

## Article

# Study on the Decontamination Effect of Biochar-Constructed Wetland under Different Hydraulic Conditions

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**Abstract:** To explore the purification effect of biochar-constructed wetlands on rural domestic sewage, six types of biochar-constructed wetlands were constructed for experiments. Under different hydraulic conditions, the removal effects of each biochar-constructed wetland on chemical oxygen demand, ammonia nitrogen, total nitrogen, and total phosphorus in sewage were analyzed. The results showed that the removal rates of the four types of pollutants in each biochar-constructed wetland first increased and then decreased with the increase in hydraulic retention time, and the optimal hydraulic retention time range was 36–48 h. The highest removal rates of chemical oxygen demand, ammonia nitrogen, total nitrogen, and total phosphorus in the wetland were  $97.34 \pm 0.84\%$ ,  $95.44 \pm 1.29\%$ ,  $98.95 \pm 0.52\%$ , and  $97.78 \pm 0.91\%$ , respectively. The chemical oxygen demand (COD) removal rate of each biochar-constructed wetland increased first, then decreased with the increase in hydraulic load, and the optimal hydraulic load was 10 cm/d. The removal efficiency of ammonia nitrogen, total nitrogen, and total phosphorus of each biochar-constructed wetland gradually weakened with the increase in hydraulic load, and the optimal hydraulic load range was between 5 and 10 cm/d. Under these conditions, the highest removal rates of chemical oxygen demand, ammonia nitrogen, total nitrogen, and total phosphorus in the wetland were  $92.15 \pm 2.39\%$ ,  $98.32 \pm 0.48\%$ ,  $96.69 \pm 1.26\%$ , and  $92.62 \pm 2.92\%$ , respectively. Coconut shell and shell-constructed wetlands with the highest proportion of biochar in the matrix have the best removal effect on pollutants under different hydraulic conditions, and the wastewater purification effect is stronger, indicating that the addition of biochar is helpful for the removal of pollutants in constructed wetlands.

**Keywords:** constructed wetland; biochar; hydraulic retention time; hydraulic load



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## 1. Introduction

Rural sewage has become one of the important sources of rural environmental pollution. Due to the randomness, volatility, low level of harmful substances, and good biodegradability of rural domestic sewage discharge, combined with the existing rural domestic sewage purification methods, constructed wetlands are a form of low-cost, easy-to-manage, highly efficient, and environmentally friendly water purification system [1,2]. Many scholars have applied constructed wetlands to the research on the purification of rural domestic sewage, showing the feasibility of constructed wetlands for the decontamination of rural domestic sewage [3–6]. Xingyuan Xu proposed that it is easy for nitrification reaction to occur in constructed wetlands, which is conducive to the removal of ammonia nitrogen [7]. Tingliang Jiang and Pozhen Chen held that the construction of constructed wetlands can not only increase the hydraulic load of purification facilities but also improve the anti-impact ability of the system [8,9]. Sylla concluded that constructed wetlands can provide a favorable environment for various organic and inorganic reactions and promote the removal of pollutants [10]. However, traditional constructed wetlands have low pollutant load, low pollutant removal efficiency, and the substrate is likely to clog, which also

restrict their application. Therefore, improving the purification efficiency of pollutants and the sewage purification load of constructed wetlands is extremely critical for their future development.

Biochar refers to a carbon-rich insoluble solid material obtained by pyrolysis of biomass at a certain temperature in hypoxia or an anaerobic airtight environment [11] with high carbon content, large specific surface area, strong cation exchange capacity, abundant surface functional groups [12], and stable physical and chemical properties. Moreover, it is easily prepared and can effectively adsorb pollutants in water and reduce the carbon footprint [13,14]. Generally, the source of raw materials of biochar can be divided into straw, shell, wood, feces, sludge, etc. The physical and chemical properties are mainly determined by biomass materials and pyrolysis temperatures, while the temperature determines the biochar's aromatization, the number of surface functional groups, and the size of the surface area, which is the key to purify contaminated water by biochar [15]. As the temperature increases, the number of surface functional groups of biochar will decrease constantly. The good pore structure and large specific surface area can improve retention of sewage in system and prolong the hydraulic retention time. The pH of biochar is generally alkaline. A large number of studies have shown that constructed wetlands combined with biochar can enhance the purification effect of constructed wetlands on sewage [16–18].

