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Short Communication

How Temperature Affects Wastewater Nitrate Removal in a Bioelectrochemically Assisted Constructed Wetland System

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Abstract

A novel bioelectrochemically assisted constructed wetland system (BECW) was investigated using a laboratory-scale experimental apparatus for treating nitrate-contaminated water without an organic carbon source. The BECW was operated at 29±1 and 18±1ºC, respectively, to explore the effects of temperature on the autotrophic denitrification process. The results showed that higher TN removal efficiency (76.30±5.08%) was obtained at higher temperature when compared to a lower temperature (48.18±4.40%). The effluent concentrations of NO_2^--N and NH_4^+-N at 18±1ºC were 0.40±0.11 and 0.50±0.42 mg N L^{-1}, whereas those at 29±1ºC could be neglected. Besides, significant accumulations of NO_2^--N and NH_4^+-N were observed in the cathode region at 18±1ºC through quantifying different forms of nitrogen that varied along the flow path.

Keywords: constructed wetland, bioelectrochemically, nitrate removal, temperature

Introduction

Nitrate pollution of groundwater in many regions of the world has become a serious concern since its potential health threat to infants and pregnant women [1-2]. Thus many countries and organizations have set standards for the content of nitrate in drinking water. The World Health Organization (WHO) has suggested a guideline value for nitrate of 11 mg NO_3^--N L^{-1} in drinking water [3], and China's Ministry of Environmental Protection in 2006 established a strict standard of 10 mg NO_3^--N L^{-1} for nitrate concentrations in drinking water (Ministry of Health, 2006). Conventional physicochemical methods, such as ion exchange [4], reverse osmosis [5], and electrodialysis [6] are not feasible for large applications due to low efficiency, generation of secondary pollutants, and mostly high cost [7]. Biological denitrification is considered to be an environmentally friendly and cost-competitive alternative for eliminating nitrates from water and wastewater [8].

Constructed wetlands (CWs) are economical, ecological, and effective engineering systems with the

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unique advantages of higher effluent quality and low operational costs [9-10]. In recent years, CWs have been widely used in the purifications of nitrate-rich water and wastewater, such as agricultural runoff, municipal wastewater treatment effluent, and polluted groundwater [11-14]. Nitrate nitrogen can be removed in CWs by the multiple functions of aquatic plants, substrates, and microorganisms. Among them, biological denitrification is generally considered to be the major nitrate removal process, particularly in those receiving high-nitrate loadings [15]. However, wastewater with low C/N ratio, such as groundwater and secondary effluent-polluted with nitrates, mostly contain relatively low organic matter, thus leading to the requirement of additional electron donors (e.g., methanol, ethanol, and plant materials) to enhance the conventional biological denitrification process [16]. Previous studies have reported that adding external electron donors can effectively improve the denitrification process while simultaneously bringing some other problems, including secondary pollution caused by the unused carbon source and nitrite accumulation due to incomplete denitrification [17-18].

Recently, a newly bioelectrochemically assisted constructed wetland (BECW) was used to remove nitrate in wastewater with organic-free influent, and the highest nitrate removal efficiency was achieved with the applied current of 15 mA [19]. The BECW system was constructed by integrating a biofilm-electrode reactor with a continuous up-flow constructed wetland, in which hydrogen gas was produced by water electrolysis and denitrifying bacteria cultured on the cathode surface used hydrogen as the sole electron donor to reduce nitrate nitrogen.

Temperature, known as a key environmental factor, is related to the denitrification process by affecting the activities of the denitrifying bacteria in CWs [20]. Nitrate reduction is accomplished by autotrophic hydrogen-dependent denitrifying bacteria in BECWs, which is rather different from conventional constructed wetlands. The aim of this study was: 1) to investigate the effect of temperatures (29±1 and 18±1ºC) on the denitrification performance of the BECW system and 2) to quantify different forms of nitrogen varied along the flow path for clarifying the nitrogen removal mechanism in this integrated system. Investigating the effect of temperature on the autotrophic denitrification process in the BECW reactor is necessary and will facilitate optimizing the integrated system.

