600 °C - 10 °C/min - 10 h	SA(123 m^2/g); PV(0.098 cm^3/g); PS(6.2 nm) pH(8.9)	C (69%); H (3.4%); O (17.6%); N (6.1%); S (4.4%)	(Kizito et al., 2017)
Corn cob	600 °C -2 h	SA(263.0 m^2/g)	–	(Gotore et al., 2022)
	500 °C - 2 h		–	

Table 1 (*continued*)

Feedstock	Pyrolysis temperature	Surface characteristics (SA, PV,PS) and pH	Composition	Reference
Giant reed straw		SA(345.92 m^2/g); PV(0.2467 cm^3/g); PS (1.95 nm)		(Deng et al., 2019)
Corn straw	450 °C, 2 h - 10 °C min^{-1} - N_2	SA(232.715 m^2/g); PV(0.098 cm^3/g); PS (1.286 nm)	C (77.30%) H (2.35%) N (0.87%) O (11.26%) S (0.02%) P (1.43%) Cl (l0.38%)	(Wang et al., 2022)
Nut shells	450 °C - 2 h	SA(14.76 m^2/g)-pH(8.1)	C (68.6%); K (5.1%); Ca (4.0%)	(Chang et al., 2022)
Sludge	600 °C - 2 h - 10 °C/min	SA(13.13 m2/g); PV(0.12 cm3/g); PS (18.71 nm) pH(7.9)	–	(Zheng et al., 2022)
Walnut shells	450 °C - 2 h- N_2	SA(14.76m^2/g)	C (68.6%); K (5.1%); Ca (4.0%)	(Chang et al., 2022)

SA: Surface area; PV: Pore volume; PS: Particle size.

biochars obtained under different experimental conditions (e.g., different feedstock, conversion temperature, and contact time) will be better or worse depending on the contaminant to be removed. Accordingly, researchers used materials produced at very different temperatures for achieving the removal of their target contaminants. For example, the pyrolysis temperature of the sludge-based biochar at 400 °C showed optimal ammonia adsorption, while pyrolysis temperatures at 350 °C or 550 °C were not favorable for the biochar's adsorption capability (Tang et al., 2018), i.e., without any clear consistent effect of pyrolysis temperature on biochar adsorption performance towards ammonia (Tang et al., 2018). However, Ajibade et al. (2020) and Huggins et al. (2016) were prepared the biochar at high pyrolysis temperature (700 and 1000 °C) and justified the choice of these temperatures to their high surface area and pore volume that will serve as a niche for microbes for the effective treatment of pollutants (Ajibade et al., 2020).

2.3. Biochar characteristics for wastewater treatment

The physicochemical properties of biochar, such as pore distribution and size, surface functional groups, alkalinity, SSA, etc., which strongly depend on the feedstock and thermal conversion conditions, are responsible for pollutant adsorption capacity, and biofilm adhesion (Wang et al., 2019; Tan et al., 2015). As a result, biochar's ability to remove inorganic and organic contaminants is determined by its characteristics as well as the characteristics of the molecules to be eliminated, such as the size, charge and chemical moieties. As mentioned above, biochar produced at low temperatures has more oxygen-containing functional groups, favorable for the adsorption of polar compounds, and may show a higher mechanical strength for being used preferably in CWs. In contrast, biochar produced at high temperatures has a larger porosity and SSA, a higher aromaticity, a higher carbon content, and overall a higher hydrophobic character (Del Bubba et al., 2020; Castiglioni et al., 2021). The net surface charge of the chars (commonly evaluated by the pH of the point of zero charge and/or Boehm's titration), which mainly depends on the surface functional groups of the material and is often related to its ash content, is a further crucial parameters to explain the adsorption behaviours of biochars, particularly towards ionized or ionisable compounds (Castiglioni et al., 2022). Accordingly, best performing biochars can be obtained a lower or higher temperatures, depending on the target molecule to be removed.

For example, phenol adsorption was higher for biochars produced at 900 °C than for those prepared at lower temperature 600 °C, probably due to the relative increase in SSA at the higher pyrolysis temperature (Mohammed et al., 2018). Similarly, Xu and Lu (2019) reported an increasing removal efficiency of biochar towards bisphenol from aqueous solutions with increasing the preparation temperature. However, Del Bubba et al. (2020), studying the removal of 16 alkylphenols and alkylphenol ethoxylates from real wastewater, with biochar produced at 450, 650 and 850 °C, observed higher absolute absorption maxima for materials produced at the two highest temperatures, depending on of the investigated molecule.

The biochar can be modified chemically, physically or biologically to increase its properties and achieve greater adsorption and catalysis capacities for the target pollutants (Xu and Lu, 2019). In addition, the pH of the solution played a key role in controlling the deprotonation and hydrophobicity of the compounds, which is in agreement with the correlation analysis of the maximum sorption capacity. The pH of biochar produced to be used as a substrate in CWs was generally alkaline and varied between 7.9 and 9.8 (Table 1) (Enaime et al., 2020; Kizito et al., 2017; Zheng et al., 2022).

The carbon content can give an early indication of biochar quality. Generally carbon (C) was the main compositional element of biochar, varying approximately from 50% to 90%, followed by oxygen (O) and nitrogen (N) and other elements that were present at much lower percentages (Table 1) (Gupta et al., 2016; Kizito et al., 2017). In Kizito's study, element C was found at 69% in biochar derived from corn cobs and 90% in wood, confirming that biochar characteristics are feedstock dependent (Kizito et al., 2017). The biochar generally had a high surface area of several hundreds m^2/g (Abedi and Mojiri, 2019; Deng et al., 2019); for example, in Abedi's study, the BET surface area of biochar was around 809 m^2/g (Abedi and Mojiri, 2019). However, other investigations have found it as low as a few tens of m^2/g (Ji et al., 2020; Zheng et al., 2022). For example, the study by Zheng, who works on two feedstocks, the cattail (*Typha latifolia*) and sludge, shows that the two feedstocks give low specific surfaces of 6.14 and 13.13 m^2/g, respectively (Zheng et al., 2022). With increasing pyrolysis temperature, the porosity, surface area and carbon content of biochar increased. However, bio-assimilation decreased. The percentage of carbon in biochar grew from 57.8% to 63.2% as the pyrolysis temperature increased from 300 to 500 °C. On the other hand, the surface area increased by more than one magnitude from 10.0 m^2/g to 281 m^2/g (Li et al., 2018a). This shows that the porosity is extremely sensitive to temperature variation compared to the percentage of carbon. These properties will probably influence their function in CWs. According to Liao et al. (2022), the biochar must have a large pore volume and surface area to adsorb pollutants and provide adhesion of microorganisms (Liao et al., 2022). In most cases the biochar used in CWs has a higher specific surface area (>200 m^2/g) to provide a higher number of adsorption sites (Shen et al., 2020; Zhang et al., 2021; Gotore et al., 2022).

3. Configurations of biochar-based CWs and their removal efficiency

The performance of a CW depends on the type of CW, temperature, vegetation, water flow regime (hydraulic regime), dissolved oxygen (DO), substrate nature, redox potential (Eh) and applied hydraulic load (Parde et al., 2021; Malyan et al., 2021). Table 2 shows the order, dose, dimension of substrates, different plants used in CW and the removal efficiency of pollutants of each configuration.

3.1. Integration mode of biochar in CWs

3.1.1. Biochar in vertical flow CW

When used as substrate in VF-CWs, biochar can potentially promote contaminant removal. As illustrated in Fig. 1-a, most CWs are implemented by positioning the biochar between two layers of inert material (see Table 2), thereby avoiding the clogging of the filtration system (Ji et al., 2020; Liang et al., 2020; Liao et al., 2022). In this interlayer, the biochar is used alone or mixed with other materials, namely sand, gravel, etc. (Table 2) (Ajibade et al., 2020; Liao et al., 2022; Zhong et al., 2021; Zhou et al., 2018).

Several authors have used the biochar substrate alone as an interlayer of the filter system in order to increase the removal rate of different pollutants. For example, in the study of Nguyen et al. (2020), the biochar substrate is used under two sand and sandy soil layers. This distribution increases the removal efficiencies of total coliforms up to 70% (Nguyen et al., 2020). Moreover, using biochar substrate under a coarse stone substrate allows the removal of total phosphorus up to 91% and organic matter such as BOD and TSS up to 95% and 99.7%, respectively, from municipal wastewater (Saeed et al., 2020). Another study placed the biochar substrate under a coarse pebble layer to improve nitrate removal performance up to 92% and orthophosphate up to 67.7% (Gupta et al., 2016). However, using gravel substrate over biochar increases the removal performance up to 94.9% TN, 99.4% NH_4^+ and 99.84% COD (Liang et al., 2020; Liao et al., 2022). On the other hand, the modification of biochar with iron shows high removal performance of pollutants such as Abamectin (99%), COD (98%), NH_4^+ (65%) and TP (80%) (Sha et al., 2020).

Biochar can be mixed with gravel (Feng et al., 2021a), sand (Ajibade et al., 2020), or zeolite (Yuan et al., 2020) to form a single substrate to filter various micropollutants from wastewater. Zheng et al. (2022) found that mixing biochar with gravel at a volume ratio of 1:4 resulted in high removal efficiency of COD (90.99%), NO_3^- (99.50%), TN (90.94%), NH_4^+ (99.59%), and TP (51.59%).On the other hand, mixing biochar with sand with a low volume ratio of biochar (2%) gave low removal rates (TOC (29.3%); NH_4^+ (13.5%); TN (11.7%); TP (8%)) except for *E. coli*, TSS and coliforms, which show high removal efficiency, coming up to 87.1% and 71.1% for *E.coli* and TSS, respectively (Chen, 2018). Similarly, Ajibade et al. (2020), also mixed biochar with sand. Still, this time gave a high performance compared to the study of Lun and Chen (2018), where the removal efficiency of some pollutants reached 89.1% for COD, 90.2% for TN and 81% for NH_4^+ (Ajibade et al., 2020). The ratio of biochar can explain the difference between these two studies that is higher in the second one. Yuan et al. (2020) reported that mixing biochar with zeolite can improve the removal percentage up to 63% for TN, 94% for NH_4^+, 93% for NO_3^- and 87% for COD. This result may be justified by the fact that the biochar inhibited the formation of quinolone resistance genes and enhanced the COD removal efficiency by increasing the abundance of bound microorganisms (Yuan et al., 2020). In most studies, biochar substrates mixed with gravel showed higher removal efficiency of various pollutants compared to biochar substrates mixed with sand (Table 2).