Haiyan Zou explored the effect of sludge biochar on the adsorption and immobilization of low-temperature mixed bacteria and the removal efficiency of pollutants in constructed wetland water under low temperature conditions. The results showed that the addition of sludge biochar increases the specific surface area of the immobilized pellets, which can protect microorganisms from the disturbance of hydraulic erosion. When the quality of polyvinyl alcohol (PVA), sodium alginate (SA), and sludge biochar carrier is 6%, 2%, and 1.4%, respectively, the pollutant removal efficiency of wastewater is greatest. The removal rate of chemical oxygen demand (COD), total nitrogen (TN), ammonia nitrogen (NH<sub>3</sub>-N), and total phosphorus (TP) in constructed wetland can be up to 92.21%, 94.70%, 91.08%, and 89.75%, respectively [19]. Chaoren Deng explored the removal effect of biochar on wetland pollutants and N<sub>2</sub>O emissions by building a biochar micro-subsurface flow constructed wetland system in a greenhouse. The study concluded that, as the amount of biochar continues to increase, the removal effect of ammonia and total nitrogen also increases significantly, and N<sub>2</sub>O emissions are significantly reduced. The removal rate of COD all reached 90%, and the average removal rate of NH<sub>3</sub>-N and TN was  $34.76 \pm 14.16\%$ ~ $57.96 \pm 10.63\%$  and  $70.92 \pm 5.68\%$ ~ $80.21 \pm 10.63\%$ , respectively [20]. Joseph combined anaerobic ammonium nitriding process technology with biochar and applied it to constructed wetlands to treat landfill leachate, indicating that anaerobic bacteria combined with biochar-embedded purification technology can treat landfill leachate with a higher pollution index. The combined purification system demonstrated purification efficiencies as 100% of ammonia, 98.7% of nitrite, 98.2% of nitrate, 80.9% of phosphate, 79.7% of COD, and 69.9% of conductivity [21]. These studies have shown that different amounts of biochar in the substrate of constructed wetlands have different effects on sewage decontamination; however, the amount of biochar is not the only factor that affects sewage purification. The hydraulic retention time and hydraulic load of the wetland are also important factors affecting the removal capability of biochar-constructed wetland. Therefore, the aim of this article is to discuss the pollutant removal effects of different biochar-constructed wetlands by adjusting the hydraulic retention time [22] and hydraulic load [23,24] and obtain the optimum hydraulic retention time and hydraulic load. Finally, the development of a low-cost ecological purification system coupled with biochar substrates using constructed wetlands strengthens the research on the related mechanisms and technical parameters and provides theoretical and technical support for the sustainable ecological purification of microsewage [25,26].

## 2. Materials and Methods

### 2.1. Experimental Design

For this study, six subsurface flow constructed wetlands were constructed. Each constructed wetland was made of brick concrete, with a length:width ratio of 3:1, dimensions of 510 cm length, 170 cm width, and 80 cm height, and a wall thickness of 15 cm. The construction was composed of ceramsite, zeolite, melon seed stone, and biochar as the substrate; with the exception of biochar, the laying order of the substrate, descending from bottom to top according to the particle size, was ceramsite, with a particle size of 3 cm; zeolite, 0.8–1.6 cm; ceramsite, 0.4–0.8 cm; and melon seed stone, less than 0.4 cm. To study the purification effect of different types of biochar, different placement locations of biochar, and different dosages of biochar on the purification of rural domestic sewage in constructed wetlands, coconut shell biochar and nutshell biochar were used in this experiment. Based on their placement and amount, the constructed wetlands were divided into six groups of controlled trials: Coconut shell ceramsite, Coconut shell zeolite, Coconut shell, Shell ceramsite, Shell zeolite, and Shell. Coconut shell biochar was added to Coconut shell ceramsite, Coconut shell zeolite, and Coconut shell, Shell ceramsite constructed wetlands, and shell biochar was added to the constructed wetlands of Shell ceramsite, Shell zeolite, and Shell. Biochar was placed in the small ceramsite layer at a 1:1 volume ratio in the constructed wetlands of the Coconut shell ceramsite group. In the Coconut shell zeolite group, biochar was placed in the zeolite layer at a 1:1 volume ratio in the constructed wetland. In the Coconut shell group, biochar was placed in the small ceramsite layer and zeolite layer at the volume ratio of 1:1, that is, the amount of biochar in the Coconut shell group was twice as much as that in the Coconut shell ceramsite and Coconut shell zeolite groups, and each layer of the matrix had a thickness of 15 cm. The plant selection of the six subsurface flow constructed wetlands was yellow flag, and the planting density was 25 plants/m<sup>2</sup>. The plan of the constructed wetland is shown in Figure 1. The profile of the constructed wetland is shown in Figure 2.

