A Study on the Effect of the Modified Bioretention Pond to Remove Nitrogen Pollution from Rainwater Runoff

Peiqiang Li¹, Youyuan Chen¹,²,³*, Ping Sun¹, Xinyue Zhao¹ and Jie Li¹

¹College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China
²Key Laboratory of Marine Environment and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China
³Shandong Provincial Key Laboratory of Marine Environment and Geological Engineering; Ocean University of China, Qingdao 266100, China

*Corresponding author’s e-mail: youyuan@ouc.edu.cn

Abstract. The bioretention pond plays an important role in controlling stormwater runoff pollution. However, the removal efficiency of the traditional bioretention pond is unstable. In this study, we used NaOH (2 mol·L⁻¹) to modify Enteromorpha prolifera biochar (BC), preparing alkali-modified biochar (KBC). We tried to study the removal capacity of biochar as a kind of bioretention filter and optimization of operating conditions of the bioretention pond. The results showed that: (1) When modified biochar was used as the filler medium, the maximum removal rate of TN, NH₄⁺-N, NO₃⁻-N, NO₂⁻-N in effluent were 59.1%, 79.0%, 54.3%, and 76.7%, respectively; In short, the average removal rate of experimental columns added with primitive biochar increased by 1%-12%. (2) The hydraulic retention time and setting of the saturation region had a clear influence on removing nitrogen from rainwater runoff in the bioretention pond. When TL=2 h, DS=10 cm, the average removal rates of NH₄⁺-N, NO₃⁻-N, NO₂⁻-N in effluent reached 80%, 60%, and 70%, respectively.

1. Introduction
With the rapid process of urbanization, a large number of impervious surface is increasing. Rainfall runoff carries many pollutants into the city’s water system and drainage network, leading to serious pollution. As one of the “sponge” facility, the bioretention pond is mainly composed of the covering layer, planting soil layer, filler layer, gravel layer and drainage pipe [1]. According to research, the average removal efficiency of COD in bioretention ponds can reach 60%, however, the efficiency of N is uncertain [2]. In the bioretention pond, it is significant to study the improvement of fillers to remove nitrogen effectively [3]. Biochar is solid product carbonized by pyrolysis of biomass under anoxic conditions [4]. It has high cation exchange capacity, rich pore structure and large specific surface area [5]. In recent years, many research has focused on biochar as filler medium in bioretention ponds [6]. Ashoori conducted a series of column tests to simulate the pollutant removal in rainstorm runoff. The column packing was filled with wood chip biochar prepared at 520 °C. The results showed that TSS and NO₃⁻-N in effluent were reduced by 86% [7].

Enteromorpha prolifera is a common kind of seaweed in Qingdao sea area. The effect of Enteromorpha prolifera biochar, used as filler medium in the bioretention ponds to remove nitrogen from rainwater runoff, is yet unknown The purpose of this study is to explore the efficiency of primitive
and modified biochar, and clarify the effect of operating conditions of the bioretention pond in removing nitrogen. We try to provide a theoretical basis for bioretention filter research.

2. Materials and methods

2.1 Preparation of Enteromorpha prolifera biochar

We took an appropriate amount of Enteromorpha prolifera powder in the crucible, placed it in a precise temperature-controlled muffle furnace, and raised it to 400 °C at 4 °C·min⁻¹. After remaining constant temperature for 2 h and cooling down, we took it out to get primitive biochar (BC). Then, we put 30.0 g BC into a conical flask, added 100 mL 2 mol·L⁻¹ NaOH solution. Next, using a magnetic stirrer to stir it at 125 r·min⁻¹ for 12 h. Immersing with deionized water, suction filtering and cleaning time and again, until the pH was stable. It was dried to constant weight at 70°C to obtain NaOH modified biochar (KBC).

