Study on the Effectiveness of Constructed Wetlands in Purifying Polluted Water from Rivers and Greenhouse Gas Emissions

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Abstract

In order to investigate the effect of different substrates of constructed wetlands on the purification of polluted water in rivers and their greenhouse gas emissions, this study designed three small-scale constructed wetland experimental systems with traditional gravel (CW-G), volcanic rock (CW-V) and biomass carbon (CW-B) as filler substrates to investigate the effect of different constructed wetland systems on the removal of COD and nitrogen pollutants and to further analyse their effect on greenhouse gas emissions. The results showed that the removal rates of organic matter in all three groups of constructed wetlands reached over 90% and 49.29% to 58.71%, respectively, with CW-V and CW-B significantly improving the removal of NH₄⁺-N and NO₃⁻-N compared to CW-G (P < 0.05). A comparison of greenhouse gas emissions reveals that although CW-B resulted in the highest N₂O emissions due to its better removal of NO₃⁻-N, its share in nitrogen removal was still the smallest. In addition, the rapid consumption of organic

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matter in the influent water and the oxidation of some CH$_4$ to CO$_2$ resulted in no detectable CH$_4$ in any of the three groups of constructed wetlands. The results of this study show that the differences in treatment effects and greenhouse gas emissions between the three types of substrate constructed wetlands are significant, and this study can provide some scientific reference for the construction and operation of wetlands for the purification of polluted water bodies in rivers.

**Keywords:** Constructed wetlands, river water pollution, biochar, greenhouse gases.

### 1 Introduction

As China’s economy continues to develop, a large number of pollutants are continuously discharged into rivers and the water environment continues to deteriorate [1]. Traditional technical methods to deal with polluted water bodies in rivers include physical methods such as water diversion and water exchange, substrate dredging [2], chemical methods such as flocculation and sedimentation, oxidative degradation, and biological methods such as ecological ponds and constructed wetlands [3], among which, constructed wetlands, compared with other technologies, have mature technology, good treatment effect, strong nitrogen and phosphorus removal capacity, easy operation and maintenance management, low engineering infrastructure and operation costs, as well as the ability to adapt to load changes. The scope of application in the field of ecological restoration and purification of polluted water bodies in rivers is becoming increasingly widespread [4–6]. However, the massive emission of greenhouse gases such as carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O) during the treatment of wastewater in constructed wetlands has become a global problem and is of great concern to all sectors of society [7, 8]. Therefore, there is an urgent need to find a green and efficient method to achieve efficient removal of river pollutants and mitigation of greenhouse gas emissions simultaneously.

Wetland fill is a living vehicle for aquatic plants and animals and a stable attachment substrate for microorganisms in wetlands [9]. Different fillers, with different physicochemical properties, have different water treatment effects. Suitable fillers and proportional composition not only enhance the wastewater treatment effect of constructed wetlands and reduce construction and maintenance costs, but also regulate the internal environment and ecological bodies that produce and oxidise greenhouse gases [10]. On the
one hand, for the internal environment of the wetland, differences in the spatial structure of the substrate can directly influence the distribution of dissolved oxygen, with substrates of large particle size or high porosity having a high oxygen enrichment capacity, determining that the end products of organic matter degradation are dominated by CO$_2$ rather than CH$_4$. At the same time, an increase in dissolved oxygen also inhibits denitrification and increases N$_2$O emissions. When the substrate contains organic matter, it can be directly involved as a substrate in the microbial reaction process, e.g. the carbonaceous substrate in the denitrification process takes on the function of a carbon source, providing an electron donor for the complete heterotrophic denitrification, thus reducing the production of the intermediate product N$_2$O [11]. Therefore, finding substrates that can simultaneously remove pollutants efficiently and achieve greenhouse gas reduction is important to further promote the application of constructed wetlands in polluted rivers.