Experimental

Configuration and Setup of the BECWs

The BECW system with a holding bucket 25 L (700 mm height, 160 mm in diameter) was established and shown in Fig. 1. The configuration and experimental setup of the BECWs have been described by Xu et al. [19]. Briefly, there were five layers from the bottom upward:

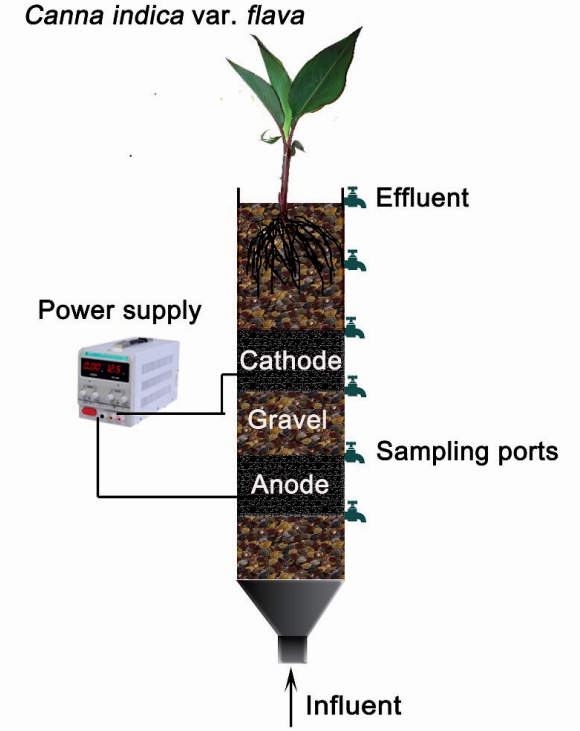

Fig. 1. Schematic representation of the BECWs used in this study.

bottom gravel layer, the anode compartment, the middle gravel layer, the cathode compartment, and then following the upper gravel layer planted with *Canna indica var. flava*. The upper gravel layer was 200 mm height while the other four layers were 100 mm high. The anode and cathode chamber were filled with granule active carbon (GAC, diameter 3-5 mm), and graphite felts (300 mm length × 100 mm wide× 6 mm thick) were inserted into the randomly packed GAC to collect or release electrons. All graphite components were pre-treated by washing in 1 N HCl and 1 N NaOH [21].

In addition, a constant current of 15 mA was applied to the circuit by connecting the positive pole of a DC power supply (LongWei PS-305DM, Shenzhen, China) to the anode, and the negative pole to the cathode.

Experimental Operation and Sample Analysis

The inoculation process and inflow water quality of reactors were described by Xu et al. [19]. Synthetic wastewater was augmented with sodium nitrate to a target concentration of 30 mg NO_3^--N L^{-1} without supplemental organic carbon. The BECWs were operated in a continuous up-flow mode with a flow rate of 1.493 ml min^{-1} (giving an HRT of 2 d). To determine the influence of temperature on denitrification behavior, the experimental study was divided into two different periods: Period 1 with an average temperature of 29±1ºC for 23 days and period 2 with an average temperature of 18±1ºC for 17 days.

Water samples were collected from the BECW effluents and sampling ports arranged at intervals of

100 mm throughout the height of the reactors. TN, NH_4^+-N, NO_2^--N, and NO_3^--N were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). Prior to analysis, except for TN, the samples were centrifuged at 5,000 rpm for 10 min to spin down any suspended solids from the liquid phase. The pH and dissolved oxygen (DO) values were immediately measured using a portable Orion Star meter (520M-01A, Thermo, USA) equipped with a pH electrode (8107UWMMD, Thermo, USA) and a DO electrode (086030MD, Thermo, USA).

Results and Discussion

pH and DO Profiles along the BECW System

The distributions of pH and DO along the BECW reactors at two different temperatures (29±1 and 18±1ºC) are shown in Figs 2(a-b), respectively. Both of the pH values along the BECW reactors at 29±1 and 18±1ºC decreased gradually with the increased reactor height until they reached 20 cm due to the generation of H^+ during water electrolysis in the anode region, and then they increased gradually to the maximal pH values at a height of 40 cm because of the generation of OH^- during the denitrification process and water electrolysis in the cathode region. The lowest pH values were in the anode region with 5.85±0.04 at 29±1ºC and 5.95±0.05 at 18±1ºC, whereas the highest pH values were in the cathode region with 9.10±0.06 at 29±1ºC and 10.02±0.02 at 18±1ºC. Furthermore, the pH value of the BECW at 29±1ºC decreased again after leaving the cathode region to the outlet, whereas the pH value of the BECW at 18±1ºC decreased first but increased a little. The effluent pH were 8.03±0.06 at 29±1ºC and 7.65±0.08 at 18±1ºC. The decrease of pH values after leaving the cathode region were due to that root secretion and putrefaction of dead plants mitigating some alkalinity [11].