Sometimes th whole filter is filled from top to bottom with biochar (Fig. 1-**c**) (Table 2) mixed at low rate (10%) with another material (quartz sand, soil, LECA), to avoid the clogging of the system. For example, Jia et al. (2020) mixed 10% biochar with quartz sand and soil to fill the entire filter and obtained an increase of the removal efficiency of pollutants (NO_3^-(95.30%); TN (86.68%); NH_4^+ (86.33%); NO_2^- (79.35%); COD (63.36%)) (Jia et al., 2020).

3.1.2. Biochar substrate in the horizontal flow CW

The use of biochar in horizontal flow CWs (HF-CWs) is still limited, and a little number of articles was found (Gao et al., 2018; Bolton et al., 2019; Gao et al., 2019; Jia and Yang, 2021; Wu et al., 2022). For example Bolton et al. (2019) implemented two small pilot-scale HF-CWs planted with *Melaleuca quinquenervia* trees, each one consisting in two cells separated by a polyethylene baffle. The first wetland contained two cells in series filled with gravel (control wetlands), while in the other wetland the first cell was filled with gravel to trap sediments, thus avoiding blockages in the downstream cell, the latter filled with an enriched biochar cell (biochar wetlands). This study showed that the removal efficiencies of PO_4^{3-}-P in the biochar wetland was up to 97%

Table 2
Characteristics of CWs integrated with biochar.

Implementation mode of the substrate (by order)	Plant species and density	Wastewater	CW size	Aeration	Feeding	HLR	HRT	Experiment duration	Removal efficiency	Reference
- Sand (0.5–2 mm) h = 50 mm - Biochar (2.95%) + gravel: h = 300 mm - Gravel (10–20 mm) h = 50 mm	*Acorus calamus L.* 4 rhizomes	Tail water	VF-CW h = 450 mm d = 160 mm	No	–	0.055 $m^3 \cdot (m^2 \cdot d)^{-1}$	3 days	2 months	COD (76%) - TP (52%) - TN (82%) – NH_4^+ (84%) – $N0_3^-$ (89%)	(Wang et al., 2022)
- Zeolite (d = 2 mm–4 mm) h = 30 cm - Biochar (d = 3 mm–5 mm) h = 30 cm - Cobblestone (d = 20 mm–30 mm) h = 5 cm	*Phragmites australis*	Synthetic wastewater	VF-CW h = 75 cm d = 14 cm V = 2 L	No	–	260 $L \cdot m^{-2} \cdot d^{-1}$	12 h	4 months	NH_4^+ (95.49%) - $N0_3^-$ (83.24%) – TN (83%)	(Zhong et al., 2021)
- Clay ceramite (d = 2–5 mm) h = 7 cm - Biochar (d = 2–5 mm) h = 14 cm - Clay ceramite (d = 2–5 mm) h = 7 cm	*Lythrum salicaria*	Domestic wastewater	HF-CW l = 30 cm w = 15 cm h = 30 cm	Yes	Manually 4 L	–	24 h	6 months	COD (75.5%) - TP (76.2%) - TN (59.2%) – NH_4^+ (62.5%)	(Ji et al., 2020)
- Gravel (d = 7–8 mm) h = 3 cm - Biochar (d = 6–8 mm) h = 10 cm - Gravel (d = 7–8 mm) h = 3 cm	*Plants hydroponics*	Synthetic wastewater	VF-CW d = 12 cm	–	–	–	–	6 months	COD (99.84%) – NH_4^+ (92.00%) – TP (88.63%)	(Liao et al., 2022)
- Gravel (d = 1–3 cm) - Biochar (d = 1–2 cm) h = 3–6-9 cm - Gravel (d = 1–3 cm)	*Acorus calamus* 30 rhizomes$\cdot m^{-2}$	Synthetic Wastewater	VF-CW h = 35 cm d = 33 cm	–	Manually 10 L	0.05 m^3. $m^{-2}.d^{-1}$	48 h	6 months	COD (89.88%) TN (86.36%) - NH_4^+(63.51%)	(Deng et al., 2019)
- Pebbles (d = 90 mm) h = 5 cm - Biochar (d = 10 cm) -Gravel (d = 15 mm) h = 17 cm - Gravel (d = 10 mm) h = 5 cm	*Canna sp*	Synthetic wastewater	HF-CW 1 m × 0.3 m x 0.3 m	Yes	32 L	–	72 h	–	COD (91.3%) - TN (58.3%) - NH_3^- (58.3%) – NO_3^- (92%) - TP (79.5%) - PO_4^{3-} (67.7%)	(Gupta et al., 2016)
- Pebbles (d = 5-7 mm); h = 5 cm - Coke (d = 3–5 mm); h = 74 cm - Fe-modified biochar (50 mm×10 mm×5 mm) - Pebbles (d = 5-7 mm); h = 5 cm	*Canna*	River water	VF-CW h = 100 cm d = 30 cm	–	–	–	–	5 months	Abamectin (99%) – COD (98%) - NH_4^+ (65%) – TP (80%)	(Sha et al., 2020)
- Sandy soil h = 10 cm - Sand (d = 2 mm) h = 20 cm - Biochar (d = 1–3 cm) h = 40 cm - Gravel (d = 2–3 cm) h = 10 cm	*Colocasia esculenta* 64 seedlings/m^2	Domestic wastewater	VF-CW h = 1.0 m d = 0.5 m	Yes	–	–	–	6 months	COD (73%) - DBO_5 (79%) - NH_4^+ (91%) – TSS (71%) - Total coliforms (70%)	(Nguyen et al., 2020)
- Sand (d < 2 mm) h = 15 cm - Gravel + Biochar (*v*/v = 1:1): (d = 1–2 cm) h = 15 cm - Gravel + Biochar (v/v = 1:1): (d = 2–4 cm) h = 25 cm - Gravel (d = 5–7 cm) h = 10 cm	*Iris pseudacorus* 6 rhizomes	Swine wastewater	VF-CW h = 65 cm d = 20 cm	Yes	–	33.74 g. $m^{-3}.d^{-1}$	72 h	2 months	COD (77.18%) – NH_4^+ (96.54%) - TN (40.12%) ARGs (99.3%)	(Feng et al., 2021a)
- Sand (d = 1–2 mm) h = 150 cm - Biochar + fine gravel (*v*/v = 3:1): (d = 10–20 mm) h = 150 mm - Gravel (d = 20–40 mm) h = 250 mm - Gravel (d = 50–70 mm) h = 100 mm	*Oenanthe Javanica* 12 rhizomes	Domestic wastewater	VF-CW h = 65 cm d = 20 cm	Yes	5.5 L	–	72 h	3 months	COD (91.80%) - NH_4^+ (50.05%) - TN (49.90%)	(Zhou et al., 2018)

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Table 2 (*continued*)

Implementation mode of the substrate (by order)	Plant species and density	Wastewater	CW size	Aeration	Feeding	HLR	HRT	Experiment duration	Removal efficiency	Reference
- Gravel (d = 5–8 mm) h = 0.1 m - Biochar (sludge) + gravel (*v*/v = 1:4) h = 0.2 m - Gravel (d = 5–8 mm) h = 0.1 m	*Typha latifolia*	Synthetic wastewater	VF-CW h = 0.5 m d = 0.2 m	No	–	–	72 h	60 batches	COD (90.99%) – NO_3^- (99.50%) – NH_4^+ (99.59%) - TN (90.94%) - TP (51.59%)	(Zheng et al., 2022)
- Gravel (d = 5–8 mm) h = 0.1 m - Biochar (cattail) + gravel (*v*/v = 1:4) h = 0.2 m - Gravel (d = 5–8 mm) h = 0.1 m	*Typha latifolia*	Synthetic wastewater	VF-CW h = 0.5 m d = 0.2 m	No	–	–	72 h	60 batches	COD (77.41%) - NO_3^- (84.72%) - NH_4^+ (96.12%) - TN (80.73%) - TP (43.95%)	(Zheng et al., 2022)
- Gravel (d = 2–6 mm) h = 0.05 m - Biochar (v/v = 1%) + sand (d = 2–10 mm) h = 0.2 m - Gravel (d = 2–6 mm) h = 0.05 m - Gravel (d = 2–10 mm) h = 0.05 m	*Iris pseudacorus* 5 rhizomes	Synthetic wastewater	VF-CW h = 0.45 m d = 0.15 m	No	–	–	72 h	4 months	COD (89.1%) - TN (90.2%) - NH_4^+ (81%)	(Ajibade et al., 2020)
- Soil h = 10 cm - Quartz sand h = 5 cm - Zeolite d = 8–10 mm + biochar d = 2–4 mm (*v*/v = 1:1): h = 30 cm - Cobblestones (d = 7–10 cm): h = 10 cm	*Phragmites communis* 6 plants	Synthetic wastewater	VF-CW l = 50 cm w = 40 cm d = 60 cm	Yes	30 L	$0.050\ m^3.m^{-2}.d^{-1}$	72 h	4 months	TN (62.98%) - NH_4^+ (93.93%) - NO_3^- (93.28%) - COD (86.64%) – CIPH (88.05%) – SMZ (56.57%)	(Yuan et al., 2020)
- Sand (d = 2–4 mm) h = 2 cm - Biochar (2%) + Sand (98%): (d = 5–10 mm) h = 15 cm - Sand (d = 2–4 mm) h = 3 cm	*Phragmites australis*	Synthetic stormwater	VF-CW h = 25 cm d = 11 cm	–	–	10–40 cm/h	5 days	3 months	TSS (71.1%) – TOC (29.3%) - NH_4^+ (13.5%) - TN (11.7%) - TP (8%) - *E.coli* (87.1%)	(Chen et al., 2018)
- Sand - Biochar + gravel: *v*/v = 50%. - Gravel	*Iris pseudacorus* 6 rhizomes	Synthetic wastewater	VF-CW h = 50 cm d = 10 cm	Yes	–	–	72 h	5 months	COD (93.21%) - NH_4^+ (98.30%) - TN (72.22%) – TP (53.32%)	(Li et al., 2019)
- Gravel (d = 8–10 mm) h = 0.1 m - Biochar + gravel (*v*/v = 4:1): h = 0.2 m - Gravel (d = 8–10 mm) h = 0.1 m	*Typha latifolia*	Synthetic wastewater	VF-CW l = 0.3 m w = 0.3 m h = 0.5 m	–	–	–	5 days	60 batches	NH_4^+ (66.3%) – TN (65.4%) – COD (90%)	(Guo et al., 2020a, 2020b)
- Biochar (d = 2–3 cm) h = 25 cm - Zeolite (d = 2–3 cm) h = 25 cm - Gravel (d = 2–3 cm) h = 25 cm	*Phragmites australis*	Synthetic Wastewater	VF-CW h = 80 cm d = 40 cm	Yes	–	–	57.4 h	3 months	COD (99.9%) - NH_3^- (99.9%) - Phenols (99.9) - Pb (99.9%) – Mn (99.9%)	(Abedi and Mojiri, 2019)
- Biochar (20%) + sand (80%): h = 20 cm - Gravel: h = 5 cm	*O. javanica* 12 rhizomes	Synthetic wastewater	VF-CW h = 50 cm d = 25 cm	NO	–	$0.13\ m^3m^{-2}$ batch -1	7 days	8 months	COD (78.71%) - NO_3^- (92.72%) - TN (93.26%) - NH_4^+ (94.26%)	(Li et al., 2018a)
- Biochar + sand: (d = 0.5–1 mm) h = 15 cm - Gravel (d = 4–6 mm) h = 10 cm - Gravel (d = 8–12 mm) h = 10 cm - Rocks (d = 20–21 mm) h = 5 cm	*Colocasia esculenta* 10 rhizomes	Domestic wastewater	VF-CW h = 37 cm d = 33.5 cm	Yes	–	–	10 days	40 days	COD (96.8%) - NO_3^- (57.85%) - TN (68.02%) - NH_4^+ (88.16%) - PO_4^{3-} (75.26%) - SO_4^{2-} (80.50)	(Chand et al., 2021)
- Biochar (corn cobs) (d = 2–10 mm) h = 0.6 m - Gravel (d = 50 mm); h = 0.1 m	–	Industrial wastewater	VF-CW h = 0.9 m d = 0.2 m	No	–	–	–	5 months	COD (59%) - BOD_5 (75%) - TN (37%) – NH_4^+ (76%) - PO_4^{3-} (71%)	(Kizito et al., 2017)
- Biochar (wood) (d = 2–10 mm) h = 0.6 m	–	Industrial wastewater	VF-CW h =	No	–	–	–	5 months	COD (72%) - BOD_5 (83%) - TN (47%)	