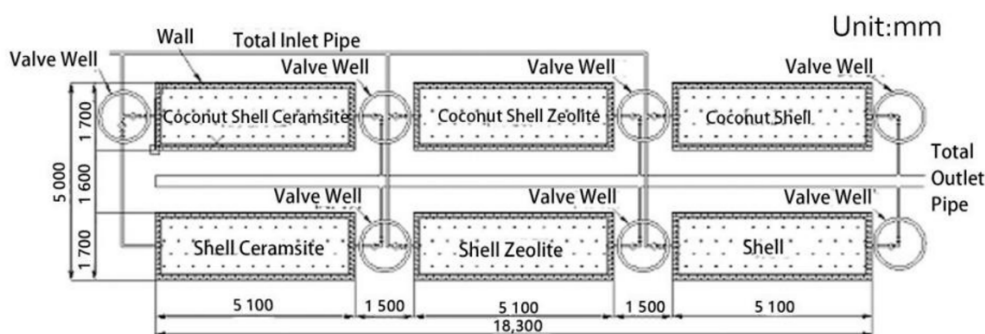
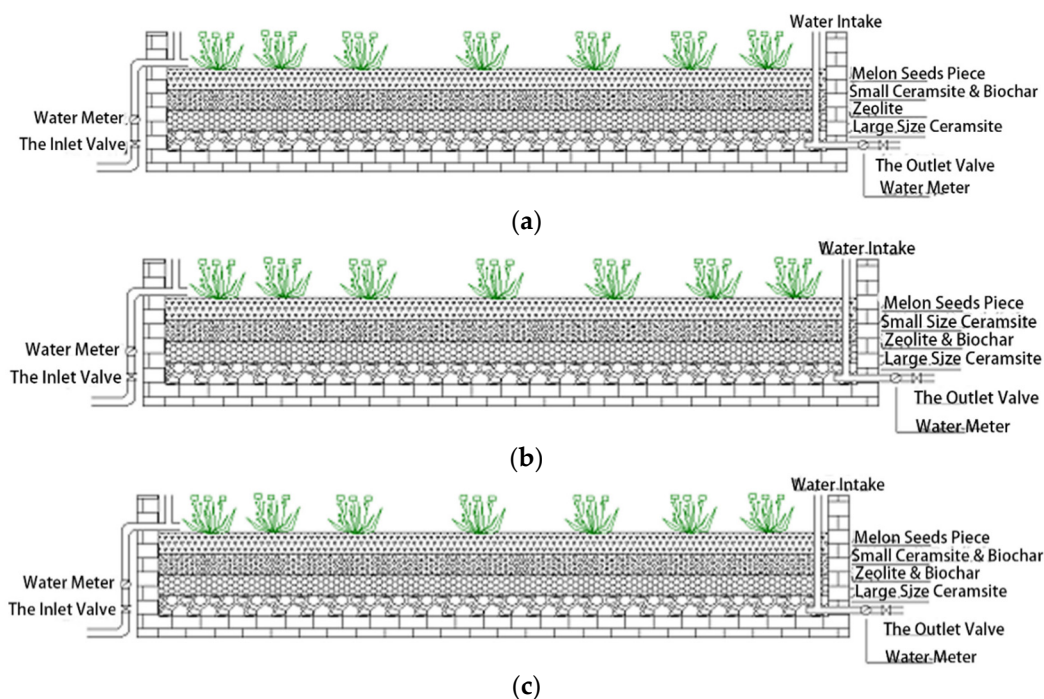


Figure 1. The plan of the constructed wetland.

### 2.2. Inflow Water Quality

The experiment adopted the method of intermittent water supply. To simulate different concentrations of rural domestic sewage, the inlet water used by the system was configured synthetic sewage, diluted with potassium dihydrogen phosphate, ammonium chloride, and glucose. The sewage indicators tested this time are mainly chemical oxygen demand (COD), ammonia nitrogen (NH<sub>3</sub>-N), total nitrogen (TN), and total phosphorus (TP). The chemical oxygen demand refers to the amount of oxidant consumed when a certain strong oxidant is used to treat water samples under certain conditions. The higher the chemical oxygen demand, the more organic pollutants in the water. Ammonia nitrogen refers to nitrogen in the form of free ammonia (NH<sub>3</sub>) and ammonium ions (NH<sub>4</sub><sup>+</sup>) in water. Total nitrogen refers to the total amount of various forms of inorganic and organic nitrogen in water. Total phosphorus is the result of the transformation of phosphorus from various forms into orthophosphate after water digestion. Switches and water meters were installed

at the inlet and outlet pipes of each wetland to control the flow of water in and out. A vertical pipe was positioned at the inlet and outlet pipes for adding samples and collecting water samples. The water source used to simulate domestic sewage was a fishpond, which had a pollutant concentration that exceeded the standard. Therefore, the pollutant concentration of the water in the fishpond plus the theoretical pollutant concentration after the addition of drugs was the actual input of the constructed wetland for this test (Tables S1–S4). The reagents used in the experiment (potassium dihydrogen phosphate, ammonium chloride, glucose) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The equipment used in the experiment is UV-vis spectrophotometer provided by Beijing Purkay General Instrument Co., Ltd. (Beijing, China). The monitoring indexes and methods of water quality are shown in Table 1, and the actual inlet water quality of the test is shown in Table 2.



**Figure 2.** Biochar was added to the small particle size ceramsite layer (a); biochar was added to the zeolite layer (b); biochar was added to the small particle size ceramsite layer and the zeolite layer (c).

**Table 1.** The monitoring indexes and methods of water quality.

Water Quality Monitoring Index	Method or Instrument
Chemical oxygen demand	Bichromate method (HJ 828-2017)
Ammonia nitrogen	Nessler’s reagent spectrophotometry (HJ 535-2009)
Total nitrogen	Alkaline potassium persulfate digestion UV spectrophotometry (HJ 636-2012)
Total phosphorus	Ammonium molybdate spectrophotometric method (GB/T 11893-1989)

**Table 2.** The actual inlet water quality of the test. Unit (mg/L).

Type of Pollutant	NH <sub>3</sub> -N	TN	TP	COD
Theoretical pollutant concentration	30.636	30.636	5.917	173.382
Concentration of pollutants in fishponds	0.374	5.79	0.09	22
Actual influent pollutant concentration	31.01	36.426	6.007	195.382

### 2.3. Experimental Scheme

The hydraulic retention times selected were 12, 24, 36, 48, 60, 72, and 84 h, and the hydraulic loads were 5, 10, 20, and 30 cm/d. These hydraulic retention times and loads were achieved by adjusting the in and out flows of the gate valve. After a period of stable operation of the wetland, 100 mL water samples were taken from the water outlet of each wetland and immediately put into a 4 °C incubator for the monitoring of pollutant concentration in the laboratory (Tables S5–S8). Each test was repeated twice, and the average value was taken. Before each experiment, the water inside the wetland was emptied to reduce the influence of the original sewage on the experimental results.

