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Long term effect of biochar on the efficiency of subsurface flow wetland pollutant treatment

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ABSTRACT

Biochar is a product pyrolyzed from agricultural biomass waste and has been gradually applied to promote the pollutants removal efficiencies in constructed wetland (CW). To investigate the long-term effects of biochar on subsurface flow CW, different biochar doses (40%, 30%, 20%, 10%, and 0% v/v) were added to five constructed microcosm wetlands (named BW-40, BW-30, BW-20, BW-10, and CW-K), respectively. The results showed that the concentration of effluent dissolved oxygen (DO) was less than 0.5 mg L^{-1}, and there were no significant correlations between biochar addition and the effluent DO. Additionally, the effluent pH in BWs was almost decreased to 7.0 during the operation. However, the oxidation–reduction potential (ORP) and the conductivity (Cond) were found to be significantly increased and decreased with the increasing of biochar. After a long-term operation, the stable chemical oxygen demand removal rates, higher than 90%, were observed in all CWs, indicating no significant effects resulted from adding biochar. At the early operating stage, the ammonium (NH_4^+–N) removal showed a cascade increase with the increase of biochar, while the unremarkable differences were found among all CWs after a long run. However, the NH_4^+–N removal efficiency could be improved by adding massive biochar.

Keywords: Biochar; Subsurface flow constructed wetland; Organic matter removal; Nitrogen removal; Long-term

1. Introduction

Due to a strong purification ability, constructed wetland has been widely studied and applied [1]. In the traditional denitrification process, nitrogen removal is highly dependent on nitrification. But in the subsurface flow wetland, the nitrification process cannot be effectively carried out due to the restricted oxygen supply [2,3]. As a result, a low efficiency of denitrification in the subsurface flow wetland, limits the application of subsurface flow wetland [4]. The research on the packing medium selection has drawn great attention in constructed wetland system. Aunsary and Chen [5] reported that the subsurface flow constructed wetland with the upper layer of light filler and the lower layer of gravel could improve the nitrogen removal efficiency. Fogwe et al. [6] found that the constructed wetland with limestone, clay particles, and other active media could effectively improve the treatment effect.

Biochar is a kind of pyrolysis product of agricultural biomass waste, and with characteristics of large specific surface area, high porosity, strong stability, low cost, and no pollution. It plays the important role in regulating wetland oxygen environment and strengthening wetland denitrification [7]. The research on the application of biochar has drawn great attention in constructed wetland, however, the long-term operation effect of biochar constructed wetland remain unclear, which are very important for practical application.

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This research aims to provide scientific evidences for keeping efficient and stable operation in long-term operation. In this study, the system constructed with different biochar doses was constructed, and pollutants removal performance was investigated.

2. Materials and methods

2.1. Biochar subsurface flow constructed wetland set-up

The investigation was carried out using two identical CWs, with a diameter of 35 cm and a depth of 35 cm. The containers are made of cylindrical polyethylene. Five identical subsurface flow CWs packed with different biochar doses (40%, 30%, 20%, 10%, and 0% v/v) were constructed, respectively, and named BW-40, BW-30, BW-20, BW-10, and CW-K. A parallel reactor was set up for every group. The wetland reactor adopts the form of submerged wetland. The bottom part is filled with gravel (particle size is 1–2 cm), and the upper part is filled with biochar, made of the reed bamboo at 500°C, a length of 1–2 cm. A layer of approximately 3 cm crushed stones were laid on the surface to prevent the biochar filler from floating. The wetland reactors were filled with a height of 33 cm, and planted with *Acoruscalamus* L. The center of the CWs was set a perforated tube with a diameter of 3 cm, used for siphon drainage, sampling, and determination of various physical and chemical parameters. Ten identical CWs are shown in Fig. 1.

Synthetic wastewater was used in this research. The composition of the nutrients in the synthetic media fed to the ten reactors are the same as below (per liter): 390 mg $C_6H_{12}O_6$; 220 mg KNO_3; 75 mg NH_4Cl; 200 mg $NaHCO_3$; 11 mg KH_2PO_4; 18 mg $K_2HPO_4{\cdot}3H_2O$; 10 mg $MgSO_4{\cdot}7H_2O$; 10 mg $FeSO_4{\cdot}7H_2O$; 7.6 mg $CaCl_2$ and trace of 0.15 g H_3BO_3; 0.03 g $CuSO_4{\cdot}5H_2O$; 0.18 g KI; 0.12 g $MnCl_2{\cdot}4H_2O$; 0.06 g $Na_2MoO_4{\cdot}2H_2O$; 0.12 g $ZnSO_4{\cdot}7H_2O$; 0.15 g $CoCl_2{\cdot}6H_2O$; and 10 g EDTA-Na_2. The characteristics of the influents was shown in Table 1. The dissolved oxygen (DO) was controlled at 7.0 ± 0.5 mg L^{-1}, the retention time was 2 d, the treatment load kept 0.05 m^3 m^{-2} d^{-1}, the inflow loadings was 10 L, and the water level can be adjusted by the water level control valve at the top.