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Table 2 (*continued*)

Implementation mode of the substrate (by order)	Plant species and density	Wastewater	CW size	Aeration	Feeding	HLR	HRT	Experiment duration	Removal efficiency	Reference
- Gravel (d = 50 mm); h = 0.1 m			0.9 m d = 0.2 m						– NH_4^+ (83%) - PO_4^{3-} (85%)	(Kizito et al., 2017)
- Biochar (d = 2–4 mm) h = 120 mm	*Salicaria seedling*	Synthetic wastewater	VF-CW d = 110 mm h = 150 mm	Yes	550 mL	–	24 h	> 3 months	Hg (>94%) – COD (>88%) – NH_4^+ (92.1) – TP (74.7%)	(Chang et al., 2022)
Mixture of Quartz rock d = 2–4 mm (*v*/*v* = 25%), Bioceramic d = 3–6 mm (*v*/*v* = 25%), and biochar d = 1–7 mm (v/v = 50%) h = 200 mm	*Cyperus alternifolius*	Synthetic wastewater	HF-CW l = 670 mm h = 310 mm w = 300 mm	NO	30 L	–	25 h	–	NO_3^- (67.16%) – TP (74.25%) – TN (64.31%) - NO_2^- (51.6%) - PO_4^{3-} (96.73%)	(Gao et al., 2018)
Mixture of quartz sand + soil (*v*/*v* = 1:1) and Fe-modified biochar (v/v:10%)	*Iris hexagonus* 13 plants/m^2	Tailwater	VF-CW l = 100 cm w = 60 cm d = 75 cm	–	–	–	96 h	–	NO_3^- (95.30%) - TN (86.68%) - NH_4^+ (86.33%) - NO_2^- (79.35%) - COD (63.36%)	(Jia et al., 2020)
Mixture of biochar (v/v = 10%) (d < 20 mm) and LECA (d = 2–4 mm)	*Typha latifolia* 10 plants/ mesocosm	Municipal wastewater	HF-CW l = 1.5 m w = 0.6 m d = 0.6 m	–	–	60 L/d	48 h	4 months	TN (20.0%) - TP (22.5%)	(Kasak et al., 2018)
- Gravel (d = 2–6 mm) h = 0.05 m - Biochar (v/v = 1%) + sand (d = 2–10 mm) h = 0.2 m - Gravel (d = 2–6 mm) h = 0.05 m - Gravel (d = 2–10 mm) h = 0.05 m	*Iris pseudacorus* 5 rhizomes	Synthetic wastewater	VF-CW h = 0.45 m d = 0.15 m	No	–	–	72 h	4 months	COD (75.9%) – TN (69.2%) – NH_4^+ (70.8%) – NO_3^- (74.7%) – SMX (65.3%)	(Ajibade et al., 2021)
- Biochar + sand (d = 0.25–1 mm) h = 6 cm - Gravel (d = 4–6 mm) h = 10 cm - Gravel (d = 8–12 mm) h = 10 cm - Boulders (d = 20–21 mm) h = 5 cm	*Colocasia*	Synthetic wastewater	VF-CW d = 33.5 cm h = 37 cm V = 30 L	No	–	–	–	–	COD (88.8%), NH_4^+ (83.1%), and NO_3^- (64.9%) AMX (75.51%) - CF (87.53%) - IBU (79.93%)	(Chand et al., 2022)
Sand h = 15 cm Biochar h = 20 cm Gravel h = 15 cm	*G. maxima*	Synthetic wastewater	VF-CW d = 15 cm h = 55 cm	No	–	2 L/ 4d	–	3 months	PPCPs (99.99%)	(Kang et al., 2019)
Stones (d = 5-10 mm) h = 0.05 m Biochar (d = 5-10 mm) h = 0.76 m Stones (d = 5-10 mm) h = 0.05 m	*Phragmites*	Municipal wastewater	VF-CW h = 0.91 d = 0.15 m	No	–	–	–	–	NH_4^+ (89.8%) - NO_2^- (38.5%) - TN (82.5%) – TP (91%) –BOD (95%) - COD (96.2%) – TSS (99.7%)	(Saeed et al., 2020)
Gravel (d = 2 cm) Biochar *v*/*v* = 30% (d = 2 cm) Gravel (d = 2 cm)	*Cyperus alternifolius L*	Synthetic wastewater	VF-CW h = 35 cm S = 0.1 m^2	Yes	–	–	24 h	–	COD (93.4%) - TN (94.9%) - NH_4^+ (99.4%)	(Liang et al., 2020)
Fe-modified biochar v/v = 1/3 (d = 1–2 mm) + gravel (diameter of 2–4 mm) h = 50 cm	*Acorus calamus*	Synthetic wastewater	VF-CW h = 60 cm d = 25 cm	–	–	–	3 days	–	NH_4^+ (44.8%) – NO_3^- (51.8%)	(Kang et al., 2023)
Cu-Biochar (40%) + sand (60%): h = 50 cm	*Iris pseudacorus* 6 plants/unit	Synthetic wastewater	VF-CW h = 75 cm d = 25 cm	No	–	–	3 days	2 months	COD (75.33%) – NO_3^- (91.11%) – Phenanthrene (94.09%)	(Shen et al., 2020)
				No	–			7 months	PO_4^{3-} (97%)	

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Table 2 (*continued*)

Implementation mode of the substrate (by order)	Plant species and density	Wastewater	CW size	Aeration	Feeding	HLR	HRT	Experiment duration	Removal efficiency	Reference
Two cells: first one with gravel and second with biochar	*Melaleuca quinquenervia*	Domestic wastewater	HF-CW 1.2 m × 0.76 m × 0.4 m			0.023 m/day	5.1 days			(Bolton et al., 2019)
Gravel (v/v = 80%; d = 1–2 cm) + soil (v/v = 10%) + biochar (v/v = 10%; d = 0.1–0.5 mm)	*Hydrocotyle verticillata* + *Iris germanica 100 clumps/m²*	Tail wastewater	HF-CW S = 900 m^2	No	–	–	1 day	3 months	TN(62.62%) - TP (52.99%) - NO_3^-(73.28%) - NH_3(53.11%) - PO_4^{3-}(67.58%)	(Gao et al., 2019)
Zeolite (d = 20 cm) Biochar (d = 10 cm) Gravel (d = 20 cm)	*Canna indica* 16 plant/m^2	Synthetic wastewater	HF-CW 110 cm × 40 cm × 60 cm	No	–	–	–	11 months	NH_4^+(89.1%) – TN (88.1%) – TP (75.9%)	(Wu et al., 2022)

HRL: Hydraulic loading rate, HRT: Hydraulic retention time.

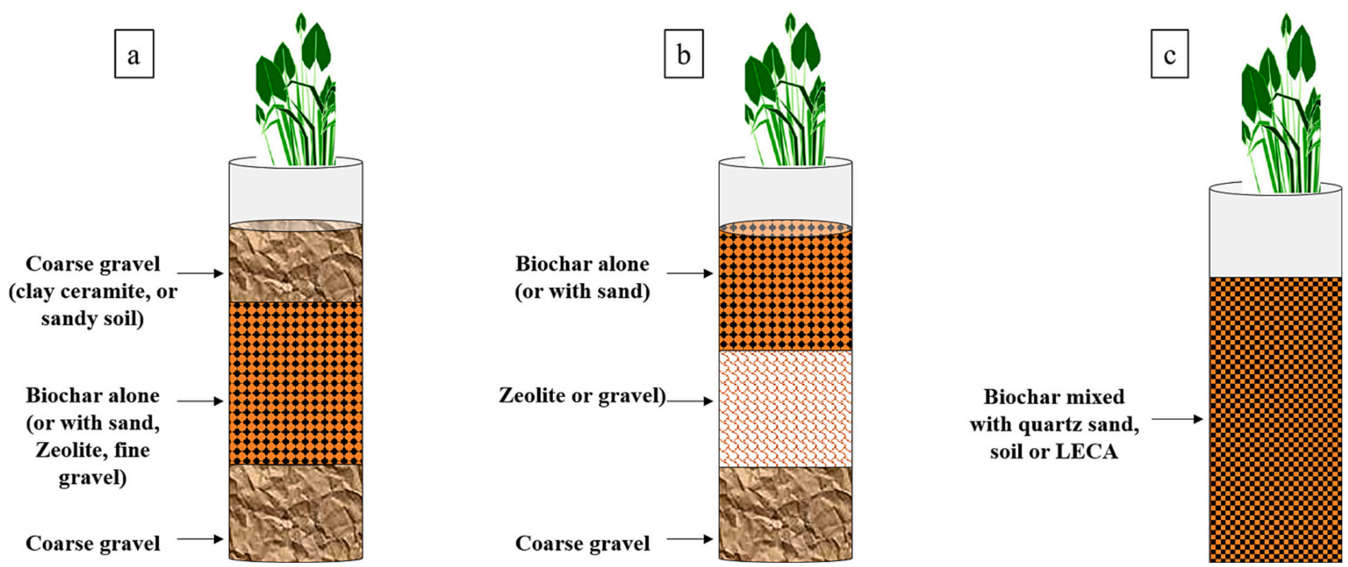

Fig. 1. Position of biochar substrate (a): as interlayer of VF-CW, (b): on top of the VF-CW, (c): filling all the VF-CW.