## 3. Results and Discussion

### 3.1. Analysis of Decontamination Efficiency of Biochar-Constructed Wetlands under Different Hydraulic Retention Time

#### 3.1.1. Removal Effect of Chemical Oxygen Demand (COD) in Biochar-Constructed Wetlands

As shown in Figure 3, the removal rate of COD in sewage by each biochar-constructed wetland increases rapidly and then stabilizes with the extension of hydraulic retention time. When the hydraulic retention time was between 0 and 36 h, the COD removal rate increased with the increase in hydraulic retention time. In particular, within the range of 0–12 h, the COD removal efficiency of each wetland increased rapidly; the coconut shell constructed wetland reached  $75.82 \pm 3.68\%$ , and the removal efficiency of shell zeolite, coconut shell zeolite, and shell ceramsite was about 55%. When the hydraulic retention time was extended to 36 h, the removal rate of COD in each constructed wetland exceeded 75%. Among the tested wetlands, the removal efficiency of the coconut shell-constructed wetland and the shell-constructed wetland were highest, with removal rates reaching  $97.34 \pm 0.84\%$  and  $93.896 \pm 3.31\%$ , respectively. The removal rate was higher than that of the former (92.21% of Haiyan Zou's and 90% of Chaoren Deng's). The coconut shell biochar-constructed wetland achieved slightly higher COD removal from domestic sewage than the shell biochar-constructed wetland. However, the removal effects of shell zeolite-, coconut shell zeolite-, shell ceramsite-, and coconut shell ceramsite-constructed wetlands were almost the same, being  $83.21 \pm 3.72\%$ ,  $79.86 \pm 3.17\%$ ,  $79.82 \pm 7.26\%$ , and  $85.69 \pm 1.56\%$ , respectively. As the hydraulic retention time continued to increase until 84 h, the removal effect of each wetland on the COD in domestic sewage no longer continued to increase but is in a dynamic equilibrium (Table S9).

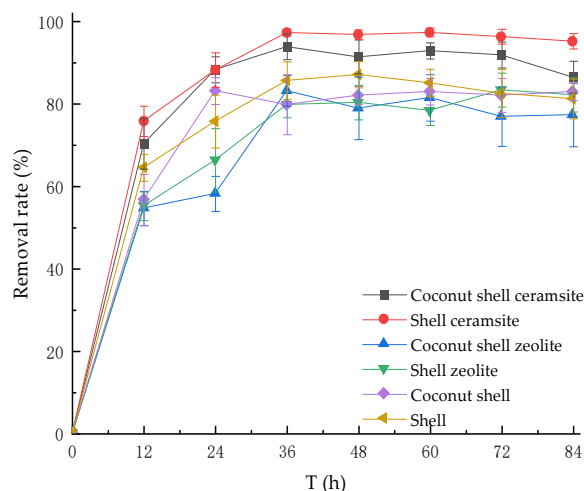


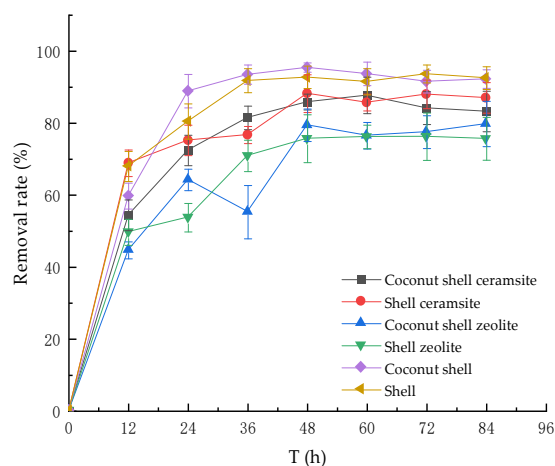
Figure 3. Removal effect of chemical oxygen demand (COD) in biochar-constructed wetlands.

To summarize, it can be seen that, the larger the proportion of biochar in the constructed wetland matrix, the higher the removal rate, as well as that the result of analysis of

variance (ANOVA) shows that the addition of biochar significantly improves the removal efficiency of COD ( $p < 0.05$ ), whereas the position of the biochar has no effect on the COD removal effect.