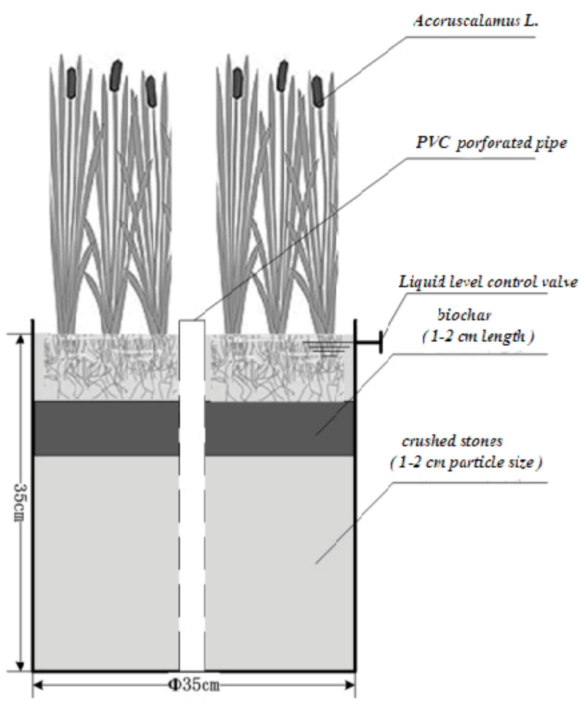

Fig. 1. Schematic diagram of the experimental systems.

2.2. Chemical analysis in the reactors

The chemical oxygen demand (COD), total nitrogen (TN), ammonium nitrogen (NH_4^+–N), nitrite nitrogen (NO_2^-–N), and nitrate nitrogen (NO_3^-–N) were determined according to the standard methods [8]. DO, pH, oxidation–reduction potential (ORP), and conductivity (Cond) were measured by a DO meter (YSI Pro ODO, U.S.A), a pH meter (PB-10, Germany), a ORP meter (YSI PH100, U.S.A), and a Cond meter (DDS-307, China), respectively.

2.3. Data analysis

The test data was compiled and mapped by Origin 8.5, and the data analysis was performed by PASW Statistics 18.0. All test data are expressed in terms of average plus or minus standard deviation. The correlation between subjects was analyzed by correlation and tested by Pearson (test levels include significant $p < 0.05$ and extremely significant $p < 0.01$). One-way ANOVA was used for the analysis of differences between subjects (test levels included significant $p < 0.05$ and extremely significant $p < 0.01$).

3. Results and discussion

3.1. DO, pH, ORP, and Cond

The DO, pH, ORP, and Cond, the factors of the microbial activity in reactors, would affect the removal efficiency of the reactors [9,10]. Fig. 2 summarizes DO, pH, ORP, and Cond in different CWs under different stages, Stage I(a) and Stage II(b). In the stage I, effluent DO concentrations of CWs were always below 0.5 mg L^{-1}. In stage II, effluent DO concentrations were below 0.2 mg L^{-1}. So, effluent DO concentrations of CWs in the stage II were lower than in the stage I, but they had no significant difference in the CWs ($p > 0.05$). Previous studies have shown the decomposition of organic matter increased for the mass multiplication after long-term operation, resulted in an increase in dissolved

Table 1
Characteristics of the influent

Parameter	Value
COD (mg L^{-1})	420
NH_3–N (mg L^{-1})	20
NO_3^-–N	30
TP (mg L^{-1})	5
pH	7.5 ± 0.3

