Enhance nitrogen removal in bioretention cells with addition of hydrothermal pre-treated pine barks as external carbon source

Jing Tuo (✉ tjyx914@163.com)

Nanjing Forestry University <https://orcid.org/0000-0003-2338-381X>

Shiwei Cao

Nanjing Forestry University

Muzi Li

Nanjing Forestry University

Rong Guo

Nanjing Forestry University

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Abstract

The problem of poor carbon source is a common factor limiting the nutrients removal in bioretention cells (BRCs). This study aimed to investigate the feasibility of using modified biomass in BRCs filled with a mixture of fly ash ceramsite and pumice fillers to enhance nitrogen removal. Different pretreatment methods (hydrothermal-treated, acid-treated and alkali-treated) were attempted, and hydrothermal pretreatment showed a best performance in carbon release ability. The scanning electron microscopy showed that the lignin in hydrothermal pretreated pine barks (H-PBs) was destroyed, and the fiber structure became thinner with more irregular folds, which improved the accessibility of cellulose and attachment of microorganisms. The addition of H-PBs significantly enhanced the nutrients removal in BRCs, and the removal rates of TN and NO_3^- -N increased by 23.25% and 38.22% compared with those in BRC-A (without external carbon source), but the removal rate of NH_4^+ -N was inferior to BRC-A. Besides, the large carbon release amount of H-PBs did not deteriorate the effluent quality, with COD removal rate of 87.98% in the 48 d. These results indicate that the BRCs by adding H-PBs could intensify the denitrification process.

1. Introduction

The nitrogen removal performance of bioretention basins is variable, especially for NO_3^- -N, owing to the lack of carbon source and anaerobic conditions (Zhang et al., 2021). The application of natural materials (sawdust, wood bark, straw, calamus and other agricultural waste products) for an additional carbon source to solve the carbon shortage in bioretention cells (BRCs) for rainwater with a low C/N (COD/nitrogen ratio) is well-known (Wang et al., 2021). One of the promising biomass carbon source is pine bark (PB) representing wastes of timber harvesting and timber processing. It's because of the large-yield and easy availability of PB that its comprehensive utilization has received much attention. It can be used in many areas, for example, it is now widely used in landscaping, environmental protection, agricultural planting and other fields. Also, it can be used as biological filter material because of its high porosity, which has good adsorption, water retention and microbial carrying benefits in biological treatment systems. At the same time, PB has stable physical and chemical characteristics, containing large quantities of N, P, K, Ca, Mg and other elements (Augoustides et al., 2021). In addition, PB, as a lignocellulosic material, can be decomposed into glucose and oligosaccharides by microorganisms, and its high organic matter content makes it a novel denitrifying carbon source. Biomass carbon source such as PBs are cheaper and environmentally friendly compared with traditional carbon source (Luo et al., 2018). Due to secondary pollution, lignin encapsulation and instability of release (Hu et al., 2019), many researches have explored the influence of carbon source modification or pretreatment on denitrification performance. Different pretreatment methods lead to different degrees of damage to plant structure, as well as different carbon release patterns and total amounts. Pretreatment of lignocellulosic biomass is a prerequisite step for biological conversion because of the structural complexity of cellulose, hemicellulose and lignin, limited degradability of lignin and formation of inhibitory products during microbial fermentation. Therefore, the selection of appropriate pretreatment methods is of great

significance to improve the availability of biomass carbon source. The most common ones are the shearing, grinding, ultrasonic treatment, acid treatment, alkali treatment and hydrothermal treatment of the carbon source. In liquid hot water pretreatment, water in the liquid phase at high temperature and pressure was used to breakdown the celluloses and hemicelluloses structure that was bound by lignin. For most BRCs, the carbon source cannot be guaranteed, so many researchers have added biomass such as agricultural wastes for BRCs and achieved good nitrogen removal. Zhu et al. (2021) found that denitrifications and organic-degrading bacterial were enriched after the addition of rotten fruits as external carbon source. Zhong et al. (2019) explored the feasibility of using microalgae biomass to enhance the denitrification rate and found that nitrate removal and total nitrogen removal were improved by 27.9% and 17.7%, respectively. Saliling et al. (2007) evaluated wood chips and wheat straw as substrates for denitrification process and it showed that both wood chips and wheat straw produced comparable denitrification rate. However, research on PBs as the BRCs carbon source is limited, lacking the effects of carbon release and nitrogen removal of PBs, especially for the pre-treated PBs. PB, as a kind of agricultural waste, has a large yield. If it can be pretreated effectively, it will be an effective and cheap denitrification carbon source.