Biochar can also be placed at the top (Fig. 1-**b**) (Table 2) of the filtration system with large grain size (2–30 mm) in order to avoid the clogging phenomenon (Abedi and Mojiri, 2019; Kizito et al., 2017). In Abedi and Mojiri (2019), the top biochar layer played an important role in decreasing the content of various pollutants such as COD, NH_4^+, phenols, Pb, and Mn. This study showed the best removal performance compared to the literature, since the removal efficiency was quantitative for COD, NH_4^+, phenols, Pb and Mn (Abedi and Mojiri, 2019). This result can be explained because biochar is mainly attributed to the greater adsorption capacity and microbial culture in the porous medium of biochar (Kizito et al., 2017). Furthermore, the use of biochar at the upper filter level revealed that adding biochar in VF-CWs improves the oxidative removal of NH^{4+}-N, SO_4^{2-}, and PO_4^{3-} and contributes to the uptake of other plants (Chand et al., 2021). Another study conducted by Chand et al. (2021) used biochar on top of a system with small grain size (d = 0.5–1 mm), but to avoid clogging, they mixed the biochar with sand, which allowed them to increase the treatment efficiency and thus removed up to 97% COD, 58% NO_3^-, 68% TN, 88% NH_4^+, 75.26% PO_4^{3-} and 80% SO_4^{2-} (Chand et al., 2021).

probably due to the higher number of adsorption sites in the substrate. In contrast, the control achieved only an average PO_4^{3-}-P removal of 91%, indicating a rapid saturation of the gravel. Another study realized by Gupta et al. (2016) revealed that HF-CWs with biochar were more efficient to reduce various pollutants (organic and inorganic) as compared to the wetland with gravels alone. Hence, the removal efficiencies achieved were arround 58% of TN, 79% of TP, 92% of NO_3-N, 58% of NH_3-N, 68% of PO_4^{3-}-P and 91% of COD. The high removal of NH_4^+-N obtained in HF-CWs is probably related to the enhanced microbial nitrification when adding biochar (Gupta et al., 2016). The improved NO_3-N removal efficiency is attributed to a higher denitrification, due to the anoxic conditions in HF-CWs. These results indicate clearly that integrating of biochar in HF-CW can be primarily used for a secondary treatment of municipal and domestic wastewaters leading to nutrients removal. In general, the use of biochar in HF-CWs can be a cost-effective and sustainable wastewater treatment option with a smaller energy footprint (Wu et al., 2022; Gupta et al., 2016).

3.2. Effect of substrate nature, biochar dose and granulometry on CWs efficiency

The fundamental element of the CW system is the substrate or media, which is essential for removing contaminants from wastewater.It serves as a platform for biofilm development, macrophyte root growth, and a reaction site for pollutants' immobilization and supporting matrix (Wu et al., 2015). Therefore, the choice of bed materials is highly important in a CW. Inexpensive and locally available materials can be used depending on the size of the media, its hydraulic conductivity, texture, porosity, and other factors (Wu et al., 2015). Gravel, biochar, zeolite, composite materials and activated carbon have been used as CW substrates (Kataki et al., 2021). Substrates such as sawdust, light expanded clay aggregate (LECA), zero-valent iron, and gravel can effectively remove phosphorus, organic matter, arsenates, and sulfates (Parde et al., 2021).

Biochar-based CWs show promising wastewater treatment efficiency (Enaime et al., 2020). However, granular biochar is more suitable for applications than powdered ones. This can be explained by its good pore size distribution, low abrasion index, durability, high bulk density, and ability to regenerate (Louarrat, 2019). In addition, this type of biochar has sufficient mechanical strength and is suitable for ensuring the stability and hydraulic permeability of the matrix (Deng et al., 2021). In addition, particle size has a significant effect on pollutants adsorption. Nitrate-nitrogen content, ammonia nitrogen content, and denitrification intensity of the wetland substrate decreased by 51%, 47%, and 35%, respectively, after the introduction of biochar with a particle size ranging from 1 to 2 mm in CW (Zhou et al., 2018), when compared to biochar with a particle size lower than 1 mm. Biochar with a 1–3 cm diameter is widely used as a substrate in CWs to avoid clogging (Table 2) (Nguyen et al., 2020). Other factors influence the adsorption of pollutants, such as increasing of the contact time, pH, temperature, and concentration of NH_3. But adsorption is decreasing with increasing the size of biochar particles (Kizito et al., 2015). According to these results we can state that the biochar granulometry has a significant effect on the efficiency of the treatment of the pollutants.

On the other hand, the biochar dose in CW substrate strongly influences the removal performance of various pollutants. However, a study conducted by Deng et al. (2019) was built based on different volumes of biochar in common gravel (0%, 10%, 20%, and 30%) to see the effect of increasing biochar substrate depth on the characteristics of metabolites and microbes. This experiment found that increasing the biochar dose in the gravel medium enhanced the contaminant removal efficiency in CWs. Hence, Illumina MiSeq sequencing reported that the microbial community showed some obvious variations. The relative abundances of *Candidatus competibacter, Thauera, Dechloromonas, Chlorobium, Thiobacillus and Desulfobulbus* were significantly improved with the biochar dose. On the other hand, the content of total Extra Polymeric Substances (EPS) decreased with increasing the biochar percentage.

Furthermore, the increase in biochar dose in CWs substrate reflects an improvement in the biodegradation of EPS and the richness of microbial communities, which promotes the removal of organic and nitrogenous substances (Deng et al., 2019). Similarly, Liang et al. (2020) used 4 CW microcosms with different volume ratios of biochar (0%, 10%, 20%, and 30%) to analyze the improvement of pollutant removal performance. The results showed that the increase in biochar dose increased the average removal efficiencies of total nitrogen (TN) and ammonium (NH_4^+-N). At the same time, nitrous oxide (N_2O) emissions were reduced. The increase in biochar dose can explain this change in the diversity and similarity of the microbial community. In addition, the relative abundance of functional microorganisms such as Nitrospira, Nitrosomonas, Pseudomonas, and Thauera increased due to the increase in biochar content, which favored nitrogen cycling and reduced N_2O emissions.

3.3. *Effect of macrophytes used and its role in CWs implemented with biochar*

Plants are essential in removing pollutants, as they generally play an indirect role in the wastewater treatment performance in CWs (Fu et al., 2022). The choice of appropriate plant species is crucial for the best performance (Guittonny-philippe et al., 2015; Srivastava et al., 2008; Kulshreshtha et al., 2022). Hence, the right choice was based on several parameters; the species that are preferred are characterized by high ecological adaptability, adaptation to local climatic and nutritional conditions, high biomass productivity, resistance to pests and diseases; having good coverage with high prospects of successful establishment, tolerance to pollutants and hypertrophic waterlogging conditions, low tendency to dominate or forming monocultures, a high capacity for pollutant removal, easy propagation, and rapid establishment (Nuamah et al., 2020; Kataki et al., 2021). According to literature the *Phragmites australis* was the most used plant in the studies (Table 2), due to its effect on the efficiency of CW, resistance to pests and diseases, tolerance to pollutants and hypertrophic waterlogging conditions, high capacity for pollutant removal, easy propagation and adaptation to local climatic and nutritional conditions (Zhong et al., 2021; Yuan et al., 2020; Chen, 2018). However, a comparative study done by Qadiri et al. (2021) has demonstrated that the CWs transplanted with *Phragmites* has more capacity in removing TN, COD, TP and TSS than *Sagittaria latifolia* and *Iris kashmiriana*, due to its well developed roots in the substrates which gives a better remediation effect. Furthermore, the presence of a biochar substrate in the CW promotes plant growth, microbial metabolism and substrate characteristics in many aspects (Qadiri et al., 2021). Another key parameter in selecting CW species is the higher water use efficiency index (Stefanakis, 2020). Several studies have shown that plants with fibrous root systems provide a greater surface area for biofilm enhancement, sedimentation, and particulate matter trapping. They show higher photosynthesis and radial oxygen loss levels and are more effective in removing contaminants than plants with thick roots (Kataki et al., 2021); (Borne et al., 2013; Lai et al., 2012). In addition, previous studies have shown that plant density affects CWs performance at 5 to 50 plants/m^2. A low density (16 m^2) CW planting may result in lower nitrogen removal than a CW with a high plant density (32 m^2) (reduced by almost half) (Hernández et al., 2017). Another factor to consider is the age of the plant, as oxygen release and contaminant uptake are lower in older plants due to the presence of older lignified roots (Valipour and Ahn, 2015).