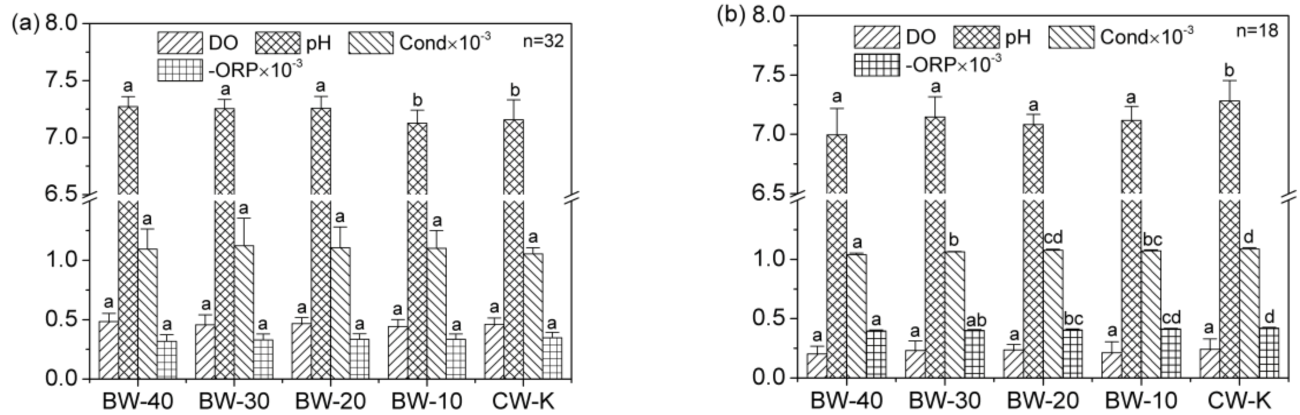

Fig. 2. DO, pH, ORP, and Cond in different CWs under different stages, stage I (a) and stage II (b).

oxygen [11–15]. A similar conclusion was obtained in this study. The pH decreased slightly, compared with initial operating stage. However, the biochar addition had no significant influence on pH ($p > 0.05$). The higher proportion of the biochar addition had a significant effect on ORP and Cond. The ORP in the BW-40 and the BW-30 was significantly greater than others, while the Cond in the BW-40 and the BW-30 was significantly lower than those rectors with a low proportion of the biochar addition. This suggested that the micro-environment of the wetland was changed by the addition of biochar, due to the porous structure of the biochar filler, which was conducive to the mass transfer of oxygen. On the one hand, it strengthened the nitrification process for the reducing environment. On the other hand, the Cond was decreased for more consumption of ion.

3.2. Pollutants removal

Table 2 shows the treatment performance of different constructed wetlands during the experimental period. The effluent NO_3^-–N was not detected in all CWs, which is related to the denitrification performance of CWs. The TN removal efficiency is mainly related to the NH_4^+–N removal, which will be discussed later.

Fig. 3 shows the influent and effluent COD concentration and removal rate in different CWs. The COD removal was related to the aerobic and anaerobic biological metabolic, precipitation, etc. From the Fig. 3, the COD can be removed with conversion efficiency of over 90%, which demonstrated the subsurface flow wetland can help removal of organic matter. Moreover, the effluent COD becomes less with the addition of the biochar addition. This implied that the biochar addition could improve the COD removal, but it influenced not significantly ($p > 0.05$).

As Fig. 4 shows, the NH_4^+–N removal efficiency of BW-40, BW-30, BW-20, and BW-10, respectively, improved by 66.43%, 47.08%, 39.54%, and 21.05%, compared with the control in stage I, which implied that the biochar addition can improve NH_4^+–N removal efficiency. According to the precious studies [16,17], the CWs with the biochar addition showed a better diffusion of DO, adhesion of the biofilm, and good activity for microorganism, also the nitrification,

Table 2
Treatment performance of different constructed wetlands during the experimental period

Pollutants	Stages	Influents (mg L^{-1})	Effluents (mg L^{-1})				
			BW-40	BW-30	BW-20	BW-10	CW-K
COD	Stage I	419.62 ± 6.94	39.93 ± 7.78	42 ± 8.33	42.93 ± 8.48	50.93 ± 8.34	49.43 ± 13.51
	Stage II	403.72 ± 8.58	39.42 ± 10.62	48.93 ± 17.78	50.13 ± 19.73	49.81 ± 16.60	49.96 ± 17.63
	Average	414.12 ± 10.67	39.73 ± 8.77	44.71 ± 12.96	45.75 ± 14.03	50.51 ± 11.77	49.63 ± 14.86
TN	Stage I	49.98 ± 1.76	9.42 ± 1.61	10.21 ± 3.52	11.35 ± 2.07	11.91 ± 3.04	15.13 ± 2.90
	Stage II	50.25 ± 2.19	10.63 ± 1.36	11.85 ± 1.27	11.93 ± 1.03	12.18 ± 1.41	13.40 ± 1.13
	Average	50.08 ± 1.88	9.85 ± 1.61	10.78 ± 3.01	11.56 ± 1.78	12.00 ± 2.57	14.53 ± 2.55
NH_4^+–N	Stage I	19.74 ± 1.57	7.61 ± 2.40	9.15 ± 2.94	10.04 ± 2.39	11.87 ± 3.53	13.70 ± 3.69
	Stage II	19.52 ± 1.63	9.47 ± 1.47	10.44 ± 1.34	10.28 ± 1.07	10.56 ± 1.37	11.37 ± 0.98
	Average	19.67 ± 1.57	8.04 ± 2.54	9.40 ± 2.71	9.93 ± 2.20	11.23 ± 3.03	12.71 ± 3.21
NO_3^-–N	Stage I	30.17 ± 1.02	ND[a]	ND	ND	ND	ND
	Stage II	32.14 ± 0.51	ND	ND	ND	ND	ND
	Average	31.40 ± 1.02	ND	ND	ND	ND	ND