Traditional BRCs usually use a mixture of local soil, quartz sand, and other pretreated materials as substrates (Luo et al., 2020b). In order to improve the combination of fillers in BRCs, Fly ash ceramsite (FC) and Pumice (PC) were chosen as substrates in this experiment. FC has the advantages of large specific surface area, high porosity, good impact load resistance, and stable chemical properties (Qin et al., 2015). Moreover, it is a cheap adsorbent as it has strong adsorption in the presence of active sites such as aluminum and silicon oxides and is easy to regenerate (Cheng et al., 2018). PC is a kind of good microbial carrier material because of its high porosity, and it is also widely used in water treatment (Rashad et al., 2019).

In this study, PBs were selected as an external carbon source through experiments, and hydrothermal pretreated pine barks (H-PBs) were prepared to solve the carbon shortage in BRCs. The main objectives of this study are to (a) compare pretreatment conditions and analyze pretreatment mechanism of PBs;(b) study the feasibility of utilizing H-PBs as external carbon source to enhance denitrification process in BRCs. Therefore, this study will be helpful for the practical application of PBs in nitrogen removal intensification of BRCs.

2. Materials And Methods

2.1 Agricultural material

The PBs were collected in the field of Jiangsu Province, China. They were washed with ultrapure water, air-dried at room temperature and cut into 2 cm pieces. Then, the PBs were dried in the oven at 105°C (GZX-9140MBE, Shanghai, China) to a constant weight. Finally, the prepared PBs were stored in a dryer until used.

2.2 Experimental design

2.2.1 Optimization of pretreatment conditions

Different pretreatment conditions of PBs carbon source were compared in the leaching experiments. Firstly, 10 g PBs were added to the 250 mL Erlenmeyer flasks with 100 ml ultrapure water, 100 mL 1% H₂SO₄ and 100 mL 2% NaOH, respectively. The carbon sources for study were untreated, hydrothermal-treated, acid-treated and alkali-treated PBs. To obtain H-PBs, PBs were treated in an autoclave at 140 °C for 1 h. To obtain acid-treated and alkali-treated PBs, PBs were treated in 100 mL 1% H₂SO₄ and 100 mL 2% NaOH respectively at 25 °C for 1 h. Then, 2.5 g different pre-treated PBs after washing with ultrapure water and air-dried were added to 250 mL Erlenmeyer flasks with 200 mL ultrapure water respectively. Finally, leachate of pretreated PBs in the flasks were detected at 24, 48, 96, 150, 240, 264, 360, 720 h, soluble and insoluble COD contents in the leachate were measured.

2.2.2 Characteristic analysis

PBs and H-PBs were subjected to the leaching experiment (Tao et al., 2021) according to the methods in the previous section. The lignocellulose composition of PBs before and after pretreatment was analyzed by Van Soest (Van Soest et al., 1991). The surface morphology of PB samples were assessed by scanning electron microscopy (SEM, Ultra 55, Zeiss, Oberkochen, Germany). Each dried sample before and after pretreatment were sliced, fixed and gold-sputtered before observation. Moreover, for kinetic study, 2.5 g H-PBs were added to 250 mL Erlenmeyer flasks with 200 mL ultrapure water. Then, leachate in the flasks was taken on 24, 48, 96, 150, 240, 264, 360, 720 h. Finally, soluble COD contents in the leachate were measured and Ritger-Peppas equation (Ritger and Peppas., 1987) was employed to simulate the release behavior of H-PBs as follows:

$$\frac{M_t}{M_\infty} = a * t^n \quad (1)$$

Where t is carbon release time; a is release rate constant; n is release exponent; M_t and M_∞ show amounts of soluble COD at time t and after infinite time, respectively.