### 3.1.2. Removal Effect of Biochar-Constructed Wetland on Ammonia Nitrogen

The ammonia nitrogen removal effect of each biochar-constructed wetland is shown in Figure 4. The ammonia nitrogen removal effect of all constructed wetlands increased rapidly within a range of 0–12 h. During this time period, the removal of ammonia nitrogen mainly depends on the adsorption of the matrix. Among the tested wetlands, the ammonia nitrogen removal effects of the shell ceramsite-constructed wetland and shell-constructed wetland were greatest, with the ammonia nitrogen removal rate reaching  $68.88 \pm 3.69\%$  and  $68.00 \pm 4.18\%$ , respectively. The increasing trend of ammonia nitrogen removal effect within 12–48 h decreased obviously. This is because the adsorption of ammonia nitrogen by the substrate is in equilibrium at this time, and the microorganisms help to continually increase the removal efficiency of ammonia nitrogen. At 36–48 h, the removal rate of ammonia nitrogen in each wetland basically reached its maximum. After 48 h, as the hydraulic retention time continued to increase, the removal effect of ammonia nitrogen in each wetland no longer continued to increase, and the removal rate of ammonia nitrogen was in a dynamic balance. Among the tested wetlands, the removal effect on ammonia nitrogen of coconut shell- and shell-constructed wetlands was greatest, with the maximum removal rate reaching  $95.44 \pm 1.29\%$  and  $92.73 \pm 3.12\%$ , respectively; it was higher than that of the former (91.08% of Haiyan Zou's and 57.96% of Chaoren Deng's), followed by coconut shell ceramsite- and shell ceramsite-constructed wetlands, with removal rates of  $87.73 \pm 5.06\%$  and  $88.23 \pm 5.23\%$ , respectively. The removal effects of shell zeolite- and coconut shell zeolite-constructed wetland were the worst but also reached  $79.78 \pm 6.29\%$  and  $76.26 \pm 6.56\%$ , respectively (Table S10).



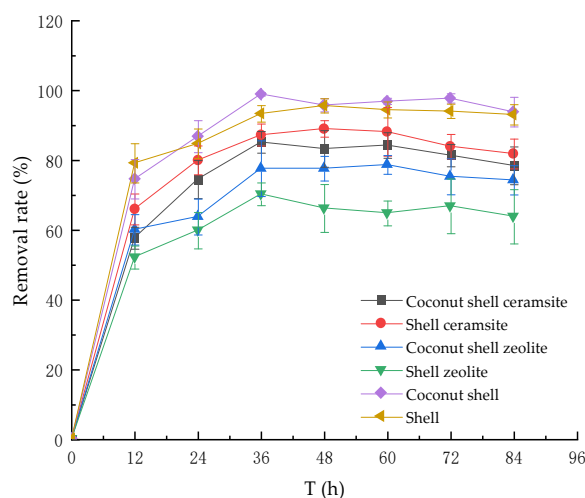
**Figure 4.** Removal effect of biochar-constructed wetland on ammonia nitrogen.

Therefore, for ammonia nitrogen, increasing the proportion of biochar helps with the removal of pollutants ( $p < 0.05$ ). In addition, the removal effect of ammonia nitrogen is dependent on the filling location of the biochar. Adding biochar to the upper layer of the substrate results in a higher removal rate of ammonia nitrogen.

### 3.1.3. Removal Effect of Biochar-Constructed Wetland on Total Nitrogen

As shown in Figure 5, during 0–12 h, the removal effect of wetlands on total nitrogen increased rapidly. Within the range of 12–36 h, the removal rate of each wetland also increased with the increase in hydraulic retention time, but the upward trend gradually decreased. The removal rate gradually reached the maximum value within the hydraulic retention period of 36–48 h. The removal effects on total nitrogen of coconut shell- and

shell-constructed wetlands were highest, reaching  $98.95 \pm 0.52\%$  and  $95.64 \pm 2.01\%$ , respectively. The removal rate was higher than that of the former (94.7% of Haiyan Zou's and 70.92% of Chaoren Deng's) The removal effects on total nitrogen of coconut shell zeolite- and shell zeolite-constructed wetlands were worst, with rates of  $70.30 \pm 3.26\%$  and  $78.71 \pm 2.69\%$ , respectively. This is because, within a certain range of hydraulic retention time, as the hydraulic retention time increases, the nitrification and denitrification effects in each biochar-constructed wetland are strong. As the hydraulic retention time continued to increase, the dissolved oxygen in the wetland gradually decreased, inhibiting the progress of the nitrification reaction, and the removal rate of total nitrogen of wetlands stabilized. At the same time, if the hydraulic retention time was too long, that is, after the hydraulic retention time reaches 72 h, the removal effect was weakened (Table S11).

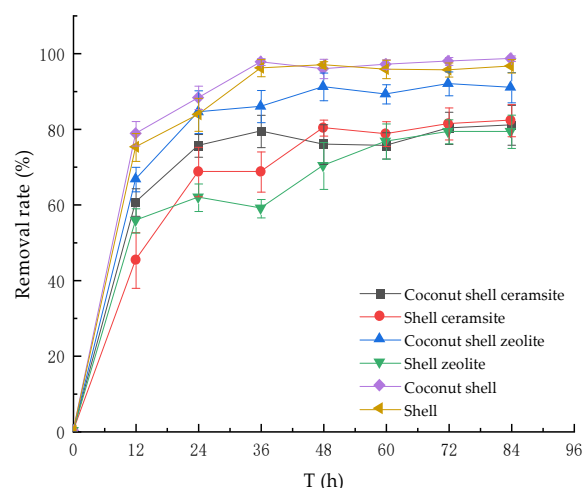


**Figure 5.** Removal effect of biochar-constructed wetland on total nitrogen.

Similarly, the greater the amount of biochar, the stronger the removal effect of the wetland on total nitrogen ( $p < 0.05$ ). Furthermore, the removal effect is better when biochar is placed on the substrate.