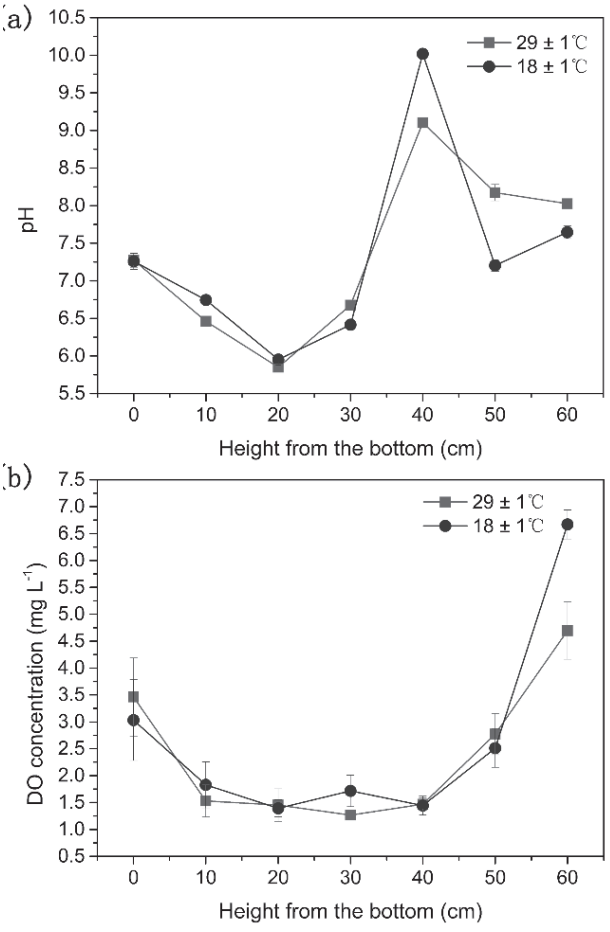

Fig. 2. pH a) and DO b) concentrations varied along the flow path in the BECWs.

Dissolved oxygen (DO) is the measure of the oxidizing (aerobic) and reducing (anaerobic) condition of the aquatic environment. As shown in Fig. 2b, with the increasing reactor height, the DO concentrations along the reactors at 29±1 and 18±1ºC showed a similar trend that first decreased due to the consumption of O_2 and then increased because of atmospheric reoxygenation and the root release of oxygen. Moreover, the DO concentration of the reactor effluent at 18±1ºC (6.67±0.27) was higher than that at 29±1ºC (4.70±0.53) due to the fact that DO concentration increased with the decrease of temperature.

Nitrogen Removal Performance of the BECW System

As illustrated in Table 1, the effluent concentrations of TN in the BECW reactors were about 7.14±1.53 mg N L^{-1} at 29±1ºC and 16.49±1.40 mg N L^{-1} at 18±1ºC, whereas 76.30±5.08% and 48.18±4.40% TN removal efficiencies were accomplished at 29±1 and 18±1ºC, respectively. Moreover, we observed that nitrate removal efficiencies at higher temperatures were also much higher than those at lower temperatures. It is known that microbial denitrification processes are strongly linked to temperature. In general, higher temperatures lead to higher biological activity and growth rates, whereas lower temperatures will hinder biological activity [22-25]. Sirivedhin and Gray found that the overall nitrate removal rate was significantly higher in summer than in winter [23]. Beutel et al. also observed a significant positive correlation between the nitrate loss rates and water temperature [24]. It is also noticed that the effluent concentrations of NO_2^--N and NH_4^+-N at 29±1ºC was a bit higher than those at 18±1ºC.

In order to ascertain the reason for the difference of N removal efficiencies between the BECWs with two temperatures, the concentrations of various forms of nitrogen varied along the reactor height were investigated (see Fig. 3). When the BECW reactor was operated at 29±1ºC, the concentration of TN declined gradually from 30.13±0.31 to 27.69±2.19 mg N L^{-1} until they reached the reactor height of 20 cm, and then decreased drastically to 5.93±0.14 mg N L^{-1} from the reactor height of 20 to 40 cm, yet it increased to 7.45±1.05 mg N L^{-1} at the

Table 1. Effluent N characteristics in the BECWs.