2.3 Design and operation of experimental BRCs

Three lab-scale BRCs (BRC-A, BRC-B, BRC-C) were established in the laboratory at Nanjing Forestry University in Nanjing, China (Fig. 1). Each system was composed of a 9 cm-pumice layer and a 30 cm-ceramsite layer. Specific information of fillers was shown in Table 1. There was a 6 cm-H-PBs covering for BRC-C, a 6 cm-untreated PBs covering for BRC-B and no covering for BRC-A. The diameter and height of each device was: 0.1m×0.7m, planted with *Cyperus alternifolius* L. The detailed information of simulated rainwater could be found in Table 2. The rainfall intensity with rainfall return period of 5 years and rainfall duration of 120 min was calculated, and the total catchment area and integrated runoff coefficient were used to calculate influent area. The experiment used submersible pumps to enter the simulated rainwater, and the hydraulic retention time of each device was 1 d.

2.4 Water Quality Analysis

The effluents and influent were taken after 1 d. The water quality of each device were analyzed, including TN, NO_3^- -N, NH_4^+ -N and COD, according to the standard methods (APHA, 2012). NH_4^+ -N, NO_3^- -N and TN were detected by a UV spectrophotometer (Shimadzu UV-2600, Japan), and the determination of COD was performed using the Potassium dichromate rapid method. Furthermore, TN, NO_3^- -N, NH_4^+ -N and COD removal rate (R , %) were calculated by using Eq. (2):

$$R = \frac{C_i - C_0}{C_i} \times 100\% \quad (2)$$

Where C_i and C_0 are the TN/ NO_3^- -N/ NH_4^+ -N/COD concentration of the influent and effluent, respectively.

3. Results And Discussion

3.1 Comparison of pretreatment conditions

In this study, four kinds of pretreated PBs (untreated, hydrothermal-treated, acid-treated and alkali-treated) were compared and their release of COD were analyzed. The specific experimental results were shown in Fig. 2. The COD release amount of H-PBs was significantly greater than that of the others, with the total COD reaching to 213.24 mg/g and the soluble COD reaching to 188.16 mg/g within 24 h. While the COD release amount of acid-treated PBs was lower than that of untreated PBs, and the COD release of acid-treated PBs was only half of that of untreated PBs at the end of the experiment. After 5 d, the COD release rate of PBs was accelerated. The total COD release of hydrothermal treatment was the highest with concentration of total COD and soluble COD as high as 716.27 mg/g and 505.25 mg/g on the 30th day, while the total COD release of alkali treatment, untreated treatment and acid treatment was 490.68 mg/g, 457.64 mg/g and 272.13 mg/g, and the soluble COD was 378.96 mg/g, 335.48mg/g and 192.81mg/g, respectively. After hydrothermal treatment, the soluble COD released from PBs accounted for about 70% of the total COD release, which is an effective carbon source that can be utilized in the initial rainwater runoff denitrification. Many researches found the hydrothermal treatment can destroy the structure of lignocellulosic biomass and dissolve the hemicelluloses contents, thus exposing the cellulose surface and increasing enzyme accessibility to the cellulose microfibrils (Jeong et al., 2020). Alkali treatment were found to cause swelling, resulting in a decrease in the degree of polymerization (Li et al., 2021) and an increase in internal surface area, which is beneficial to the continuous carbon release of PBs. While Selig et al. (2007) found droplets composing of lignins and possible lignin-carbohydrate complexes were formed on the surface of residual corn stover following acid pretreatment, and these droplets were shown to have a negative effect on the enzymatic saccharification of the substrate, which can account for the low COD release of acid treatment.

It showed that hydrothermal pretreatment could significantly improve the carbon release of PBs comparing the proper 4 pretreatment methods. Also, hydrothermal treatment is an ideal pretreatment method for biomass carbon sources which is more environmental friendly than alkali and acid treatment.