3.4. *Effectiveness of biochar in removing various pollutants*

Biochar is a solid material with high porosity, a high surface area, and diverse surface functional groups and properties, making it an attractive option for wastewater treatment. Biochar has been proposed as an effective substrate for capturing wastewater supplements that may be connected to soil alteration. The adsorption properties and high porosity allow pollutants to accumulate on its surfaces, resulting in supplement-rich biochar and a clean effluent (Peiris et al., 2017; Yaashikaa et al., 2020). Biochar adsorbents have been used to remove various contaminants (Table 2) such as antibiotics (Ahmed et al., 2017), pesticides (Mandal et al., 2021), pharmaceuticals (Masrura et al., 2021; Solanki and Boyer, 2017), and personal care products from aquatic environments (Keerthanan et al., 2020). The use of biochar for wastewater treatment is becoming more viable due to the low cost of the raw material and the ease of the manufacturing process, as well as the various improved physicochemical characteristics of biochar, which have been successfully used in a diverse range of applications for the contaminated wastewater remediation, including toxic heavy metals adsorption (the following techniques have been used: chemisorption, physical sorption, ion exchange, and precipitation) and dyes from aqueous solutions, as immobilization support for microorganisms, as a support for catalysts, and as an adsorbent for inhibiting substances during anaerobic digestion, thanks to its unique and very versatile characteristics. Overall, it is clear that biochar has multiple potential economic and environmental benefits, and its effectiveness in removing various contaminants on a laboratory scale has been widely reported (Ahmad et al., 2021; Enaime et al., 2020; Chen et al., 2022).

Biochar added to CW substrate can considerably enhance the wastewater purification effect (Kizito et al., 2017), as biochar can remove more nutrients and reduce greenhouse gas (GHG) emissions than other substrates, e.g., ceramite, while promoting more diverse bacterial communities and greater abundances of available taxa (Ji et al., 2020). The average N_2O and CO_2 fluxes were significantly lower, while CH_4 fluxes were significantly greater in the biochar-added and non-biochar CWs (Guo et al., 2020a, 2020b). Biochar combined with sand, zeolite, and other artificial CW substrates can enhance microbial activity and compensate for the lack of carbon sources (Wang et al., 2020b). Abedi and Mojiri (2019) reported that CW containing three substrate layers, namely biochar, gravel and zeolite layers, showed high performance in wastewater treatment compared to the other CWs containing gravel as a substrate; the first CW can remove pollutants from wastewater better than the second one. At an optimum retention time (57.4 h) and pH (6.3), this biochar integrated CW can remove up to 99.9% of COD (1000 mg/L), ammonia (1000 mg/L), phenols (50 mg/L), Pb (50 mg/L) and Mn (50 mg/L). In addition, the emission of nitrous oxide was lower in gravel CW than in the integrating biochar CW (Abedi and Mojiri, 2019). These results can explain that the introduction of biochar considerably improved the abundance of biological bacteria in CW, consequently increasing the efficiency of removing various contaminants in wastewater (Li et al., 2018a). This agrees with the results of Liang's study (Table 2), which explains the increase in nitrogen removal efficiency and the decrease in N_2O emissions resulting from the increase in biochar addition ratio. This shows that biochar addition changed the diversity and similarity of the microbial community (Liang et al., 2020).

In general, the removal efficiency of pollutants was increased due to biochar adsorption (Meng et al., 2019). In addition, the total amount of extracellular polymeric substance (EPS) decreased significantly with the addition of biochar, which is explained by the change in the functional groups of EPS, including amide, carbonyl, and hydroxyl groups of proteins. Furthermore, biochar has the potential to convert metabolized high molecular weight compounds into low molecular weight compounds (Deng et al., 2019).

The biochar can be used at various stages of the wastewater treatment process to increase treatment capacity and recover value-added by-products. The adsorption, buffering, and immobilization mechanism of microbial cells may influence the use of biochar in the wastewater treatment system. For example, properly modified biochar could effectively adsorb nutrients such as phosphorus and nitrogen from treated effluent, allowing it to be used for soil rehabilitation as a nutrient-enriched material. In addition, biochar could help develop activated sludge's treatment and settling capacity by adsorbing inhibitors and hazardous chemicals or providing a surface for microbial immobilization when used in the treatment process. The introduction of biochar to the biological system can also help increase the soil amendment capabilities of biosolids, extend the value chain, and provide other economic benefits as interest in its use in soil applications increases (Mumme et al., 2014). The following sections discuss biochar's role in removing various contaminants from wastewater.

3.4.1. Removal of organic pollutants

Numerous studies have been conducted in recent years to test the effectiveness of biochar in removing various organic substances from water, such as antibiotics, drugs, agrochemicals, polycyclic aromatic hydrocarbons (PAHs), cationic aromatic dyes, and volatile organic compounds (VOCs) (see Table 2) (Adeel et al., 2016; Mondal et al., 2016).

3.4.1.1. Removal of conventional pollutants. Organic pollutants are another important type of pollutant in the aquatic environment, the biochar has shown a high removal efficiency towards this kind of pollutants. Based on the literature, the biochar prepared at a higher pyrolysis temperature will improve non-polar organic compounds' removal efficiencies due to higher microporosity and surface area (Mohamed et al., 2016; Mohanty et al., 2013). On the other hand, the biochar prepared at a temperature below 500 °C comprises a higher amount of hydrogen and oxygen-containing functional groups, so it is more likely to have a high affinity for polar organic molecules (Suliman et al., 2016). For example, biochar derived from rice husk and pyrolyzed soybeans at 600–700 °C facilitates the removal of trichloromethylene (VOC) and non-polar carbofuran (pesticide) from contaminated water (Suliman et al., 2016). In addition, at $T > 700$ °C, red gum wood chips and chicken litter-derived biochar efficiently removed pyrimethanil and diesopropylatrazine (fungicide/pesticide), whereas the same biochar at $T < 500$ °C proved ineffective (Chen and Chen, 2009; Yu et al., 2010). And for the removal of polar insecticides and herbicides such as norflurazon, 1-naphthol and fluridone was performed using biochar produced at <300 °C, as a result of the pollutant's interaction with the biochar's functional groups (Li et al., 2016; Sun et al., 2011). On the other hand, the biochar with more O and H functional groups (<400 °C) showed higher sorption of aromatic cationic dyes such as methyl-blue and methyl-violet. Still, the process strongly depended on pH (Adeel et al., 2016; Teixid et al., 2011). In addition, the polar antibiotic sulfamethazine (SMZ) exhibits pH-dependent interactions when sorbed to softwood/hardwood-derived biochars (pyrolyzed at 300–700 °C) (Mohan et al., 2014). Therefore, it can be considered an important parameter for biochar interactions and polar organic contaminant removal.

Generally, organic matter from wastewater may be removed by filtration, adsorption, hydrolysis, chemical reduction or oxidation by microbial degradation, etc. (Vymazal and Tereza, 2015). The degradation by the microbiota attached to the substrates is responsible for the elimination of organic matter in aqueous solutions (Faulwetter et al., 2009). Conventional organic compounds such as chemical oxygen demand (COD) and biological oxygen demand (BOD_5) can be removed effectively due to the coupling role of anaerobic and aerobic degradation in CW systems (Saeed and Sun, 2017; Zhao et al., 2020). Thus, the integration of biochar into CWs plays an important role in COD removal, even though organic matter can be leached from biochar (Zhou et al., 2019). However, Several studies have shown that biochar amendment promotes COD removal in CWs (Deng et al., 2019; Guo et al., 2020a, 2020b). This result can be explained by the good adsorption capacity of biochar toward organic molecules and provides a heterogeneous surface with very high porosity for oxygen filling and habitation by various organic degradation microbes. Moreover, biochar can promote plant growth, releasing additional oxygen into CW substrates for aerobic COD decomposition. A recent finding by some researchers show that the introduction of biochar into CWs can reduce the quantity of microbial extracellular polymeric substances (EPS) accumulated in the wastewater matrix and induce their metabolization of heavy molecular weight EPS metabolites into lower molecular weight compounds because biochar increases the metabolic and abundance activities of heterotrophic bacteria, thus reflecting organic decomposition, which is conducive to mitigating the clogging of wastewater treatment substrate.

3.4.1.2. Emerging pollutants. Emerging hazardous organic pollutants that can be contained in stormwater, livestock wastes, agricultural waters, and industrial wastewaters, etc., such as dyes, pesticides, herbicides, endocrine disruptors (e.g., phthalic acid esters, polycyclic aromatic hydrocarbons, and bisphenol A), and antibiotics (Table 2), pose serious long-term threats to ecosystems and public health, even at minute concentrations (Vymazal and Tereza, 2015). Hydrophobic effects, electrostatic attraction, conjugation of aromatic-donors and cationic-acceptors, pore filling, and hydrogen bonding are all processes that biochar can use to adsorb these contaminants (Xiang et al., 2020; Zhang et al., 2019). Most importantly, biochar possesses catalytic and redox-reactive activities, allowing it to accept/donate electrons or promote generate ROS and electrical conduction, thus accelerating the abiotic decomposition of adsorbed organic pollutants (Devi and Saroha, 2015; Zhang et al., 2019). In addition, biochar substrates may stimulate the reproduction and development of microbes involved in decomposing organic pollutants. However, this augmentation role of biochar has only been studied profoundly so far (Yan et al., 2017; You et al., 2020). The mechanisms involved depend mainly on biochar properties, operating conditions and contaminants. Due to the exceptional ability of biochar to adsorb bisphenol A, Lun and Chen (2018) found that the integrating biochar into CWs improved the elimination of bisphenol A from stormwater and increased the life of CW systems. According to the same authors, the biochar prepared at 700 °C performed significantly better than biochar prepared at 300 and 500 °C. In addition, the biochar substrate supported the increase of functional microbes and served as an excellent biofilm carrier to indirectly enhance the decomposition of bisphenol A. Improved plant growth in CWs also facilitates the removal of organic pollutants (Chen, 2018). Tang et al. (2016) used plant-derived biochar that was planted in a *Cyperus alternifolius* CW and then modified with $Fe(NO_3)_3$ solution to achieve higher removal efficiencies (>99%) and constant rate for four pesticides in wastewater than the non-biochar control (64–99%) (Tang et al., 2016). The cause is that biochar adsorbs the pesticides and promotes their microbial decomposition. The use of biochar derived from fruit pits in zeolite-based CWs significantly increased antibiotic removal rates (sulfamethazine and ciprofloxacin) while also decreasing the production of sulfonamide and quinolone resistance genes, which was attributed to the biochar's ability to facilitate antibiotic biodegradation and adsorption (Yuan et al., 2020). Biochar is a good attachment medium for microbes that degrade organic matter. For example, Mahmood et al. (2015) used corn-derived biochar manufactured at 400 °C as a biofilm support for *Pseudomonas putida* cells to adsorb and reduce dyes and Cr (VI) in a continuous flow bioreactor for the efficient treatment of tannery wastewater containing azo dyes, aniline and Cr (VI).