In this study, the effects of traditional gravel, volcanic rock and biomass carbon on the removal of pollutants from river channels were compared and investigated by constructing constructed wetlands with different substrate fillers, and the effects of substrate characteristics on the reduction of CO$_2$, CH$_4$ and N$_2$O emissions were further investigated to reveal the mechanisms by which substrate configuration affects pollutant removal and greenhouse gas emissions. This will provide a new solution and theoretical basis for enhancing the performance of constructed wetlands in treating polluted water in rivers while mitigating the warming potential.

2 Materials and Methods

2.1 Substrate Filler

The three matrix fillers used in this experiment, gravel, volcanic rock and biomass carbon, were purchased from Henan Longrun Water Treatment Materials Co. The substrates were washed repeatedly with ultrapure water and dried to a constant mass in a blast dryer at 105$^\circ$C before use.

2.2 CWs Set-up and Operation

As shown in Figure 1, the test set-up had an internal diameter of 10 cm, a column height of 60 cm and a substrate fill height of 50 cm. All batches were tested at room temperature (25 ± 1)$^\circ$C. Three different submerged wetlands with different fill types were designed for this experiment: Type CW-G wetland substrate consisting of 10 cm of soil on the surface, 5 cm of
quartz sand in the middle (to separate soil and substrate) and 30 cm of thick gravel on the bottom; Type CW-V wetland substrate consisting of 10 cm of soil on the surface, 5 cm of quartz sand in the middle (to separate soil and substrate) and 15 cm of thick gravel and 15 cm of volcanic rock on the bottom; Type CW-B wetland substrate consisting of 10 cm of soil on the surface, 5 cm of quartz sand in the middle (to separate soil and substrate) and 15 cm of thick gravel on the bottom. The CW-B wetland substrate consists of a surface layer of 10 cm soil, a middle layer of 5 cm quartz sand (to isolate the soil from the substrate) and a bottom layer of 15 cm gravel and 15 cm biochar.

The experimental wastewater was disposed according to the water quality of Yongxing river. The artificial simulated wastewater quality index is shown in Table 2.
Table 2  Simulated wastewater quality indicators

<table>
<thead>
<tr>
<th>Projects</th>
<th>COD/(mg L$^{-1}$)</th>
<th>TN/(mg L$^{-1}$)</th>
<th>NH$_4^+$-N/(mg L$^{-1}$)</th>
<th>TP/(mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scope</td>
<td>206.9 ± 21.1</td>
<td>52.12 ± 8.4</td>
<td>48.1 ± 9.2</td>
<td>4.7 ± 1.6</td>
</tr>
</tbody>
</table>

2.3 Operational Conditions
During the experiment, the peristaltic pump was continuously fed with 10 L/D water, the hydraulic load of the constructed wetland was 0.14 m$^3$·m$^{-2}$·d$^{-1}$, and the hydraulic residence time was 4 days. The experiment was carried out in two stages: the first stage was to collect domestic sewage, which was injected into subsurface flow wetland for 30 days, and the second stage was to drain the water in the subsurface flow wetland every 24 hours, after stable operation for 7 days, 1 L of water samples were taken from the outlet of the wetland system each time, and the corresponding indexes were determined in 3 parts in parallel.

2.4 Analytical Methods
The water quality was determined by the national standard method, in which COD$_{Cr}$ was determined by potassium dichromate method and NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N, TN and TP were determined by ultraviolet Spectrophotometer.

Combined static chamber-gas chromatographic method for the determination of greenhouse gas fluxes. The gas chromatograph was equipped with a FID detector and an ECD detector, a PorapakQ column and a nitrogen carrier gas.

3 Results and Discussion
3.1 Effect of Constructed Wetland Wastewater Treatment with Different Filler Substrates
Since the nitrogen source in the experimental influent is NH$_4$Cl, NH$_4^+$-N is the main component of the influent TN. The nitrification process is the first step in the removal of NH$_4^+$-N, which is also an essential step for TN removal. However, constructed wetlands often have low oxygen levels and weak reoxygenation capacity, which inhibit aerobic microorganisms that convert NH$_4^+$-N. Therefore, the nitrification process is the main limiting step for nitrogen removal in constructed wetlands. The NO$_3^-$-N produced by nitrification needs to be removed by the denitrification process, which is the last step of nitrogen removal. The denitrification process is often limited by
the carbon source and the lack of electron donors, which eventually leads to the accumulation of NO$_3^-$-N and inhibits the removal of TN [12, 13].