3.2 Characteristics of PBs

3.2.1 Effect of hydrothermal pretreatment on fiber composition

Table 2 showed the changes in cellulose composition of PBs before and after hydrothermal pretreatment in this study. It could be seen that hydrothermal treatment increased the content of cellulose in PBs, and decreased the content of hemicellulose, hot water soluble matter, ash and lignin. The results were consistent with other studies, as Xia et al. (2020) found the hemicellulose and some lignin fractions were solubilized as the hydrolysate after liquid hot water pretreatment. Hydrothermal pretreatment can greatly denature the lignocellulosic structure and enhance the fermentable sugar recovery. Furthermore, they also soften the lignin, which acts as a binder during biomass densification (Sarker et al., 2021). Thus the hemicellulose and lignin of PBs will decrease to a certain extent after hydrothermal pretreatment, and the increase of cellulose can provide enough carbon source for denitrification process and improve the nitrogen removal rate.

3.2.2 Effect of hydrothermal pretreatment on microstructure of PB

The surface slices and cross-section slices at $\times 100$ magnification of SEM analysis before and after pretreatment are shown in Fig. 3. Untreated PBs have natural mulch on the surface, usually covered with more non-fibrous impurities such as waxy layer, ash, parenchyma cells and adhesives (Yu et al., 2016). After pretreatment, the covering on the surface of PBs were destroyed which mainly caused by the removal of impurities on the surface of fibrocells. At the same time, the internal fracture occurred, the fiber structure became thinner with more irregular folds. The main reason for the change was that hydrothermal treatment destroyed the wrapping of cellulose and hemicellulose by lignin, decreasing the strength of the fiber structure. Removal and redistribution of lignin led to an increase in pore volume and improved the accessibility of cellulose (Liao et al., 2020). Also, the fiber structure became clearer, and more fiber texture was exposed on the cell surface, which probably led to a higher surface area of the substrate and increased the living and attachment space of microorganisms. Similarly, Lee et al. (2020) showed a higher biodegradability of hydrothermally-pretreated sunflower residues compared to the untreated feedstock.

3.2.3 Kinetics of carbon release of H-PBs

As can be seen from Fig. 4, the release of dissolved COD of PBs presented a certain regularity after hydrothermally treatment. The H-PBs showed a sustained COD release time and large release amount. In the initial 24 h, the carbon release amount reached 188.16 mg/g, and the carbon release rate increased at a high level for 30 days, reaching to 505.25 mg/g at 30 d, which was about three times of the initial release amount. Tao et al. (2021) explored the dynamics of carbon release from corncob and found the release of COD increased rapidly on the first day and then tended to stabilize. Zheng et al. (2021) also

found the release of COD reached the highest on the first day and finally remained stable. The reason for the higher release of COD at the beginning of the experiment was due to the fast decomposition of small molecular substances attached to the surface of corncob and the release of soluble carbon from the plants (Liu et al., 2018). With the extension of the release time, the inside organics of PBs were further decomposed and released and the COD concentration in the aqueous solution mainly came from the hydrolysis of the cellulose material. The PBs can still release carbon source steadily at 30 d as hydrothermal treatment opened the PBs fiber structure and improved its biological availability, which can provide sufficient carbon source for denitrification reaction.

The carbon release process of H-PBs fitted the Ritger-Peppas release equation (Fig. 4) best with correlation coefficient (R^2) of 0.97. Ritger et al. (1987) found that the carbon release was mainly the diffusion process when $n < 0.45$ in the equation, anomalous (non-Fickian) transport when $0.45 < n < 0.85$ and case II transport when $n \geq 0.85$. In this carbon release fitting curve, $n = 0.34 < 0.45$ ($M_t/M_\infty = 54.14 \cdot t^{0.34}$), suggesting the carbon release from H-PBs occurred as a process of Fickian diffusion. Li et al. (2020) found spinosad/chitosan formulation displayed a long sustained-release time (> 18 d) and high cumulative release ($> 80\%$) with release dynamics fitting Fickian diffusion mechanism of Ritger-Peppas model. And Tan et al. (2021) also found materials with controlled release properties (obey the Fick's Laws of diffusion) showed more sustainable and effective activity. The fitted equation indicated H-PBs were suitable as a biomass carbon source for denitrification.