Temperature (°C)	Effluent N concentration (mg N L^{-1})				N removal efficiency (%)	
	TN	NO_3^--N	NO_2^--N	NH_4^+-N	TN	NO_3^--N
29±1°C	7.14±1.53	6.12±0.80	0.01±0.01	not detected	76.30±5.08	78.92±3.12
18±1°C	16.49±1.40	14.09±0.99	0.40±0.11	0.50±0.42	48.18±4.40	55.73±3.08

height of 50 cm, finally decreasing to 7.14±1.53 mg N L^{-1} (Fig. 3a). When constructing the reactor, the height from 30 to 40 cm was designed as the cathode region. However, the actual cathode region was lower by a few centimeters than the height of 30-40 cm owing to the matrix infiltration after a period of operation. Thus, cathodic autotrophic denitrification was considered to be the main reason for the drastic decrease of TN concentration from the height of 30 to 40 cm. The change curve of TN concentration at 18±1ºC was consistent with that at 29±1ºC. But the TN concentration varying along the reactor height at lower temperatures was distinctly higher compared to that at higher ones. It is known that lower temperatures will lead to lower denitrification efficiency in the cathode region, but the reason for the increase of TN concentration in the rhizosphere region is unknown, which needs further research. As shown in Figs 3(c-d), the concentrations of nitrite and ammonia were negligible along the reactor at 29±1ºC. Thus the change trend of NO_3^--N concentration was quite similar with that of TN concentration owing to the fact that the TN was mainly composed of nitrate. However, the nitrogen forms of the BECW along reactor height opera-ting at 18±1ºC was rather different. The effluent concentration of NO_3^--N at the height of 40 cm decreased to 2.83±0.62 mg N L^{-1} at 18±1ºC, which was lower than that at 29±1ºC (4.86±0.63 mg N L^{-1}). Moreover, both of the maximum concentrations of nitrite and ammonia occurred at a height of 40 cm, with the corresponding concentrations of 4.98±0.80 and 4.37±0.26 mg N L^{-1}, respectively. Zhou et al. demonstrated that the suitable temperature range of performing a BER was 30-35ºC, and a temperature lower than 25ºC or higher than 40ºC would lead to a significant accumulation of nitrite [26]. In this study, temperature also played an important role for nitrite evolution, and the low temperature was responsible