### 3.1.4. The Removal Effect of Biochar-Constructed Wetland on Total Phosphorus

As shown in Figure 6, when the hydraulic retention time is within 0–12 h, the coconut shell- and nutshell-constructed wetlands had the highest removal rates of total phosphorus, with the removal efficiency reaching  $78.81 \pm 3.23\%$  and  $75.23 \pm 3.69\%$ , respectively. As the hydraulic retention time continued to increase, the removal efficiency of total phosphorus in each constructed wetland continued to increase, and the increasing trend was significantly reduced. Among the tested wetlands, coconut shell-constructed wetlands, shell-constructed wetlands, and shell zeolite-constructed wetlands had maximum removal rates of total phosphorus in sewage at a hydraulic retention time of 48 h, before stabilizing, reaching  $97.78 \pm 0.91\%$ ,  $97.03 \pm 0.86\%$ , and  $92.03 \pm 3.16\%$ , respectively. The removal rate was higher than that of the former (89.75% of Haiyan Zou's). In comparison, the removal rate of total phosphorus by coconut shell ceramsite-constructed wetland and shell ceramsite-constructed wetland showed a continued upward trend after 48 h, but the increase was small. As the hydraulic retention time continued to increase, it reduced the purification efficiency of wetlands, so the reasonable hydraulic retention time for total phosphorus removal of these two constructed wetlands was still between 36 and 48 h. At this time, the removal rates of total phosphorus in coconut shell ceramsite- and shell ceramsite-constructed wetlands were  $79.43 \pm 4.26\%$  and  $80.35 \pm 2.12\%$ , respectively. The removal rate of coconut shell zeolite increased more after 48 h, and the maximum removal rate reached  $79.35 \pm 3.41\%$  (Table S12).



**Figure 6.** The removal effect of biochar-constructed wetland on total phosphorus.

By analyzing the total phosphorus removal effect of each biochar-constructed wetland, it was also found that, the higher the amount of biochar contained in the constructed wetland matrix, the higher the removal rate of total phosphorus ( $p < 0.05$ ). However, the filling location of biochar had no significant effect on the removal effect of total phosphorus.

### 3.2. Analysis of the Decontamination Effect of Biochar-Constructed Wetlands under Different Hydraulic Loads

#### 3.2.1. Removal Effect of COD in Biochar-Constructed Wetland

The removal rate of COD in each biochar-constructed wetland varied with hydraulic load, as shown in Figure 7. The removal rate of COD generally showed a trend of first increasing and then decreasing with the increase in hydraulic load. When the hydraulic load was 10 cm/d, the pollutant removal effect of biochar-constructed wetland was greatest. The highest removal rate was that of the shell zeolite-constructed wetland, of  $92.15 \pm 2.39\%$ . The removal effects of the coconut shell zeolite-, coconut shell-, and shell biochar-constructed wetlands were  $91.48 \pm 2.16\%$ ,  $91.17 \pm 3.67\%$ , and  $91.08 \pm 4.26\%$ , respectively. Compared with the experimental results of the former ( $92.21\%$  of Haiyan Zou's and  $90\%$  of Chaoren Deng's), the removal rate is almost close. However, the removal effects of the two constructed wetlands of ceramsite and coconut shell ceramsite were poor. This is because, when the hydraulic load is too small, an anaerobic state is easily formed inside the wetland, which affects the removal of COD. With the increase in hydraulic load, the anaerobic state is improved, so the removal rate of COD is also improved. However, when the hydraulic load increases, a large amount of organic matter cannot fully contact with the substrate, and the degradation effect of microorganisms is not fully exerted and is removed from the wetland system. Therefore, the removal effect of wetland on COD continues to decline. It can also be seen from Figure 7 that the removal rates of coconut shell and shell wetlands do not decrease significantly with the increase in hydraulic load, indicating that increasing the amount of biochar can improve the load-bearing capacity of the constructed wetland, while the result of ANOVA shows that the effect is not significant ( $p > 0.05$ ). In addition, when the biochar is filled in the lower layer of the matrix, the load resistance capacity also increases (Table S13).



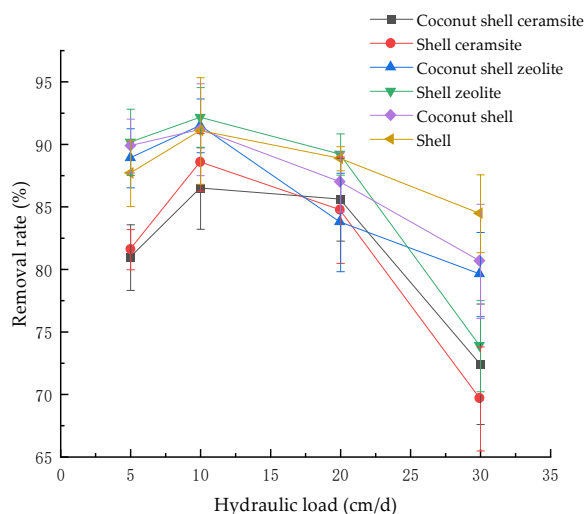


Figure 7. Removal effect of COD in biochar-constructed wetland.