Figure 2 shows the removal effects of CWs with different matrix fillers on NH$_4^+$-N, NO$_3^-$-N and TN, and the results indicate that all CWs have certain removal effects on nitrogen pollutants. Among them, the effluent concentrations of NH$_4^+$-N, NO$_3^-$-N and TN in CW-V and CW-B were significantly lower than those in CW-G (P < 0.05), and CW-V and CW-B also showed significant differences in the removal of nitrogen pollutants (P < 0.05). For NH$_4^+$-N, the average effluent concentrations of CW-V and CW-B were 3.89 ± 0.67 mg/L and 3.46 ± 0.38 mg/L, with an average removal rate of 91.25 ± 0.48% and 93.08 ± 0.31%, respectively, while the average effluent concentration of CW-G was as high as 7.98 ± 0.86 mg/L with a removal rate of 82.33 ± 0.63%. This may be attributed to the porous structure of volcanic rocks and biomass carbon which provide more favorable adsorption sites for NH$_4^+$-N removal as well as their stronger ion exchange properties for NH$_4^+$-N. It has been shown that NH$_4^+$-N is first adsorbed on the surface and in the macropores of volcanic rocks, and then further diffusively adsorbed into the micropores and small cavities inside the volcanic rocks [14]. However, conventional constructed wetlands with gravel substrates have high effluent NH$_4^+$-N concentrations and low removal efficiency due to the relatively low DO levels within their systems, which limit nitrification. In contrast, the differences in NO$_3^-$-N removal by different CWs were more significant (P < 0.05), and the effluent concentrations were CW-G (24.51 mg/L) > CW-V (20.36 mg/L) > CW-B (12.88 mg/L) in descending order, and the effluent concentration of CW-B was only half of that of CW-G, which was mainly due to the presence of biomass carbon providing sufficient carbon source supply, which enhanced denitrification and promoted the removal of NO$_3^-$-N, and likewise promoted the removal of TN to some extent [15]. As shown in Figure 2c, the effluent TN concentration of CW-B remained the lowest, followed by CW-V and CW-G, mainly because the biomass carbon not only has a large specific surface area, which can provide a large number of adsorption sites, but also can provide a certain carbon source for the denitrification of microorganisms. Therefore, overall, the substrate type had a significant effect on the nitrogen removal effect, with the best nitrogen removal effect in the biochar constructed wetland.

To further understand the removal of different forms of inorganic nitrogen at different heights within CWs, the variation of nitrogen pollutant concentrations along the CWs was measured and analyzed, and it was found that most of NH$_4^+$-N was removed in the upper layer (0–15 cm) of all CWs
Figure 2  Removal of nitrogen pollution by different CWs.
Figure 3  Along-range variation of nitrogen in different CWs.
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(Figure 3a), mainly because nitrification requires oxygen, and the deeper the packing depth, the lower the dissolved oxygen concentration, the weaker the nitrification, and the less NH$_4^+$-N is converted. And most of NO$_3^-$-N was removed in the middle and lower layers (15–45 cm) (Figure 3b). Especially in the lower and middle layers of CWs, it can be seen that the removal of NO$_3^-$-N by CW-B is significantly higher than that by CW-G and CW-V. This is mainly because the removal of NO$_3^-$-N depends on denitrification, which becomes stronger with increasing depth and is further accelerated by the release of carbon source from biochar coincided with the removal of NO$_3^-$-N, while the trend of TN variation in the middle and lower layers coincided with the variation of NO$_3^-$-N removal (Figure 3c).