3.3 Performance of H-PBs as a carbon source in BRCs

The shortage of carbon is one of the limiting factors for the denitrification in BRCs. In order to solve the problem of unstable removal of NO_3^- -N and TN in the BRCs, this experiment used PB as an external carbon source to strengthen the nitrogen removal rate of the BRCs. To determine the effect of H-PBs and PBs, the investigation on the denitrification performance was conducted with three devices (BRC-A, BRC-B, and BRC-C) with different conditions. The variations of NO_3^- -N, NH_4^+ -N, TN and COD were shown in Fig. 5.

3.3.1 NO_3^- -N, NH_4^+ -N and TN removal rate in BRCs

Figure 5a showed the impact of H-PBs on NO_3^- -N removal in BRCs. NO_3^- -N removal rate gradually increased with the operation of the system. In the initial stage of operation, the concentration of NO_3^- -N in effluent was higher than that in influent, and the removal rate was in a negative state (0–10 d), but the removal rate gradually became higher in the later stage (10–20 d). There were probably several reasons accounting for this: One possible explanation is that the number of denitrifying bacteria in the device was small and the denitrifying was not obvious in the initial stage of operation. Furthermore, the system has not set up a saturated zone at the bottom of device, which cannot provide strict anoxic area for denitrifying bacteria to carry out denitrification. In addition, the removal of NO_3^- -N by microorganisms requires sufficient hydraulic retention time (Kavehei et al., 2021), while the permeability coefficient of FC

and PC is high, thus the retention time of rainwater in the system is not enough. On the other hand, $\text{NH}_4^+\text{-N}$ is converted to $\text{NO}_3^-\text{-N}$ by nitrifying bacteria, resulting in accumulation of $\text{NO}_3^-\text{-N}$ in the system. In addition, the filler itself contains $\text{NO}_3^-\text{-N}$, which is washed down during the influent process of the BRCs to make the effluent $\text{NO}_3^-\text{-N}$ concentration even higher than the influent concentration. The $\text{NO}_3^-\text{-N}$ removal rate of the BRC-C with H-PBs was always highest than that of the other two groups, followed by the BRC-B, and the lowest in the BRC-A. The removal rate of $\text{NO}_3^-\text{-N}$ in the BRC-C was always positive after the 6th day. At the end of the experiment, the removal rate increased from -20.8% in the initial stage to 58.22%, while the removal rate of the other two groups was basically negative in the first 35 d. As we all know, a combination of organic carbon source availability, NO_3^- availability and anaerobic soils, are required for effective denitrification (Gold et al., 2018). PBs after hydrothermal treatment continued to release carbon source and released a large amount. In BRC-C, H-PBs provided sufficient and lasting carbon source for the denitrifying bacteria in the device, so that the denitrification process could proceed normally. On the other hand, after hydrothermal treatment, the specific surface area and the internal pores of PBs increased, enhancing the $\text{NO}_3^-\text{-N}$ adsorption capacity. Moreover, the addition of PBs contributed to the establishment of microbial community as denitrification is a reaction process dominated by microorganisms, in which functional microorganisms play a vital role (Wang et al., 2021). Meanwhile, the electron transfer process plays an essential role in the denitrification process, and H-PBs, as the lignocellulosic materials, can provide electron donors for denitrification (Wang et al., 2016).