Other organic compounds, such as pharmaceuticals and pesticides, are considered emerging contaminants because of their effects on human health, and have been detected in municipal wastewater treatment plants (Firouzsalari et al., 2019; Shi et al., 2021). Wastewater from the pharmaceutical industry contains pharmaceutical intermediates used in production (Karunanayake et al., 2017), antibiotics and active ingredients such as hormones (Rashid et al., 2021). However, pesticides are found in industrial wastewater through pesticide production (Pinto et al., 2018), washing of commercial containers used to store or transport pesticides (Zapata et al., 2010), and agri-food industries (Lopes et al., 2020). The biochar as adsorbent promote the degrade antibiotic and antibiotic resistance genes (ARGs) from wastewater, and dissolved organic carbon release in CWs indicated that water and alkaline media portray the optimum conditions for SMX and ARGs removal, this shows the feasibility of using biochar for regulated sulfamethoxazole (SMX) removal and ARG accumulation (Ajibade et al., 2021). However, the study of Feng et al. (2021a, 2021b) showed the relation between ARGs removal and dissolved organic matter (DOM). They, noted that the photosensitized DOM is responsible for producing reactive intermediates to remove ARGs. Hence incorporating biochar under forced aeration into CWs could remove ARGs up to 99.3% and DOM 72% effectively from swine wastewater. Abas et al. (2022) confirmed that the integration of biochar substrate has an effect in improving Chlorantraniliprole (CAP) removal, CAP mass removal was very high in biochar (99%). The biochar also enhance the efficiency of the treatment pharmaceuticals and personal care products (PPCPs) form wastewater, the presence of the colonization of arbuscular mycorrhizal fungi (AMF) in CWs enhanced the best removal performance for PPCPs in biochar added systems (more than 99.99%). These results can be attributed to the higher adsorption capacity of PPCPs of biochar, due to its large surface area and porous structures of biochar substrate, which could also promote the development and growth of microbes and the adsorption of PPCPs, thus enhancing its biodegradation (Hu et al., 2022a, 2022b).

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic compounds (Gaurav et al., 2021), with at least two aromatic rings (Kang et al., 2019). They include compounds such as phenanthrene, naphthalene, anthracene, pyrene, fluorine and benzofluoranthene (Jain et al., 2020; Kong et al., 2021). Several studies have used biochar as an adsorbent substrate to remove this pollutant, because biochar may provide a reproduction habitat for microbes and enhance the microbial community to improve denitrification and PAHs removal performance (Cao et al., 2021). Furthermore, the biochar was also tested to remove benzofluoranthene (BbFA), a typical PAH in CWs, and has shown higher BbFA with its removal efficiency exceeding 99%, which could be attributed to enhanced PAH biodegradation (Guo et al., 2020a, 2020b). In the same way Kang et al. (2023), was studying removal efficiency of representative PAH, benzofluoranthene (BbFA), using biochar modified by iron as a supplement to the CW substrate. They reached to increase the performance of BbFA removal by 20.4%, because the biochar may increase dissolved organic carbon content, particularly low-aromaticity, which contributed to PAH degradation by microorganisms. In addition, the presence of functional groups on the biochar surface may improve the electron interactions between microorganisms and PAHs.

3.4.2. Removal of inorganic pollutants

Inorganic contaminants in wastewater include compounds such as nitrite (NO_2^-), ammonium (NH_4^+), nitrate (NO_3^-), hydrogen sulfide (H_2S), phosphorus (PO_4^{3-}) and heavy metals (Cu, Cr, Cd, Pb, Fe, Hg, Zn and As ions) (Table 2) that cause a dangerous risk to human health and the environment (Cao et al., 2009). Generally, biochar produced at low pyrolysis temperature (about 500 °C) is used to remove inorganic contaminants. The nature of biochar sorption is influenced by the morphological structure and chemical composition (Abdelhafez and Li, 2016).

3.4.2.1. Nitrogen removal. Multiple pathways are used to remove nitrogen from wastewater in CW, substrate adsorption, ammonia volatilization, plant uptake and microbial processes (Saeed and Sun, 2017). Classical microbial nitrification, followed by denitrification, and finally converting N to N_2O or N_2, is considered the most common mechanism (Jia et al., 2020; Vymazal, 2011). However, the insufficient ability of sand, and gravel to adsorb nitrogen and provide habitable microsites for denitrifying microorganisms remains a major challenge in conventional CW systems filled with gravel, ceramite, or sand (Kizito et al., 2017; Yang et al., 2018), although ceramite gives better results than gravel or sand which are widely used (Vohla et al., 2011). In addition, low dissolved oxygen (DO) due to inadequate reoxygenation may limit nitrification in flooded streams, and/or denitrification can be limited by electron donors deficient for nitrate reduction (Lu et al., 2020; Vymazal, 2011). Therefore, several solutions are being investigated to improve nitrogen removal from wastewater, including introducing substrates with high nitrogen removal capacity (Jia et al., 2020; Shen et al., 2018).

Cation exchange can keep cations in biochars with a high surface charge density. Consequently, the internal porosity, high biochar surface, and presence of polar and non-polar sites on the biochar surface promote nitrifier growth and nutrient adsorption and simpler and easier atmospheric aeration and oxygen replenishment at the bottom of the CW matrix. As well as, the addition of the biochar substrate can increase the rate of nitrification, resulting in a great improvement in total nitrogen (TN) and NH_4^+ removal in CW (Kizito et al., 2017; De Rozari et al., 2018; Zhou et al., 2019). However, the leaching of dissolved organic matter (DOM) can be done with the help of biochar, which is mainly based on humic acid, which allows it to temporarily trap the influent DOM in the pores as a carbon source to stimulate denitrification after desorption (Li et al., 2018a; Zhou et al., 2019). Denitrifier proliferation may also be enhanced, resulting in nitrate denitrification for low C/N effluents (Zhou et al., 2019). On the other hand, biochar acts as a chemically redox-active material with electroactive functional groups on its surface (e.g. phenols and quinones), which promotes the biochemical transfer of the material into wastewater (Yuan et al., 2018; Zhang et al., 2019). According to Wu et al. (2018), biochar derived from cattail stalks prepared at 300 °C can increase the electron conversion efficiency between the metabolism of carbon and nitrate reduction by modulating the electron shuttle mechanism and increasing the activities of denitrifying enzymes, which can increase the rate of denitrification in wastewater, in contrast, biochar made at 800 °C inhibits these mechanisms. As a result, many studies have reported that biochar addition to domestic, swine, anaerobic, and secondary wastewater effluents improved nitrogen removal efficiency (by more than 20% on average). Removal efficiency increased proportionally with biochar dosage, although the performance improvement depended on biochar loading and preparation conditions, wastewater properties, and wastewater operating conditions. Biochar substrates in settling ponds showed better nitrogen removal than conventional gravel or sand and some functional fillers, such as zeolite and ceramite (Ji et al., 2020; Yuan et al., 2020).

3.4.2.2. Phosphorus removal. Phosphorus compounds (P) in wastewater may be eliminated by a variety of processes, including substrate precipitation, adsorption, plant uptake, and microbial uptake into wastewater, with substrate retention generally being the most widely used process (Kumar and Dutta, 2019; Saeed and Sun, 2017). Elements such as Fe, Ca, Mg, and Al in CW fillers can bind phosphorus stably; therefore, materials rich in these elements (Fe, Ca, Al, Mg) are preferable as CW substrates enable phosphorus removal efficiently and also increase the lifetime of CW systems. Conventional CW substrates consisting of sand or gravel can only effectively remove total phosphorus (TP) from wastewater for a short time (Chang et al., 2016; Shi et al., 2017). In some studies, biochar-based filters (CWs) were found to have higher phosphorus removal efficiencies than control systems filled with zeolite or gravel. Still, the improved impact for Phosphorus compounds removal was much lower than for N removal. The biochar substrates could trap more phosphorus from wastewater than gravel, especially from wastewater with a high phosphorus concentration (e.g., anaerobic digestion effluent) (Kizito et al., 2017). In addition, the incorporation of biochar into CWs can enhance plant growth and the proliferation of Phosphorus compounds accumulating microorganisms (PAOs), thereby improving biotic Phosphorus removal pathways (Ji et al., 2020; Shi et al., 2017). However, this ameliorative effect cannot be easily maintained. The chemical properties of biochar and wastewater, especially the biochar's surface charge, are important factors in removing anionic phosphates (Wichern et al., 2018). However, other studies have shown that adding biochar to gravel-filled CW did not improve phosphorus removal (Zhou et al., 2019). Mixed biochar and sand substrates are even less efficient than sand alone in phosphorus removal (De Rozari et al., 2016). These results can be explained because biochar has a negative surface charge and a low affinity for phosphate. Other negatively charged molecules in the wastewater (organic matter) can compete with phosphate for exchange sites in biochar (De Rozari et al., 2016). Biochar substrates made from /Fe/Al/Ca-rich feedstocks, such as crab shells, can improve P's recovery/removal capacity from wastewater (Dai et al., 2017). Biochar can be modified with metal salts (iron, magnesium, and aluminum compounds) to make metallic biochar before filling (Wang., 2019; Zheng et al., 2019), or combined with other fillers with high Phosphorus compounds adsorption efficiency (crab shells) to prepare biochar (Shi et al., 2017; Yang et al., 2018). There is still a need for further research and relevant applications in phosphorus removal using biochar substrates.