[a]ND: not detected

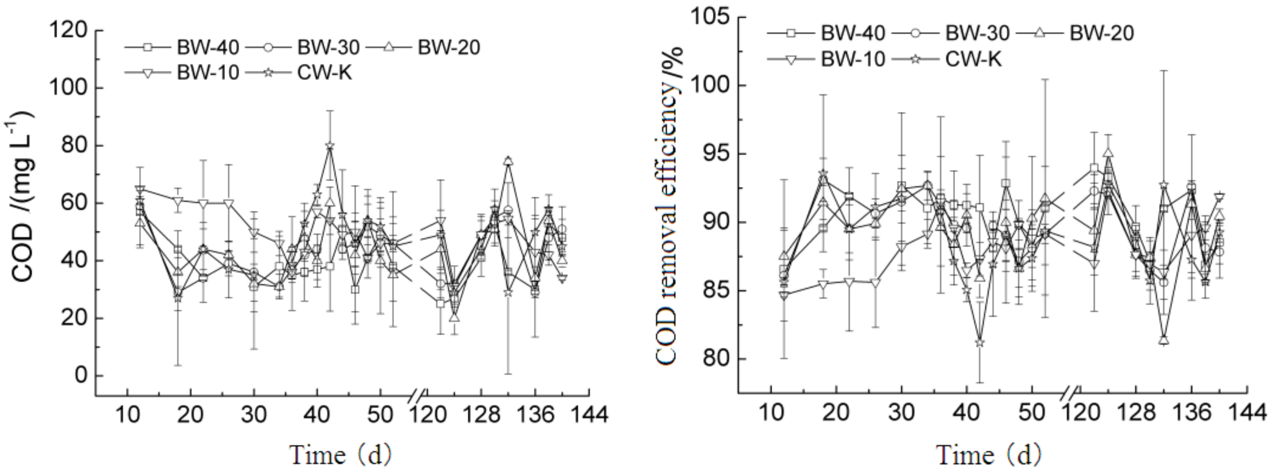

Fig. 3. Influent and effluent COD concentration and removal rate in different CWs.

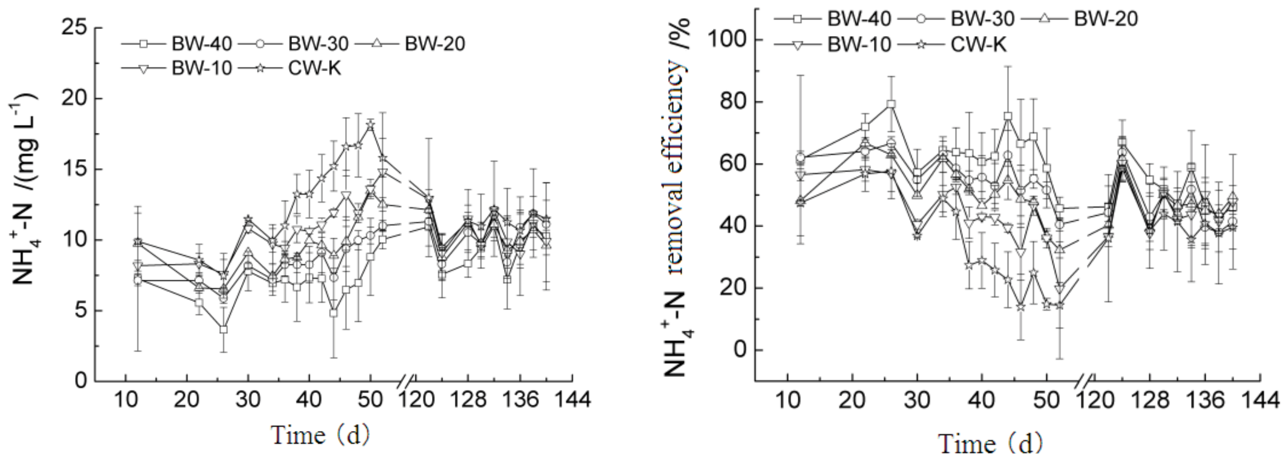

Fig. 4. Influent and effluent NH_4^+–N concentration and removal rate in different CWs during the experimental period.

a limiting step for nitrogen conversion in CWs, was promoted. Therefore, the NH_4^+–N removal can be improved by the biochar addition.