Figure 5b showed the impact of H-PBs on $\text{NH}_4^+\text{-N}$ removal in BRCs. The removal rates of BRCs for $\text{NH}_4^+\text{-N}$ were not stable. The removal rates of the three groups of devices varied from 55–85%. At the beginning of operation of the device, the removal rate of the BRC-A was as high as 90.38%, that of the BRC-B was 85.17%, and that of the BRC-C was 82.16%, all of which were at high $\text{NH}_4^+\text{-N}$ removal rates. Electrostatic adsorption is the main mechanism for removing $\text{NH}_4^+\text{-N}$ (Cheng et al., 2019). Dong et al. (2020) studied the effect of ceramsite on organic wastewater treatment and found the removal rate of $\text{NH}_4^+\text{-N}$ could reach to 85%. Wan et al. (2017) proposed that P and Mg on the surface of substrates could react with NH_4^+ , and the $\text{NH}_4^+\text{-N}$ adsorption capacity could be enhanced by the struvite ($\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$) formed. It suggested that the high removal rate of $\text{NH}_4^+\text{-N}$ in the earlier stage may be due to the larger specific surface area, strong adsorption effect and P, Mg contents of ceramsite. However, with the operation of the device, the removal rate of $\text{NH}_4^+\text{-N}$ gradually decreased. The removal rates of BRC-A, BRC-B and BRC-C were 62.02%, 62.60% and 61.93% in 48 d, respectively, which decreased by 28.36%, 22.57% and 20.23% compared with the initial stage (0–5 d). The adsorption sites of each layer of materials gradually became saturated with the increase of the operation time of the device, leading to the desorption of $\text{NH}_4^+\text{-N}$ in the process of rainfall. Since DO concentration above 1.5 mg/L is essential for nitrification (Hu et al., 2014). $\text{NH}_4^+\text{-N}$ can be converted to $\text{NO}_3^-\text{-N}$ by nitrification under aerobic conditions. The anoxic environment caused by the cover of PBs inhibited the growth and reproduction of nitrification bacteria, resulting in the lower $\text{NH}_4^+\text{-N}$ removal rate of BRC-B and BRC-C than that of BRC-A. At the same time, the water film layer

formed in the PBs during the infiltration of rainwater also greatly improved the possibility of anaerobic environment. In addition, with the extension of the system operation time, the deposition of suspended particles, the propagation of microorganisms and the development of plant roots led to the decrease of matrix porosity, system blockage and internal environment hypoxia, inhibiting the transformation of $\text{NH}_4^+\text{-N}$ into $\text{NO}_3^-\text{-N}$, which was also one of the reasons for the gradual decline of $\text{NH}_4^+\text{-N}$ removal rate. Also, large amounts of O_2 were consumed by the increasing heterotrophic microorganisms and resulted in the inhibition of growth-rate and biological-activity of ammonifying bacteria and nitrifying bacteria as H-PBs released large amount of COD (Zou et al., 2012), Zhang et al. (2019) also found that the removal for $\text{NH}_4^+\text{-N}$ of wetlands adding no biomass substrate were slightly better than other wetlands with biomass substrate. To a certain extent, this can account for the reason why the $\text{NH}_4^+\text{-N}$ removal rate of BRC-C was always the lowest among three devices. The removal rate of $\text{NH}_4^+\text{-N}$ decreased greatly after 35 d. In practical engineering, the soil can be loosened at 35 d to reduce the possibility of anoxic environment and improve the nitrogen removal performance of the system.

Figure 5c. showed the impact of H-PBs on TN removal in BRCs. Under the conditions of artificial simulated rainfall, the influent concentration was 12 mg/L on average. The effluent concentration of TN of the three groups (BRC-A, BRC-B, BRC-C) were 7.91 mg/L, 5.33 mg/L and 5.00 mg/L in 48 d operation of the device, respectively, and the removal rates were 34.08%, 55.58% and 58.33%, respectively. During the operation of the system, the TN removal rate of the three groups of devices increased continuously and gradually tended to be stable. It was worth noting that TN removal rate was improved obviously after adding H-PBs, which is similar to the research of Zhao et al. (2019) The study found that the average TN removal rates of CWs with modified canna leaves, modified rice straw, and modified peanut shells were 59.5%, 60.3%, and 61.4%, respectively, which correspondingly increased 17.1–19.0% compared with the control check. Luo et al. (2018) studied the effect of carbon source on nitrogen transformation process and indicated that CWs with husk rice achieved higher removal rate for TN (73–87%) than that of control group. The addition of PBs can improve the TN removal rate because the denitrification process is often inhibited by insufficient carbon sources and lack of anoxic environment. On the one hand, PBs can be used as an organic carbon source to promote the denitrification, On the other hand, an anaerobic environment may form inside the PBs, leading to denitrification. The results indicated that the addition of PBs could improve the denitrification rate and change the nitrification and denitrification capacity of the substrate.