2.2 Bioretention columns

The columns were labeled as No.1-No.4. The planting soil layer of 4 columns was humus + sand loam (5 cm). The No.1 had 96% gravel + 4% BC (w/w), no saturation region; No.2 had 96% gravel + 4% KBC, no saturation region; No.3 had 92% gravel + 8% KBC, no saturation region; No.4 had 92% gravel + 8% KBC, a saturation region (Figure 1). The thickness of the filler layer of 4 columns was 15 cm, the sand layer was separated by geotextile, and the gravel layer was filled with pebbles (10 cm).

2.3 Experimental water

Water used in this experiment was laboratory synthetic rainwater. It contained ammonium chloride, sodium nitrate and sodium nitrite to provide the required nitrogen source pollutants.

2.4 Experimental procedure

We carried out artificial rainwater of corresponding pollutant concentration and collected it in a water bucket. Connecting the lift pump and the water pipe at the same time. Then, we turned on the water pump. When the bioretention column drainage pipe had a stable outflow, starting the time and sampling. We took sample every 10 min for the first 20 min, every 20 min between 20 and 60 min, then every 30 min until the end of outflow. The water sample was stored in a 100mL polyethylene bottle, and the corresponding pollutant concentration was determined within 24 hours. The national standard analysis methods were adopted [8]. The measurement methods of the water quality index and model of the equipment used are shown in table 1.

| Test items | Analytical method                          | Instrument model                  |
|------------|-------------------------------------------|-----------------------------------|
| TN         | Potassium persulfate ultraviolet spectrophotometry | TU-1810 UV-Vis Spectrophotometere |
| NH₄⁺-N     | Nessler’s reagent spectrophotometer        | TU-1810 UV-Vis Spectrophotometere |
2.5 Evaluation method of removal efficiency

The calculation formula of the removal rate (R) of pollutant concentration in the bioretention pond is [9]:

\[ R = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \]  

In the formula, \( C_{in} \) is the influent pollutant concentration (mg·L\(^{-1}\)), \( C_{out} \) is the effluent pollutant concentration (mg·L\(^{-1}\)).

3. Results and discussion

3.1 Study on nitrogen removal effect of biochar with different proportions

As shown in Figure 2, the total nitrogen concentration in the effluent of the No.1 column of the experiment reached the maximum value at about 40 min, about 7.5 mg·L\(^{-1}\), and then quickly dropped to about 3.4 mg·L\(^{-1}\). Besides, the concentration of nitrogen pollutants in No.2 column increased earlier than that in No.1 column, indicating that filling KBC promoted the removal of nitrogen pollutants, especially the adsorption of NH\(_4^+\)-N. Compared with No.1 column, the average removal rates of TN, NH\(_4^+\)-N, NO\(_3^−\)-N, and NO\(_2^−\)-N in No.2 column effluent reached 57.6%, 78.0%, 57.5%, and 72.0%, respectively.

Compared with the experimental No.2 column, the total nitrogen concentration in the effluent of the No.3 column reached its maximum value at 40 min, about 5.54 mg·L\(^{-1}\), and then quickly dropped to about 3.18 mg·L\(^{-1}\). The ammonia nitrogen concentration in the effluent reaches a maximum of 2.98 mg·L\(^{-1}\) in 20 minutes, and then slowly and steadily decreases until it reaches about 1.7 mg·L\(^{-1}\). In No.3 column, the average removal rate of TN, NH\(_4^+\)-N, NO\(_3^−\)-N, NO\(_2^−\)-N in effluent reached 59.1%, 79.0%, 54.3%, and 76.7%, respectively. Therefore, the filling of alkali-modified biochar in the experimental column can obviously promote the removal of nitrogen pollutants in the bioretention pond.
3.2 The effect of operating conditions of bioretention pond on nitrogen removal efficiency

3.2.1 Different hydraulic retention time

As shown in Figure 3, when the retention time was 1 h, the removal efficiency of the biological retention column for TN and NO\textsubscript{2}--N deteriorates with time, and the removal rate was 15%~45%, 45~71%, respectively. When the residence time was 2 h, the removal efficiency of TN, NH\textsubscript{4}+-N, NO\textsubscript{2}--N were 23%~46%, 57~76%, 44~72%, respectively. It can be seen that with the residence time increasing, the removal efficiency of nitrogen increased. The reason may be that when the residence time increases, the bioretention pond nitrification and denitrification bacteria contact with nitrogen pollutants for longer time [10].