As Fig. 5 shows long-term operation has no significant effect on COD removal in the CWs ($p > 0.05$) but has an obvious influence on the NH_4^+–N removal ($p < 0.01$). In the stage I, the NH_4^+–N removal can be improved significantly with the increase of biochar addition. In the stage II, compared with the control CW-k, the NH_4^+–N removal can be improved, (by 9.73% in BW-40, 4.76% in BW-30, 5.58% in BW-20, and 4.14% in BW-40), but the difference among CWs decreases. This can attribute to the breeding of microorganism in the long-term operation, which made oxygen diffusion reduce, and affected the NH_4^+–N conversion. Overall, the NH_4^+–N removals are stable in both two stages, with the removal efficiency of 50%~60%. Precious studies showed that the NH_4^+–N removal efficiency kept 40%~55%, when the nitrogen pollutants with ammonia nitrogen as the main nitrogen source are treated by CWs [18]. This showed the same trend to CWs without the biochar addition in our research. And the removal efficiency increased with the biochar addition. Kizito et al. [19] reported that the treatment effect of biochar constructed wetland is obviously better than that of single gravel filler wetland, which is consistent with the results of this study.

3.3. *Typica periodic variations*

In a typical cycle, the DO showed a similar change in the five groups of the CWs. In 30 min, the DO dropped to 1 mg L^{-1} after feeding then there was no changes in 1 h, and kept below 0.5 mg L^{-1} after 8 h, showed as Fig. 6. This suggested that the DO keep a higher level in 2 h after feeding, which can maintain the normal metabolism of nitrifying bacteria [20], so, the nitration occurred during this time. Then the DO is less than DO < 0.8 mg L^{-1}, and anoxic condition was in favor of denitrification [21].

As Fig. 7 shows, the COD also showed a similar change in the two stages of the CWs, the occupation of COD is high in 5 h, and the removal efficiency of COD reached 85%. Then, the concertation of COD kept below 50 mg L^{-1}. Although the effluent COD of the controls was little higher than that of CWs with the biochar addition, there are no significant affection on COD removal.

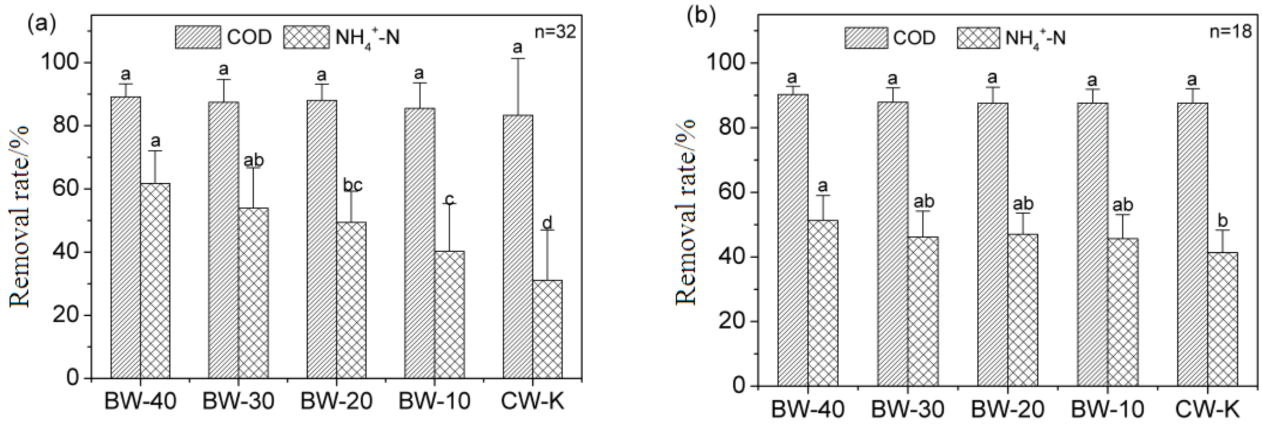

Fig. 5. COD, NH_4^+–N removal rates in different CWs under different stages, stage I (a) and stage II (b).