### 3.2.2. Removal Effect of Ammonia Nitrogen in Biochar-constructed Wetland

The change in the ammonia nitrogen removal effect of each biochar-constructed wetland with hydraulic load is shown in Figure 8. The removal rate of ammonia nitrogen generally shows a trend of decreasing with the increase in hydraulic load. When the hydraulic load was 5 cm/d, each of the biochar-constructed wetlands showed the best pollutant removal effect. The highest removal rates were those of the shell-constructed wetland and the coconut shell-constructed wetland, of  $98.32 \pm 0.48\%$  and  $98.01 \pm 0.69\%$ , respectively. It was also higher than that of the former (91.08% of Haiyan Zou’s and 57.96% of Chaoren Deng’s). The removal effects of the three constructed wetlands of coconut shells, shells, and coconut shell ceramsites increased with the increase in hydraulic load, and the removal rate of ammonia nitrogen decreased and changed little. However, the removal effects of the three constructed wetlands of ceramsite, coconut shell zeolite, and shell zeolite were poor as the hydraulic load continued to increase; at this time, the removal rate of ammonia nitrogen decreased significantly (Table S14).

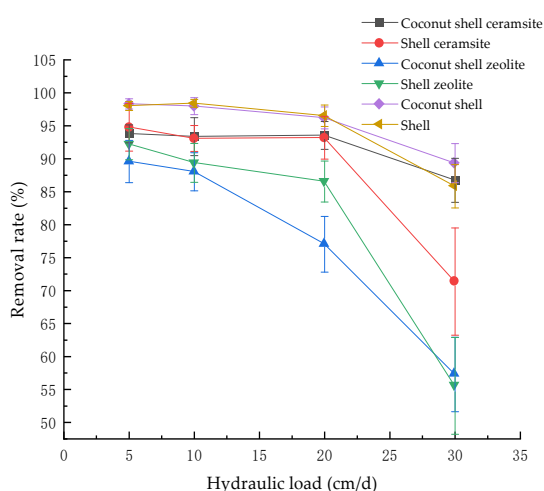


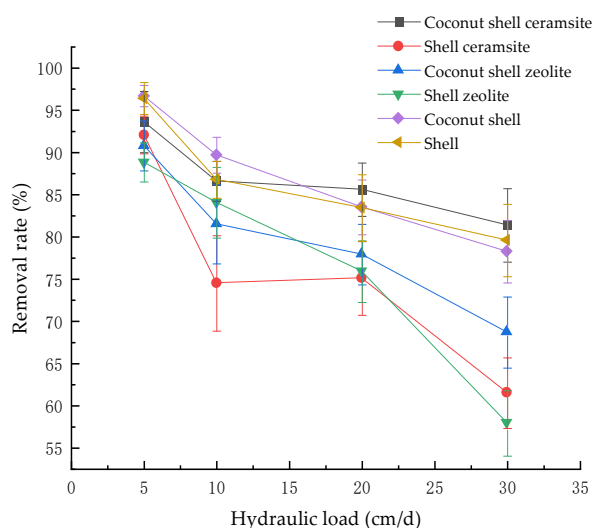
Figure 8. Removal effect of ammonia nitrogen in biochar-constructed wetland.

The study showed that a low hydraulic load, that is, a hydraulic load of between 5 and 10 cm/d, is beneficial to the removal of ammonia nitrogen in the biochar-constructed wetland. When the amount of biochar is relatively high, it not only increases the removal rate of ammonia nitrogen, but also improves the load-bearing capacity of the constructed

wetland ( $p > 0.05$ ). However, the position of the biochar has no obvious impact on the removal of ammonia nitrogen.

### 3.2.3. Removal Effect of Biochar-Constructed Wetland on Total Nitrogen

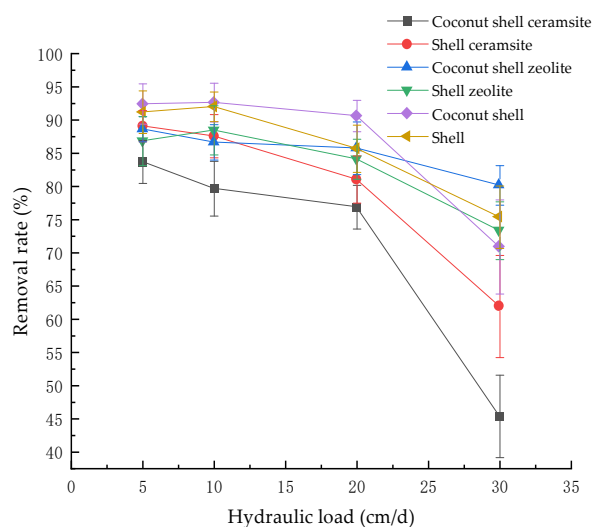
It can be seen from Figure 9 that when the minimum hydraulic load was 5 cm/d, the removal rate of total nitrogen in each biochar-constructed wetland was the highest. With the increase in hydraulic load, the removal rate of total nitrogen of each biochar-constructed wetland gradually decreased. The removal effect of coconut shell and shell constructed wetlands on total nitrogen was better than that of coconut shell zeolite-, shell ceramsite-, shell zeolite-, and other constructed wetlands, and the highest removal rates were  $96.69 \pm 1.26\%$  and  $96.40 \pm 1.88\%$ , respectively. The removal rate of total nitrogen under this condition is much higher than the experimental results of the former (94.7% of Haiyan Zou's and 70.92% of Chaoren Deng's). The removal rate of total nitrogen in the three constructed wetlands of coconut shell zeolite, shell ceramsite, and shell zeolite decreased significantly when the hydraulic load increased. In summary, it can be seen that, when the hydraulic load is small, the nitrification and denitrification effects are stronger. Thus, the nitrogen in the water can be fully decomposed, and the plants and microorganisms can more fully absorb the nitrogen in the water. With the increase in hydraulic load, the effect of nitrification and denitrification decreases, which reduces the removal rate of total nitrogen. In addition, the greater the amount of biochar, the better the removal effect of total nitrogen and the more advantageous the load-bearing capacity ( $p > 0.05$ ). The position of the biochar has no obvious impact on the removal effect of total nitrogen (Table S15).