3.3.2 COD removal rate in BRCs

Figure 5d. showed the impact of H-PBs on COD removal in BRCs. Under the conditions of artificial simulated rainfall, the influent concentration was 30 mg/L on average, and the effluent COD concentration was kept below 7 mg/L, leading no effluent water quality deterioration. The COD removal rates of BRC-A and BRC-B showed no significant difference and remained at a high level of about 85%. The BRC-C was in a state of low removal rate at the initial stage, but increased rapidly at the later stage, reaching to 87.98% at 48 d. The reduction of COD in BRCs mainly depends on the decomposition and utilization of microorganisms. Therefore, the main reason accounting for the increase of COD removal

efficiency of the three groups in the later stage may be that the reproduction of microorganisms enhanced the assimilation of organic matter. However, the low COD removal rate in the BRC-C at the early stage is related to the large amount of carbon released from the PBs at the early stage after the hydrothermal treatment, increasing the COD load of the system. With the operation of the device, the microorganisms in the system were multiplied, the denitrification of the BRC-C was continuously strengthened, with carbon source continuously being needed. So the COD released by the PBs was utilized and degraded, making the COD removal rate of the BRC-C show an increasing trend. The decreased COD was utilized by both denitrifying microbes and other heterotrophic bacteria (Li et al., 2019). Also, the removal rate of COD in BRC-C increased sharply in the initial stage (5–20 d) and then became stable, this result can be explained by rapid consumption of organics by aerobic microbes in the initial phase under conditions of adequate DO, followed by slow degradation in anaerobic phase (Ong et al., 2010).

4. Conclusions

The application of agricultural waste biomass in the advanced treatment of low C/N rainwater was evaluated in this study. The H-PBs had the highest unit carbon release, which was a suitable choice for carbon source pretreatment method. H-PBs were obtained in an autoclave at 140 °C for 1 h. Hydrothermal treatment can destroy the internal structure of lignin, dissolve lignin, and increase the relative content of cellulose and hemicellulose. Meanwhile, after hydrothermal modification, the internal fracture of PBs appeared, the fiber structure became thinner, and the specific surface area significantly increased, providing more space for microbial attachment and growth. Compared with other pretreatment methods, hydrothermal pretreatment was more environmentally friendly. With H-PBs added, TN and NO_3^- -N removal efficiency was improved by 24.25% and 38.22% compared with the BRC without external carbon source. However, the NH_4^+ -N removal rate of the system fluctuated greatly, ranging from 55%-85%, and the BRC-C was always at the lowest level among the three groups. In addition, the large carbon release amount of H-PBs in the early stage affected the COD removal rate, but did not deteriorate the effluent quality.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

Not applicable

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

Jing Tuo: conceptualization, methodology, dataacquisition, processing and analysis, write the original paper, review and revise the paper. Shiwei Cao: conceptualization, methodology, dataanalysis, funding acquisition, review and revise the paper, English language service. Muzi Li: methodology, dataacquisition, processing and analysis. Rong Guo: investigation, review and revise the paper. All authors have read and agreed to the published version of the manuscript.

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Tables

Table 2 Quality parameters of simulated rainwater

TP (mg/L)	NH ₄ ⁺ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	NO ₂ ⁻ -N (mg/L)	pH	COD (mg/L)
1.2±0.1	5.0±0.3	3±0.4	2±0.4	7.0±0.5	30±0.4

Table3 Comparison of lignocellulose

Pretreatment methods	Cellulose %	Hemicellulose %	Lignin %	Ash %	Hot water soluble matter %
Untreated	20.70	10.25	35.65	13.86	19.54
Hydrothermal-treated	42.63	2.01	29.29	9.92	16.15

Due to technical limitations, Table 1 is only available as a download in the Supplemental Files section.

Figures

Figure 1
Schematic diagram of experimental bioretention units

Figure 2

Total and Soluble COD released after pretreatment

Figure 3

Scanning electron micrograph (SEM) of PBs before (a, ×100) and after (b, ×100) hydrothermally pretreatment

Figure 4

Carbon release kinetics of H-PBs

Figure 5

Removal rates of (a) NO_3^- -N, (b) NH_4^+ -N, (c) TN and (d) COD in BRC-A, BRC-B and BRC-C

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table1.docx](#)