It is well known that denitrification is an important pathway for nitrogen transformation, and organic carbon sources, as important electron donors in the denitrification process, are essential for microbial growth and NO$_3^-$-N reduction [16, 17]. organic matter in CWs can be removed from wastewater through physical and biological processes, and substrates can often influence the physicochemical properties of the surrounding environment and microbial processes by affecting organic matter removal performance. Figure 4 shows the average COD removal performance of different CWs and its dynamics during the experimental period. The effluent COD of the experimental group was significantly lower than that of the control group throughout the experimental period, and the average COD removal performance was in the order of CW-B (97.3 ± 0.65%) > CW-V (95.47 ± 0.48%) > CW-G (93.87 ± 0.87%).

It has been noted that during the pyrolysis of biochar, cellulose compounds in the raw material are thermochemically decomposed to produce volatiles and some bioavailable organic compounds are deposited or adsorbed on the skeleton [18]. Among them, DOC released from biochar can serve as a potential carbon source for microorganisms and is an important factor in enhancing denitrification. The amount of DOC (mg) released per unit mass (g) of biochar per unit time (h) is shown in Figure 4b. The cumulative DOC release from biochar was in the order of 8.5 mg/g. One study measured DOC release from rice husk biochar at 10 mg/g over 6 days, which is similar to the amount released from biochar used in this experiment [19].

To demonstrate whether the carbon source released from biochar can be used by microorganisms, the mean TOC/COD values of biochar in this experiment were 0.31 and the ratio was close to 0.38, respectively. when the reducing materials were all carbon containing organic materials, the
corresponding TOC/COD ratio was 0.38. This indicates that the organic matter released from biochar has good solubility and degradability. One study measured the release of COD from rice straw at 178 mg/g in 30 d, while peanut shells were found to release 100.86–134.10 mg/g COD in 6 days,

Figure 4  Carbon release analysis of COD concentration of inlet and outlet water and biomass carbon for different CWs.
indicating that the amount of organic matter released from various materials is related to the type of biomass and the time of release [20]. This shows that biochar is able to release certain organic matter with good solubility and degradability, which promotes denitrification of CW-B.

3.2 Greenhouse Gas Emissions from Constructed Wetlands with Different Filler Substrates

This experiment not only monitors the effluent purification effect of constructed wetlands with different substrates, but also examines the greenhouse gas emission fluxes from constructed wetlands with different substrate types. The greenhouse gases emitted from constructed wetlands play an important role in global climate change, and the analysis of their change patterns can help further reveal the mechanism of greenhouse gas emission reduction from constructed wetlands and provide new solutions for mitigating the global greenhouse effect.

$\text{N}_2\text{O}$ is mainly produced by incomplete nitrification and denitrification of nitrogen during transport transformation, and its emissions are governed by several factors such as environmental characteristics, carbon to nitrogen ratio, pH and DO [21]. The $\text{N}_2\text{O}$ emission fluxes generated from the operation of different CWs are shown in Figure 5a. Among the three substrate types of constructed wetlands, CW-V had the lowest $\text{N}_2\text{O}$ emission of $0.21 \pm 0.06$ mg-m$^{-2}$·h$^{-1}$, followed by CW-G and CW-B with $0.26 \pm 0.04$ mg-m$^{-2}$·h$^{-1}$ and $0.31 \pm 0.07$ mg-m$^{-2}$·h$^{-1}$, respectively. The lower NO emission in CW-V $\text{N}_2\text{O}$ emissions are mainly due to the rich pore structure of the volcanic rocks, which leads to a higher DO content and promotes the nitrification process. It is worth noting that the $\text{N}_2\text{O}$ emissions in CW-B are higher than in other CWs, and the reason for this difference is mainly that different substrates lead to differences in the physicochemical properties and microbial community structure in different CWs [22].