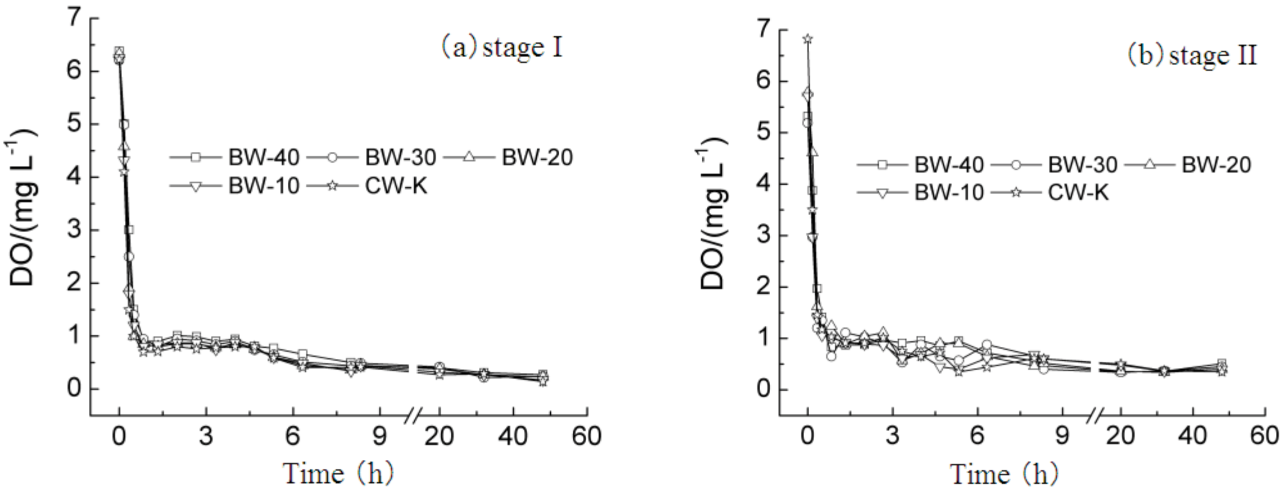

Fig. 6. DO changed with the time in different CWs under a typical cycle, stage I (a) and stage II (b).

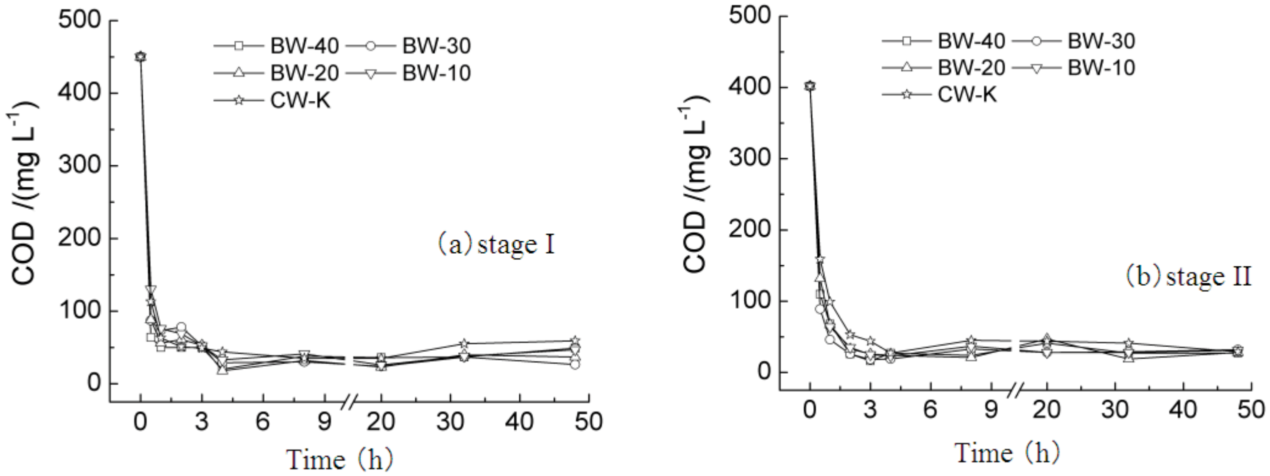

Fig. 7. COD changed with the time in different CWs under a typical cycle, stage I (a) and stage II (b).