3.4.2.3. Metals removal. Heavy metals are generally non-biodegradable and are found in large quantities in rainwater, mining effluents, and industrial wastes. Biochar with a unique pore structure, a high percentage of organic carbon, and many functional groups have a high chance of interacting with heavy metals in several ways (Oliveira et al., 2017). Heavy metals are absorbed by biochar mainly through complexation and ion exchange between heavy metal ions and functional groups of biochar (e.g., COOH, OH, R-OH) (Hsu et al., 2009; Lu et al., 2011). Additionally, the coordination of metal ions with π-electrons (C=C) of biochar (Yu et al., 2010) and the formation of metal precipitates with inorganic constituents (Ippolito et al., 2012; Lu et al., 2011) could play a role in the P removal by biochar. Adsorption through the biochar matrix is affected by its chemical properties, which are affected by feedstock type, pyrolysis temperature, application rate, pH, and other factors. For example, copper (Cu^2+) had a high affinity for OH- and COOH- groups in hardwood and crop biochars, which varied with pH and feedstock type (Lima et al., 2010). Similarly, biochars derived from soybean straw, guayule shrub, hermaphrodite sida, and wheat straw effectively removed Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} (Lu et al., 2017). The higher biochar efficiency was attributed to the high O and C contents, polarity index and high O/C molar ratio, which were regulated mainly by pH (Bogusz et al., 2015; Peng et al., 2016). In addition, the removal of mercury (Hg^{2+}) was effectively performed using alkaline biochar prepared from both manure and various agricultural residues (corn stover, soybean straw, cocoa husks, switchgrass, and corn stover). Due to its high sulfur content (SH and sulfate groups), biochar produced from cocoa hulls and animal manure was particularly effective in removing Hg^{2+}, precipitating up to 90% of the Hg^{2+} as $HgCl_2$ or $Hg(OH)_2$, mainly by co-precipitation with the anions (O, S, Cl) in the biochar (Baltrenaite, 2015; Mohamed et al., 2016). Similarly, the biochar dosage affected the removal of heavy metals such as Cd^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+}. Thus, the removal efficiency was higher with rising biochar loading in the aqueous system, due to the increase in surface area and pH (Laird et al., 2010; Xu et al., 2013).

Dissolved heavy metals in wastewater, such as hydroxides and sulfides, can be removed mainly by precipitation, adsorption from the abiotic substrate, and microbial reduction of sulfates for hydroxides and sulfides precipitation (Kosolapov et al., 2004). Adding biochar can help gravel ponds improve metal holding capacity by increasing abiotic pathways. Under ideal conditions, a study was conducted in a gravel-filled pond to remove just 58% Mn and 51.6% Pb from synthetic industrial wastewater. In comparison, adding biochar and zeolite increased the removal efficiency of both metals up to 99.9%. These results can be explained because both metals have high adsorption capacities toward biochar and zeolite (Abedi and Mojiri, 2019). In addition, the inorganic components of the biochar impart an alkaline nature to the biochar, allowing it to raise the pH value of acidic mine wastewater and subsequently reduce the metal ions solubility by inducing the formation of metal hydroxide precipitates (Gwenzi et al., 2017). Biochar substrates can be modified before amendment with heteroatoms and oxidizing agents, acids, or anionic moieties (e.g., HSO_3, OH, S_2, etc.) to enhance the metal retention capacity of CWs (Wang et al., 2019).

3.4.2.4. Pathogens removal. The removal of pathogens from wastewater is essential for protecting human health. Removal was accomplished by filtration, predation, adsorption, oxidation, and inactivation by exposure-several regulatory standards for pathogens in wastewater effluent for reuse (Wu et al., 2016). The high porosity of biochar, high specific surface area, numerous pores with a wide range of sizes, hydrophobicity and organic leaching may make biochar more suitable for removing microbial contaminants than gravel or sand. However, there has been relatively little research on removing pathogens from wastewater using biochar-enhanced CWs. According to Mohanty et al. (2014) and Lau et al. (2017), the introduction of biochar into sand-based biofilters (FBs) significantly increased the presence of *Escherichia coli* in stormwater. In addition, it decreased the remobilization of sequestered nuisance bacteria during intermittent influx and highlighted the high potential of using biochar substrate in CWs for wastewater disinfection. Furthermore, biochar with volatile content and polarity had a higher removal efficiency for *E. coli* (Mohanty et al., 2014). This improvement effect may be explained by the fact that biochar can produce antimicrobials that significantly adsorb viruses and bacteria mainly using hydrophobic interactions and reduce the driving forces that detach pathogens.

On the other hand, another recent study by Kaetzl et al. (2019) found that CWs filled with rice husk-derived biochar can remove bacteriophages and fecal indicator bacteria (FIB) from pretreated municipal wastewater much better or as much as CWs filled with sand or original rice husk (Kaetzl et al., 2019). The ability of biochar to remove pathogens varies with preparation conditions and feedstock (Mohanty et al., 2014). Modifying biochar with H_2SO_4 increases the surface area of biochar prepared from wood, reflecting a significant improvement in *E. coli* elimination in bioretention systems and reducing remobilization during drainage and intermittent flow (Lau et al., 2017). Even though biochar-based filters show high FIB removal efficiency comparable to sand-based filters (Wichern et al., 2018), biochar remains an attractive feedstock in CW systems for pathogen removal due to its economic production and performance, using locally available biological waste, and can be reused as a soil amendment.

4. Mechanisms and factors influencing the pollutants adsorption on biochar

The heterogeneity of the biochar surface allows a variety of sorption processes to occur. The chemical characteristics of the adsorbent surface and the nature of the contaminants determine the adsorption mechanism (Rosales et al., 2017). The three main adsorption mechanisms, according to Pignatello (Pignatello, 2011), are the precipitation mechanism, in which the adsorbent forms layers on the adsorbent surface, and the physical mechanism, in which the adsorbate (e.g., pollutants) is deposited on the adsorbent surface (e.g., biochar), and the pore-filling mechanism, in which the adsorbate (e.g., pollutants) condenses in the adsorbent pores (e.g., biochar). The adsorption process of organic pollutants is generally carried out by electrostatic attraction, complex adsorption, electron-acceptor- donor interaction, pore filling, hydrophobic interactions and hydrogen bonding (see Fig. 2) (Pignatello, 2011). For example, the sorption of organic contaminants by the biochar surface via the pore filling process is influenced by the total volume of the mesopores and micropores; so that the penetration of the pollutant into the internal structure of the biochar is all the more favored when its ionic radius is small, which reflects an increase in the biochar adsorption efficiency (Ahmad et al., 2014; Rosales et al., 2017). Soluble pollutants may attach to the alkaline surface of the hydrophobic biochar using their hydrophobic functional group or be precipitated. Due to the dissociation of oxygen-containing functional groups on the biochar surface, the biochar is generally negatively charged, causing an electrostatic attraction between the positively charged molecules and biochar (Ahmad et al., 2014; Qambrani et al., 2017).

The biochar produced at high temperatures lost its functional group-containing hydrogen and oxygen, making it more aromatic and less polar and, consequently, less suitable for removing polar organic pollutants. However, the electrostatic repulsion between the biochar and the negatively charged anionic organic molecules could favor the production of hydrogen bonds, leading to adsorption. On the other hand, if there is no hydrogen interaction, non-polar pollutants are more likely to penetrate hydrophobic areas (Ahmad et al., 2014). On the other hand, many mechanisms can be involved in removing inorganic pollutants such as heavy metals, such as ion exchange and complexation, surface precipitation under alkaline circumstances, and anionic and cationic electrostatic attraction (Fig. 2). Similarly, Lu et al. (2011) examined the relative contributions of different Pb adsorption mechanisms on sludge-derived biochar. They arrived at the following mechanisms: (i) co-precipitation and complexation with mineral oxides and organic matter in the biochar, (ii) electrostatic complexation due to the exchange of the metal with cations (sodium and potassium) present in the biochar, (iii) surface precipitation as lead silicate- phosphate ($5PbO.P_2O_5.SiO_2$), and (iv) surface complexation with free carboxyl and mineral oxides in the biochar.

The variation in these removal mechanisms and the physicochemical properties of biochar greatly implicates its suitability and efficacy for the remediation of the targeted pollutants. Several factors such as biochar characteristics, dosage of biochar, solution pH and temperature of the medium greatly influence the biochar's overall adsorption capacity by modifying the removal mechanisms involved in the remediation of specific pollutants aqueous systems (Abbas et al., 2018; Ambaye et al., 2021).

4.1. Characteristics of biochar

The volume of micropores in an adsorbent controls its ability to absorb an adsorbate (Lowell, 2004; Zabaniotou et al., 2008). Pores of different sizes are found in adsorbent materials, and classified into macropores, micropores, and mesopores based on the width of the opening (Mosher, 2011). The experimental conditions strongly influence the distribution and size of the pores during the preparation of the biochar, and especially the pyrolysis temperature has the greatest influence (Zhou et al., 2010). The micropores are the most abundant in the biochar structure and would be responsible for their high adsorption capacity and surface area. Zabaniotou et al. (2008) reported that biochar prepared at a high pyrolysis temperature contains a very high volume of micropores that varies between 50%–78% of the total pores. The sorption rate of the biochar is controlled by the size of the adsorbate, such that larger particles can cause blockage or exclusion of sorption sites. In comparison, smaller particles increase the van der Waal force of penetration of the adsorbate into the adsorbent and decrease the mass transfer limitation (Daifullah and Girgis, 1998). It also depends on the surface functional groups' levels and types (Qambrani et al., 2017). The

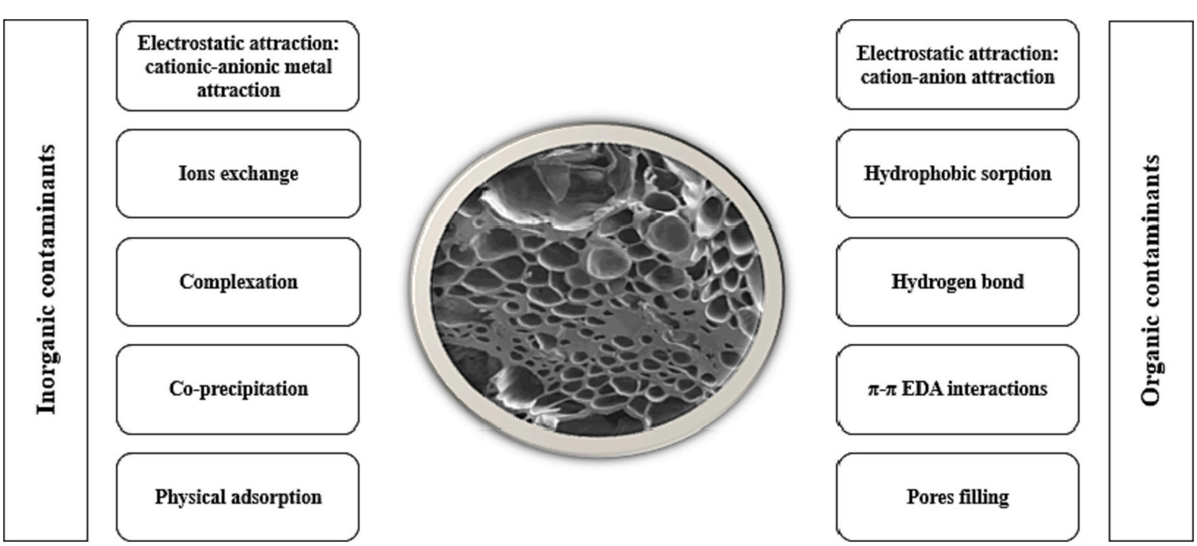

Fig. 2. Mechanisms for biochar's elimination of organic and inorganic contaminants.

carbonization process, the feedstock's chemical composition, and the carbonization temperature all influence the distribution of surface functional groups (Ahmad et al., 2012). Gascó et al. (2018) compared the properties of hydrochar and biochar produced from pig manure using HTC and pyrolysis.