3.2.2 Different depths of saturation

As shown in Figure 4, the setting of the saturation origin obviously promoted the removal efficiency of NH\textsubscript{4}+-N and NO\textsubscript{2}--N. When the depth of the saturation origin was 5 cm, the rate of NH\textsubscript{4}+-N and NO\textsubscript{2}--N reached 70%~80%, 58~72%, respectively. When the depth of the saturation origin was 10 cm, the removal rate reached 72%~86%, 55~72%, respectively. Because the saturation condition provided a good anaerobic environment for denitrification, which was conducive to the growth of denitrifying bacteria.
bacteria, and biochar can also provide electrons for anaerobic denitrification.

![Figure 4. Effect of different saturation origin depths on nitrogen removal efficiency. (a)D_3=5 cm, (b)D_3=10 cm.]

4. Conclusions  
The primitive and modified *Enteromorpha prolifera* biochar can be used as the filler medium in the biological retention, and the removal effect of the biological retention on the nitrogen pollutants in the runoff of rainwater was promoted through the functions of filtration and adsorption. Optimizing the operating conditions of bioretention pond can effectively enhance the removal of nitrogen pollutants from stormwater runoff. When T_L=2 h, D_S=10 cm, the average removal rates of NH_4^+-N, NO_3^-N, NO_2^-N in effluent reached 80%, 60%, and 70%, respectively.

Acknowledgments  
Thanks to the Shandong Key Laboratory of Marine Environmental Geology Engineering and Ecology of the Ministry of Ocean University of China for supporting this research. Others who provided assistance in the sampling and experiments, thank you here!

References  
[1] Du, X.L., Han, Q., Yu, Z.Y., (2017) Analysis of some problems in the application of biological retention facilities in the construction of sponge cities. Water Supply and Drainage., 43: 54-58.  
[2] Le, W.C., Huang Q.S., You C.Y. (2018) Simulation and impact study on the effect of biological retention ponds in the southern red soil area. Environmental Engineering., 36: 28-33.  
[3] Qiu, F.G., Wang, K., Yu, D., (2018) Research on zeolite-modified rainwater biological retention system to remove pollutants. Environmental Science and Technology., 41: 124-129.  
[4] Ronsse, F., Van, Hecke. S., Dickinson, D., (2013) Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis condition. Global Change Biology Bioenergy., 5: 104-115.  
[5] Fu, P., Song, X., Xiang, J., (2019) Effects of pyrolysis temperature on characteristics of porosity in biomass chars. Energy and Environment Technology., 1: 109-112.  
[6] Zhao, Q., Xu, S.R., Zhou, Y.C., (2019) Experimental Study on Nitrogen Removal in Bioretention System Improved by Biomass Carbon. China Water Supply and Drainage., 35: 104-109.  
[7] Ashoori, N., Teixido, M., Spahr, S., (2019) Evaluation of Pilot-Scale Biochar-Amended Woodchip Bioreactors to Remove Nitratre, Metals, and Trace Organic Contaminants From Urban Stormwater Runoff. Water Research., 154: 1-11.  
[8] Liu, X.M., (1993) Discussion on "Water and Wastewater Monitoring and Analysis Methods". China Environmental Monitoring., (1): 65-66.
[9] Zhang, R., Li, Y.G., Liu, Z.C., (2017) Effects of plants and water storage areas on the decontamination effect of southern biological retention tanks. Environmental Engineering., 8: 33-45.

[10] Zhang, C.L., Li, B., Hou, Y.R., (2019) Screening and characterization of nitrifying and denitrifying bacteria in a composite vertical subsurface flow constructed wetland. Journal of Southern Agriculture., 50: 66-74.