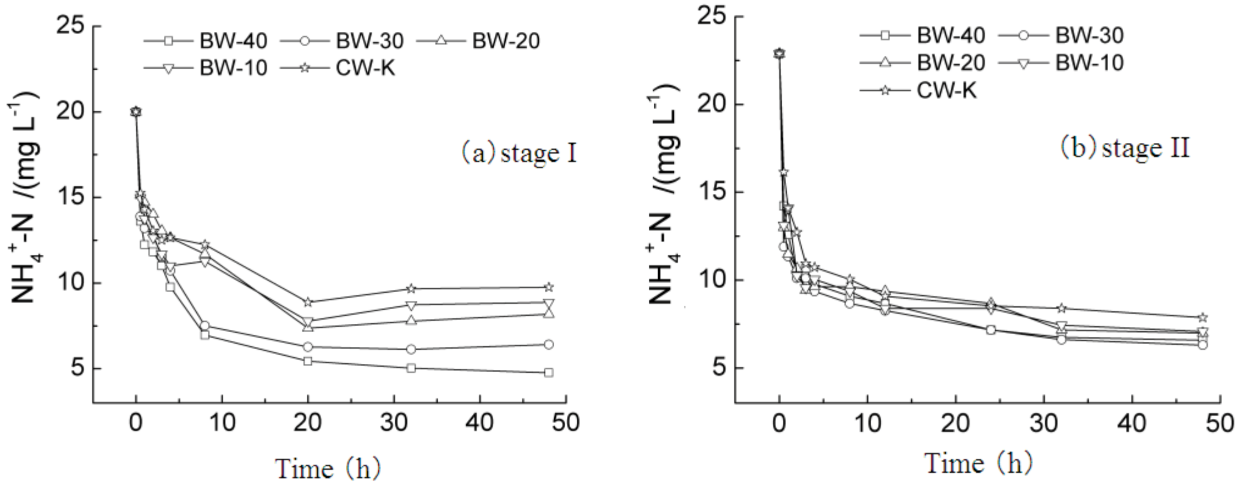

Fig. 8. NH_4^+–N changed with the time in different CWs under a typical cycle, stage I (a) and stage II (b).

The results of tracking the NH_4^+–N are shown in Fig. 8. In the stage I, BW-40 and BW-30 removed the NH_4^+–N in 10 h, while others need more time, about 20 h. This suggested that the biochar addition could improve the removal rate of the NH_4^+–N in some extent [22–24]. In the stage II, the NH_4^+–N of CWs all removed in 10 h, and there were no differences among them. Compared with the variations in the nutrient removal process, we found that the NH_4^+–N concentration of is significantly (at p = 0.01) related to the DO concentration. The higher NH_4^+–N removal was primarily due to oxygen diffusion improved; ORP increased by the biochar addition. Our results were similar to Rodriguezsanchez et al. [13], who construed CWs with mixture of gravel-wood mulch. Moreover, results show that nitrogen removal efficiency was improved by the biochar addition, this is due to multiplication of the nitrifying bacteria under favorable conditions [25–29].

4. Conclusions

The CWs with biochar addition could improve the nutrient removal. In the long-term operation, the results demonstrated the biochar addition had no significant affection on effluent DO, and pH of the CWs with the biochar addition slight decreased, compared with the control. The high ratio of the biochar addition could make ORP increase and Cond decline. We also found that the biochar addition in CWs had no significant affection on COD removal, the removal rate of the NH_4^+–N declined slighter, while the CWs with higher biochar addition ratio kept the better nitrogen removal. Finally, we found that the NH_4^+–N concentration in the CWs of was significantly related to the DO concentration. The higher NH_4^+–N removal was primarily can be due to oxygen diffusion improved, ORP increased by the biochar addition.

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References

[1] L. Huang, X. Gao, M. Liu, G. Du, J. Guo, T. Ntakirutimana, Correlation among soil microorganisms, soil enzyme activities, and removal rates of pollutants in three constructed wetlands purifying micro-polluted river water, Ecol. Eng., 46 (2012) 98–106.

[2] J. Fan, W. Wang, B. Zhang, Y. Guo, H.H. Ngo, W. Guo, J. Zhang, H. Wu, Nitrogen removal in intermittently aerated vertical flow constructed wetlands: impact of influent COD/N ratios, Bioresour. Technol., 143 (2013) 461–466.

[3] G. Fu, S.L. Huang, Z. Guo, Q. Zhou, Z. Wu, Effect of plant-based carbon sources on denitrifying microorganisms in a vertical flow constructed wetland, Bioresour. Technol., 224 (2016) 214–221.

[4] Y. Hu, Y. Zhao, X. Zhao, J.L.G. Kumar, High rate nitrogen removal in an alum sludge-based intermittent aeration constructed wetland, Environ. Sci. Technol., 46 (2012) 4583–4590.

[5] M.N. Aunsary, B.C. Chen, Sustainable water treatment management, Water Conserv. Manage., 3 (2019) 11–13.

[6] Z.N. Fogwe, S.J.P. Tume, M. Fouda, Eucalyptus tree colonization of the Bafut-Ngemba forest reserve, north west region, Cameroon, Environ. Ecosyst. Sci., 3 (2019) 12–16.

[7] A. Samsudin, M.A.A. Samah, M.Y. Ishak, Perception of government servants in Shah Alam on the utilization of food waste as a resource for biogas production in Malaysia, J. Clean WAS, 3 (2019) 16–20.

[8] A. Bialowiec, W. Janczukowicz, P.F. Randerson, Nitrogen removal from wastewater in vertical flow constructed wetlands containing LWA/gravel layers and reed vegetation, Ecol. Eng., 37 (2011) 897–902.

[9] C. Vohla, M. Koiv, H.J. Bavor, F. Chazarenc, Ü. Mander, Filter materials for phosphorus removal from wastewater in treatment wetlands—a review, Ecol. Eng., 37 (2011) 70–89.