The results showed that when the pyrolysis temperature is high, the broad peak around 3400 cm^{-1}, corresponds to the -OH stretching vibration in the hydroxyl and carboxyl groups and becomes less visible for biochars compared to the feedstock. Due to the decarboxylation and dehydration reactions during the HTC process, the HTC hydrochars revealed broadband at 3400 cm-1 with less intensity than the feedstock. Several scientists agreed that a high aromatic structure characterizes biochar prepared at a high temperature of around 600 °C. On the other hand, hydrochar prepared using the HTC method at a temperature between 200 and 240 °C for 2 h favors biochar with more aliphatic structures. According to Qambrani et al. (2017), the functional groups ($-CH_2$, O-H, C=O, C=C and $-CH_3$) of biochar have changed due to the pyrolytic conditions, which promote the hydrophobic interactions of biochar. The hydrophobic character of biochar is determined by the amount of oxygen and nitrogen-containing functional groups; the lower the nitrogen and oxygen-containing functional groups in the biochar, the higher hydrophobic the biochar (Moreno-castilla, 2004). Hence, the presence of oxygen-containing functional groups on the hydrophilic biochar surface facilitates water to penetrate through hydrogen bonds, resulting in competition between the adsorbate and water on the available sites of the biochar surface. Hydrophobic biochars are expected to contribute to insoluble adsorbate adsorption, while hydrophilic biochars are considered less effective due to water sorption. Adsorbates that are less soluble or insoluble are most likely to be absorbed into the biochar pores in aqueous solutions (Li et al., 2002).

4.2. Dosage of the adsorbent

The adsorbent dosage significantly impacts the sorbent-sorbate balance of an adsorption system. Hence, using a high adsorbent dosage increases the removal efficiency of inorganic and organic contaminants due to the availability of a larger number of sorption sites (Chen, 2013; Chen et al., 2011). On the other hand, the application of a dosage rate that is too high leads to a reduction of the adsorption capacity of the biochar and consequently, an overlapping of the adsorption layers will be produced, which protects the accessible active sites on the sorbent surface (Kizito et al., 2015; Linville et al., 2017). Therefore, the adsorbent dosing must be well optimized to achieve high elimination capacity and make the process cost-effective.

4.3. pH of the solution

The pH of the solution is a crucial factor that controls the adsorption process by influencing the ionization degree and charge of the adsorbate, the adsorbent surface charge and the speciation (Kılıc et al., 2013). The competition between protons and cationic pollutants decreases as the pH of the solution is above the point of zero charges, and a negative charge appears on the adsorbent surface as a result of the deprotonation of carboxylic groups and phenolic on the surface. Basic functional groups, such as amines, are protonated and positively charged at low pH, improving anions' adsorption (Kumar et al., 2011). This means that deprotonation of the functional groups and the pH of the medium influences the biochar adsorption behavior. Kizito et al. (2015) and Hu et al. (2019) studied the effect of pH on the adsorption capacity of biochar towards ammonium (NH_4^+). They showed that the adsorption capacity of NH_4^+ increased with the initial solution pH between 4 and 8 and then decreased when the pH was above 9.

4.4. Temperature of the medium

The medium temperature in which the biochar is applied impacts its adsorption capacity. Most studies showed that adsorption efficiency increased with temperature, confirming that the adsorption process is endothermic. The study by Enaime et al. (2017) indicated that the indigo carmine sorption on potassium hydroxide (KOH) activated biochar rises with temperature due to the endothermic nature of the sorption process. The increase in temperature leads to an increase in the mobility of the dye molecule and the possibility of an increase in the adsorbent porosity. This can be explained by the swelling effect of the adsorbent internal structure when the temperature increases, allowing more dye to penetrate further. Another study, Kizito et al. (2015) found that increasing the temperature above 300 °C to 450 °C is beneficial for maximum removal efficiency.

5. Advantages and limitations of biochar as a CW substrate

The use of biochar as a substrate in CWs solves the problem of environmental pollution (Table 3). Due to the low-cost availability of the raw materials, and the high commercial potential of biochar. The preparation of biochar has developed rapidly in recent years (Lili et al., 2017). Due to its adsorption capacity and porous structure, biochar is commonly used as a slow-release fertilizer filler (Xu and Lu, 2019). However, biochar is rarely used in water treatment due to its high cost, high ash content, and difficulty in ash removal (Kasak et al., 2018). Theoretically, biochar may considerably enhance the purification of wastewater (Deng et al., 2019), as an additional carbon source for CWs (Kasak et al., 2018), and their surface allows the adsorption of various pollutants.

Furthermore, biochar may improve the activity of the microorganisms in CWs (Tang et al., 2017). Therefore, biochar could improve the degradation of high molecular weight compounds in low molecular weight compounds in CW (Deng et al., 2019). The biochar's main objective is to increase the adsorption efficiency of the substrate and provide the carbon source to enhance the denitrification efficiency. However, the application of the CW substrate is easy to generate a blockage due to the low structural strength of the biochar and the ease of generating a powder (Saeed et al., 2019).

6. Conclusion and perspectives

The present review highlighted the constructed wetlands (CWs) a

Table 3
Limitations and advantages of biochar as a CW substrate.

Advantages	Reference	Disadvantages	Reference
- Sustainable and abundant resources, cheap and more oxygen groups present in biochar improves pollutants adsorption.	(Houben et al., 2013)	- Elimination pollutants efficiency is undetermined and heavy metals retain in soil.	(Houben et al., 2013)
- Effective medium for capturing pollutants from wastewater which can connect to the soil and result in an alteration -Reduce greenhouse gas emissions	(Yaashikaa et al., 2020)	- High cost, high ash content, and difficulty in ash removal	(Kasak et al., 2018)
- Improve the activity of microorganisms in CWs	(Tang et al., 2017)	- Easy to generate a blockage and the ease of generating a powder	(Saeed et al., 2019)
- Provide reactive sites for microbes	(Li et al., 2019)		
- Adsorb NO_3-N, NH_4^+ and PO_4^{3-} - Remove suspended solids, BOD_5, metals and coliforms	(Gao et al., 2018)	Substance release (e.g. N, P, salt, alkaline)	(Zhuang et al., 2022)

natural system that are largely investigated for different kind of wastewater (urban, industrial, mixture) treatment throw physical (porosity of substrate), chemical (adsorption, precipitation and biological processes (biodegradation, nitrification denitrifications), under vertical or horizontal flow regime. The constructed wetland has proven good performances for the elimination of organic matter (99%), nutrients especially phosphates (88%) and nitrogen (96%). However, constructed wetlands still very limited on removing recalcitrant or emergent pollutant such as heavy metals, pesticides, drugs, PAHs, volatile organic compounds (VOCs) etc., According to previous literature, removal capacity of CW depends on the type of macro-phytic plant and the substrate of the bed. According to the analyzed references, different plants can be used in CW. Nevertheless, *phragmites australis* and *Around donax* have been the most applied that are considered as the most resistant or high organic load and present the capacity to oxygenate the substrate and enhance the hydraulic conductivity in the filter. The substrate plays also an important role in constructed wetland depuration efficiency that could reach NH4 + -N (40.23%), NO3−-N (48.94%), TN (52%), and COD (35%) when sand or gravel substrate are used. Any improvement of the CW efficiency must be performed via the integration of a good substrate in the filter. Among several materials generally tested as substrate for CW such as zeolite, pozzolan, charcoal, and biochar is gaining big interest recently, due to its promising characteristics as an optimal adsorbent having the ability to remove not only conventional pollutants but owing to good removal performances for even emergent ones that are very toxic and recalcitrant. Furthermore, biochar could bring carbon to the substrate and have a great impact on the pollutants biodegradation by giving a good niche of functional group of microorganisms. The removal percentage could reach COD (99%), TP (88%), NH4+ (96%), Abamectin (99%), TSS (71%), Total coliforms (70%), TN (40%), and ARGs (99%).

Theses interesting characteristics of the biochar are obviously dependent on the processes used to prepare the material, and the conditions of the preparation including conditions of thermal conversion and the kind of feedstock used. Based on the literature review, it was found that the optimum pyrolysis temperature must be around 400 and 600 °C, with a possibility to have an oriented prepared biochar depending of the targeted pollutants basing on the temperature. Furthermore, feedstock must have some specific characteristics to give a good quality of the biochar that depends of the feedstock richness in carbon and low quantity of mineral matter. The large pore volume and high specific surface area reaching 200 m2/g, thus allowing to effectively remove pollutants and pathogens from wastewater. The biochar quality is affected by the conditions involved in preparing biochars (e.g., pyrolysis temperature, heating rate and carbonization time).

Several factors alter the removal efficiency of pollutants in CWs, such as substrate chemical and physical properties, hydraulic retention time, the oxygenation conditions, and redox conditions. In addition, configuration where the biochar is implemented as interlayer between two inert layers (sand, gravel, zeolite) has been reported as optimal design for CW integrating biochar to avoid clogging of the filtration system or biochar flotation.

Overall, the use of biochar in horizontal flow CW is still limited, and a few papers discussed this aspect. Similarly, there is only limited information on the removal of emerging organics, and pathogens from wastewaters by biochar CWs, that mean the involved mechanisms and potential capability of biochar CWs in the removal of these pollutants should be further explored and elucidated. Moreover, it is undeniable that biochar offers various economic and environmental benefits and advantages, and its effectiveness in removing various contaminants at the laboratory scale has been widely reported. However, more in situ experiments should be conducted to test the effectiveness of biochar using real effluents and to examine the actual effect of biochar on the environment before its large-scale application. Furthermore, the biochar stability after many use cycles and its regeneration should be further studied.

Declaration of Competing Interest

None.

Data availability

No data was used for the research described in the article.

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