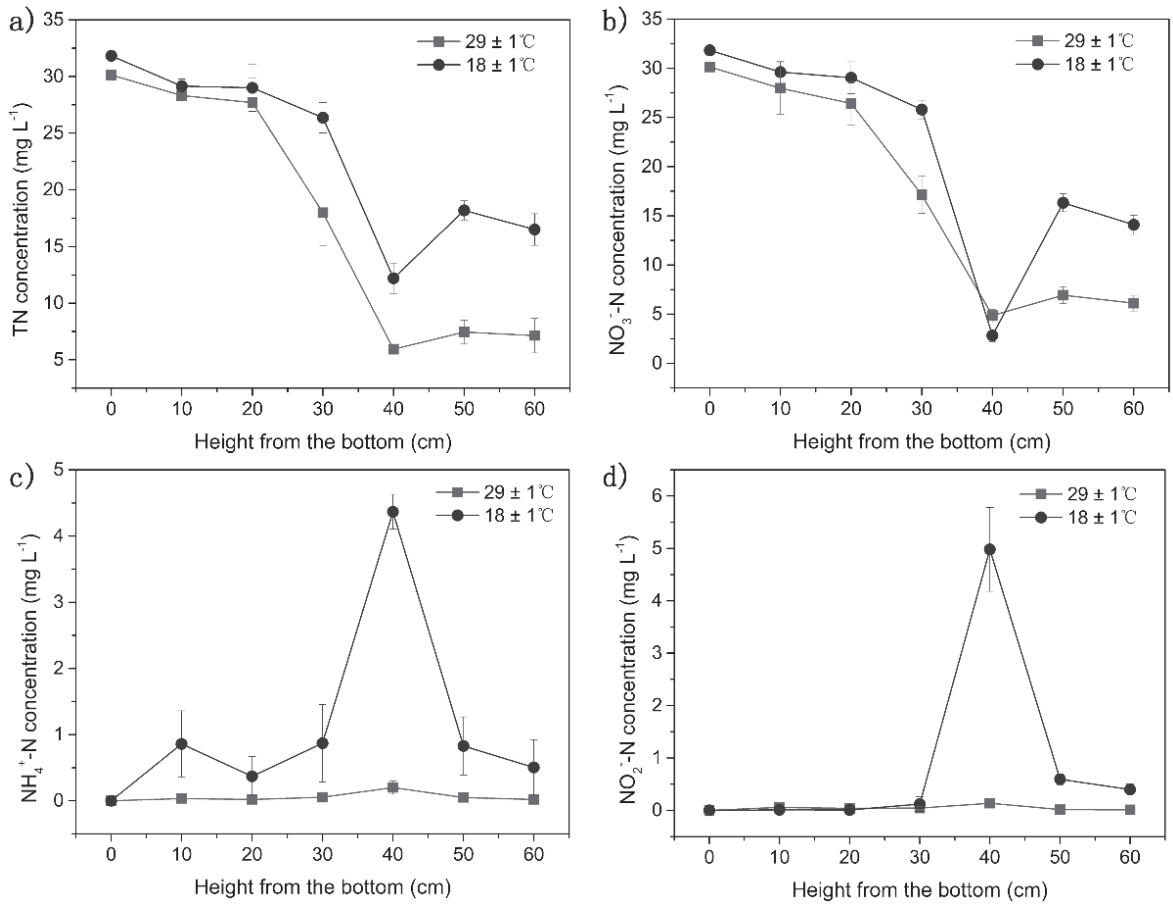

Fig. 3. TN a), NO_3^--N b), NH_4^+-N c), and NO_2^--N d) concentrations varied along the flow path in the BECWs.

for the accumulation of nitrite in the cathode region of BECW at 18±1ºC. Previous studies have reported dissimilatory nitrate reduction in constructed wetlands [27-28]. Owing to the requirement for more electrons, dissimilatory nitrate reduction, which includes the reduction of NO_2^--N and NO_3^--N to NH_4^+-N, is considered favored by carbon-rich and nitrate-limited conditions [29]. In this study, the specific conditions of the BECW system at a lower temperature may promote the growth of nitrate-ammonifying bacteria and limit the activity of nitrite-reducing bacteria for such an unconventional transformation. Besides, although the concentrations of nitrite and ammonia decreased at the rhizosphere region because of reoxygenation and the root release of oxygen [30], the effluent concentrations were still higher than those at 29±1ºC. According to the obtained results, low temperatures would limit nitrate removal of BECW through decreasing its autotrophic denitrification efficiency in the cathode region, thus measurements should be taken to improve denitrification efficiency of BECW in future studies. In order to improve the nitrate removal efficiency at a relatively low temperature, increasing the current density and HRT or combining with heterotrophic denitrification can be considered. In BERs, electrical current plays a key role in providing suitable hydrogen concentration for hydrogenotrophic bacteria and achieving a high rate of denitrification [31]. Previous studies showed that the quantity of electron donors (hydrogen concentration) are completely dependent on current density and HRT, and higher current density and longer HRT in a certain range could lead to a higher denitrification rate, thus decreasing the nitrate and nitrite concentrations of the effluent [19, 26, 32]. Besides, the co-existence of autotrophic and heterotrophic denitrification processes prevailing in BESs can improve denitrification efficiency, reduce the consumption of electrical energy, and buffer the pH [33-35]. Thus, adding a small amount of organic carbon source could also be a possible solution to enhancing the denitrification efficiency of BECW at low temperatures.

Conclusions

In this study, the effect of temperature on the autotrophic denitrification process in a novel bioelectrochemically assisted constructed wetland system (BECW) with organic-free influent was investigated. The results indicated that higher TN removal efficiency (76.30±5.08%) was obtained at higher temperatures when compared to that at lower temperatures (48.18±4.40%). The BECW system operating at a lower temperature may lead to significant accumulations of NO_2^--N and NH_4^+-N in the cathode region and higher effluent concentrations of them. Thus, measures taken to improve the denitrification efficiency of the BECW system at a relatively low temperature will be the focus of future research.

Acknowledgements

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