[10] L. Huang, Y. Chen, G. Liu, S. Li, Y. Liu, X. Gao, Non-isothermal pyrolysis characteristics of giant reed (*Arundodonax L.*) using thermogravimetric analysis, Energy, 87 (2015) 31–40.

[11] China Environmental Protection Bureau (CEPB), Standard Methods for Examination of Water and Wastewater, 4th ed., Chinese Environmental Science Press, Beijing, 2002.
[12] P. Elefsiniotis, D. Li, The effect of temperature and carbon source on denitrification using volatile fatty acids, Biochem. Eng. J., 28 (2006) 148–155.
[13] A. Rodriguez-Sanchez, A. Gonzalez-Martinez, M.V. Martinez-Toledo, M.J. Garcia-Ruiz, F. Osorio, J. Gonzalez-Lopez, The effect of influent characteristics and operational conditions over the performance and microbial community structure of partial nitritation reactors, Water, 6 (2014) 1905–1924.
[14] S.H. Wang, Theory and Technology of Constructed Wetland Sewage Treatment, Science Press, Beijing, 2007.
[15] J.S. Wang, Plant Gravel Bed Constructed Wetland Sewage Treatment Technology and Engineering Case, Environmental Science Press of China, Beijing, 2009.
[16] T. Saeed, G. Sun, A comparative study on the removal of nutrients and organic matter in wetland reactors employing organic media, Chem. Eng. J., 171 (2011) 439–447.
[17] J. Fan, B. Zhang, J. Zhang, H.H. Ngo, W. Guo, F. Liu, Y. Guo, H. Wu, Intermittent aeration strategy to enhance organics and nitrogen removal in subsurface flow constructed wetlands, Bioresour. Technol., 141 (2013) 117–122.
[18] S.A. Ong, K. Uchiyama, D. Inadama, Y. Ishida, K. Yamagiwa, Performance evaluation of laboratory scale up-flow constructed wetlands with different designs and emergent plants, Bioresour. Technol., 101 (2010) 7239–7244.
[19] S. Kizito, T. Lv, S. Wu, Z. Ajmal, H. Luo, R. Dong, Treatment of anaerobic digested effluent in biochar-packed vertical flow constructed wetland columns: role of media and tidal operation, Sci. Total Environ., 592 (2017) 197–205.
[20] P. de Rozari, M. Greenway, A. El Hanandeh, Nitrogen removal from sewage and septage in constructed wetland mesocosms using sand media amended with biochar, Ecol. Eng., 111 (2018) 1–10.
[21] J. Vymazal, L. Kropfelovu, Removal of organics in constructed wetlands with horizontal sub-surface flow: a review of the field experience, Sci. Total Environ., 407 (2009) 3911–3922.
[22] P. Gupta, W. Ann, S.M. Lee, Use of biochar to enhance constructed wetland performance in wastewater reclamation, Environ. Eng. Res., 21 (2016) 36–44.
[23] S.M. Hocaoglu, G. Insel, E.U. Cokgor, D. Orhon, Effect of low dissolved oxygen on simultaneous nitrification and denitrification in a membrane bioreactor treating black water, Bioresour. Technol., 102 (2011) 4333–4340.
[24] F. Ye, Y. Li, Enhancement of nitrogen removal in towery hybrid constructed wetland to treat domestic wastewater for small rural communities, Ecol. Eng., 35 (2009) 1043–1050.
[25] B. Borogayary, A.K. Das, A.J. Nath, Tree species composition and population structure of a secondary tropical evergreen forest in Cachar district, Assam, J. Environ. Biol., 39 (2018) 67–71.
[26] J. Liu, Y. Liu, X. Wang, An environmental assessment model of construction and demolition waste based on system dynamics: a case study in Guangzhou, Environ. Sci. Pollut. Res. Int., 27 (2020) 37237–37259.
[27] K. Singh, N. Gupta, M. Dhingra, Effect of temperature regimes, seed priming and priming duration on germination and seedling growth on American cotton, J. Environ. Biol., 39 (2018) 83–91.
[28] X. Zhou, C. Liang, L. Jia, L. Feng, R. Wang, H. Wu, An innovative biochar-amended substrate vertical flow constructed wetland for low C/N wastewater treatment: impact of influent strengths, Bioresour. Technol., 247 (2018) 844–850.
[29] Y.R. Cui, X. Qiu, Q.R. Zhang, Q. Wang, Q. Wu, J.-H. Sun, Influence of biological activated carbon on simultaneous nitrification and denitrification in inflow with different C/N ratios, Environ. Sci., 37 (2016) 4296–4301.