**Figure 9.** Removal effect of biochar-constructed wetland on total nitrogen.

### 3.2.4. Removal Effect of Biochar-Constructed Wetland on Total Phosphorus

The change of removal rate of total phosphorus in each biochar-constructed wetland with hydraulic load is shown in Figure 10. As can be seen from the figure, when the hydraulic load is between 5 and 30 cm/d, the removal of total phosphorus of coconut shell-, shell-, and zeolite-constructed wetlands first increased and then decreased; when the hydraulic load is 10 cm/d, the removal rate is the highest. In contrast, the removal rate of total phosphorus by coconut shell ceramsite-, shell ceramsite-, and coconut shell zeolite-constructed wetlands gradually decreased with the increase in hydraulic load. Among all biochar-constructed wetlands, the removal rates of total phosphorus in coconut shell- and shell-constructed wetlands were significantly higher than those in the other four types of constructed wetlands, with the highest removal rates reaching  $92.62 \pm 2.92\%$  and  $92.00 \pm 2.24\%$ , respectively (Table S16). The removal rate was also higher than that of the former (89.75% of Haiyan Zou's).



**Figure 10.** Removal effect of biochar-constructed wetland on total phosphorus.

Thus, it can be seen that when the hydraulic load is small, the removal rate of total phosphorus in each biochar-constructed wetland is high. When the hydraulic load is high, the removal effect of total phosphorus in each biochar-constructed wetland is weaker. The higher the amount of biochar, the higher the removal rate of total phosphorus and the stronger the load-resistance capacity of the constructed wetland ( $p < 0.05$ ). The position of biochar added to the constructed wetland had no obvious effect on the removal effect of total phosphorus.

#### 4. Conclusions

- (1) The removal rates of COD, ammonia nitrogen, total nitrogen, and total phosphorus in each biochar-constructed wetland increase with the increase in hydraulic retention time, and the optimal hydraulic retention time is between 36 and 48 h.
- (2) The addition of biochar is conducive to the removal of pollutants in the wetland, and increasing the proportion of biochar in the constructed wetland matrix improves the purification effect of the wetland. In addition, when biochar is added to the upper layer of the matrix, the wetland has a better effect on the removal of ammonia nitrogen and total nitrogen.
- (3) With the increase in hydraulic load, the removal of COD in every biochar-constructed wetland first increases and then decreases, and the optimal hydraulic load is about 10 cm/d. For ammonia nitrogen, total nitrogen, and total phosphorus, the removal effect of biochar-constructed wetland gradually weakens with the increase in hydraulic load, and the optimal hydraulic load range is between 5 and 10 cm/d.
- (4) The addition of biochar aids the removal of pollutants in wetlands. The coconut shell- and shell-constructed wetlands with the highest proportion of biochar in the matrix have the best removal effects on pollutants. Adding biochar to the lower layer of the wetland matrix also improves the removal rate of COD.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/2073-441/13/7/893/s1>, Table S1: Concentration of influent pollutants of first hydraulic retention time test (mg/L), Table S2: Concentration of influent pollutants of second hydraulic retention time test (mg/L), Table S3: Concentration of influent pollutants of the first hydraulic load test (mg/L), Table S4: Concentration of influent pollutants of the second hydraulic load test (mg/L), Table S5: Concentration of pollutants of outflow of first hydraulic retention time test (mg/L), Table S6: Concentration of pollutants of outflow of second hydraulic retention time test (mg/L), Table S7: Concentration of pollutants of outflow of the first hydraulic load test (mg/L), Table S8: Concentration of pollutants of outflow of the second hydraulic load test (mg/L), Table S9: The mean and the standard deviation

of removal rate of COD of hydraulic retention time test (%), Table S10: The mean and the standard deviation of removal rate of NH<sub>3</sub>-H of hydraulic retention time test (%), Table S11: The mean and the standard deviation of removal rate of TN of hydraulic retention time test (%), Table S12: The mean and the standard deviation of removal rate of TP of hydraulic retention time test (%), Table S13: The mean and the standard deviation of removal rate of COD of hydraulic load test (%), Table S14: The mean and the standard deviation of removal rate of NH<sub>3</sub>-H of hydraulic load test (%), Table S15: The mean and the standard deviation of removal rate of TN of hydraulic load test (%), Table S16: The mean and the standard deviation of removal rate of TP of hydraulic load test (%).

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