Although the addition of biomass carbon promoted the production and emission of $\text{N}_2\text{O}$, however, further examination of the proportion of $\text{N}_2\text{O}$ emission in nitrogen removal revealed that the lowest proportion in CW-B was about $0.19 \pm 0.03\%$, followed by CW-G and CW-V with $0.22 \pm 0.05\%$ and $0.27 \pm 0.07\%$, respectively, and fluctuated with the change of influent load, as shown in Figure 5b. The proportion of $\text{N}_2\text{O}$ emission in N removal in CW-B was about $0.19 \pm 0.03\%$, followed by CW-G and CW-V with $0.22 \pm 0.05\%$ and $0.27 \pm 0.07\%$, respectively, and fluctuated with the change
Figure 5  \( \text{N}_2\text{O} \) emissions from different CWs and their proportions in the nitrogen removal process.

of influent load. B, because biochar can provide carbon source by microorganisms, can promote the nitrification denitrification of microorganisms and enhance the TN removal on the one hand, and improve the \( \text{N}_2\text{O} \) emission on the other hand, however, its emission is still the lowest percentage of nitrogen removal. This indicates that the addition of both biomass carbon and
volcanic rock can reduce the production and emission of N\textsubscript{2}O in the process of nitrogen removal.

CO\textsubscript{2} is also an important greenhouse gas, and CO\textsubscript{2} in CWs is mainly produced by respiration of microorganisms and plants, but also captured by plants through photosynthesis. As shown in Figure 6, under the same experimental conditions, the CO\textsubscript{2} emission fluxes in constructed wetlands of different substrate types were CW-G, CW-V and CW-B in descending order, corresponding to CO\textsubscript{2} emissions of 508.3 ± 43.5, 415.7 ± 53.7 and 378.6 ± 48.8 mg·m\textsuperscript{−2}·h\textsuperscript{−1}, respectively. Compared with CW-G, although CW-V and CW-B had higher organic matter, the addition of limestone and biomass carbon contributed to the reduction of CO\textsubscript{2} emissions compared to CW-G. This is mainly due to the fact that limestone and biochar have a large specific surface area and can trap more organic carbon when used as substrates, which can prevent further mineralization of organic matter to produce CO\textsubscript{2}, and they can also reduce CO\textsubscript{2} emissions by reducing the abundance of two carbon mineralizing enzymes, glucosidase and cellobiosidase, as well as promoting plant growth [23]. In addition, it has been noted that high pH and high alkali metal content on the surface of biochar produce CO\textsubscript{2} that can be precipitated as carbonate [24].

However, the presence of CH\textsubscript{4} was not detected in all CWs, which may be due to the fact that the COD in the feed water was heavily consumed in
the upper layers of CWs resulting in low CH$_4$ production, while some of the generated CH$_4$ was oxidized and released as CO$_2$. It was shown that the CH$_4$ emission flux in CWs was mainly influenced by organic carbon loading, oxygen level and microorganisms, with organic matter quality being an important factor affecting the CH$_4$ emission flux. The lower C/N in this study may lead to lower CH$_4$ production, and the upper-inlet and lower-outlet inlet methods maintain a certain oxygen level in the upper layer of CWs, which further enhances the oxidation of methane.

4 Conclusion

(1) Different substrate conditions have important effects on the improvement of physicochemical conditions and microbial environment of constructed wetlands. The addition of volcanic rock and biochar can improve the removal efficiency of organic matter from polluted rivers in constructed wetlands, and the carbon release analysis of biochar found that biochar can promote the denitrification of microorganisms by releasing carbon sources.

(2) Compared with the conventional gravel matrix, the addition of volcanic rock and biomass carbon significantly improved the removal of nitrogen pollutants by CWs, and the removal of TN in descending order was CW-B ($67.89 \pm 4.28\%$) > CW-V ($52.55 \pm 5.21\%$) > CW-G ($36.78 \pm 2.33\%$), and the accumulation of NO$_3^-$-N by CW-V and CW-B was much lower than that by CW-G was much less.

(3) Biochar and volcanic rock are more beneficial to GHG emission reduction than conventional gravel substrates. CW-B exhibited the highest N$_2$O emissions due to its high NO$_3^-$-N removal, but its N$_2$O emissions remained the smallest percentage of nitrogen removal.

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References


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