

Article

## Tertiary Denitrification of the Secondary Effluent by Denitrifying Biofilters Packed with Different Sizes of Quartz Sand

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**Abstract:** Tertiary denitrification of the secondary effluent in wastewater treatment plants is necessary to control the eutrophication of receiving water bodies. Two denitrifying biofilters (DNBF), one packed with quartz sand with sizes of 2–4 mm (DNBF<sub>S</sub>) and the other of 4–6 mm (DNBF<sub>L</sub>), were operated for tertiary denitrification under empty bed retention times (EBRTs) of 30 min, 15 min and 7.5 min, respectively. Under EBRTs of 30 min, 15 min and 7.5 min, the NO<sub>3</sub><sup>-</sup>-N removal percentages were 93%, 82% and 83% in DNBF<sub>S</sub>, and were 92%, 68% and 36% in DNBF<sub>L</sub>, respectively. The nitrogen removal loading rates increased with decreasing EBRTs, and at the EBRT of 7.5 min, the rate was 2.15 kg/(m<sup>3</sup>·d) in DNBF<sub>S</sub> and 1.08 kg/(m<sup>3</sup>·d) in DNBF<sub>L</sub>. The half-order denitrification coefficient of DNBF<sub>S</sub> increased from 0.42 (mg/L)<sup>1/2</sup>/min at the EBRT of 30 min to 0.70 (mg/L)<sup>1/2</sup>/min at the EBRT of 7.5 min, while did not vary much in DNBF<sub>L</sub> with values from 0.22 to 0.25 (mg/L)<sup>1/2</sup>/min. The performance of both DNBFs was stable within each backwashing cycle, with the NO<sub>3</sub><sup>-</sup>-N removal percentage variation within 5%. Better denitrification was achieved in DNBF<sub>S</sub> but with a slightly high decreased flow rate during the operation.

**Keywords:** tertiary denitrification; denitrifying biofilters; media size; secondary effluent; empty bed retention times

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## 1. Introduction

Eutrophication is a serious environmental issue nowadays and nitrogen is one of the limiting factors inducing the occurrence of eutrophication. Dissolved inorganic nitrogen can be quickly absorbed by algae and induce their overgrowth, resulting in the occurrence or acceleration of eutrophication [1]. Therefore, it is necessary to remove nitrogen from wastewater before discharging into receiving water bodies. Furthermore, stringent regulations on nutrient discharging have also been proposed in lots of countries all over the world. For example, for sensitive water bodies in EU and north American, wastewater discharging standards such as total nitrogen (TN) concentration of below 3 mg/L and total phosphorus (TP) concentration of below 0.1 mg/L have been practiced [2]. In future, the wastewater discharging standard may approach the surface water standard and nutrient such as nitrogen should be removed with the limit of technology. Usually, nitrogen is removed from wastewater through biological processes including sequential nitrification and denitrification in the secondary treatment process. However, due to the shortage of organic carbon in influent wastewater and limits of the secondary biological treatment process, nitrogen cannot be removed to achieve a very high standard. Nitrate is the main nitrogen component in the WWTP's secondary effluent, and post-denitrification or tertiary denitrification may be required to further remove the oxidized nitrogen so as to achieve a high discharging standard. For tertiary denitrification, denitrifying biofilters (DNBFs) can effectively remove total nitrogen and total suspended solids, and have been applied commonly.

During denitrification, organic carbon is required as both the energy source and the electron donor for removing oxidized nitrogen. While only a limited amount of biodegradable organic carbon is available in the secondary effluent. External organic carbon is required for tertiary denitrification and commonly used ones include methanol, ethanol and glucose [3]. Ledwell *et al.* [4] obtained that with methanol as the carbon source, denitrification possessed both low carbon requirement and biomass yield. The low carbon requirement means a low operating cost as the carbon dosage is a major investment for denitrification [5]. In addition, the low biomass yield in denitrification filters will not only reduce the effluent turbidity and the energy consumption for backwashing, but also alleviate the clogging problem of biofilters. Therefore, methanol has been used in common for tertiary denitrification.

In nitrifying biofilter systems, the size of the filter media affects the system performance, and usually, the smaller the media size, the better the nutrient removal efficiency [6,7]. However, there are few related studies in denitrifying biofilters. In addition, the head loss and backwashing frequency will be increased with decreasing the media size, resulting in the increased energy consumption [6]. Biofilters with different media sizes have been applied for different purposes [8]. For example, the filter with media sizes above 6 mm is commonly used in pretreatment, 3–6 mm used in the secondary treatment process, and around 3 mm used in tertiary biofilters [9–14]. Empty bed retention time (EBRT) is also a key factor affecting the performance of denitrifying biofilters. A high EBRT provides adequate reaction time for denitrification and leads to better nutrient removal efficiency, while a large

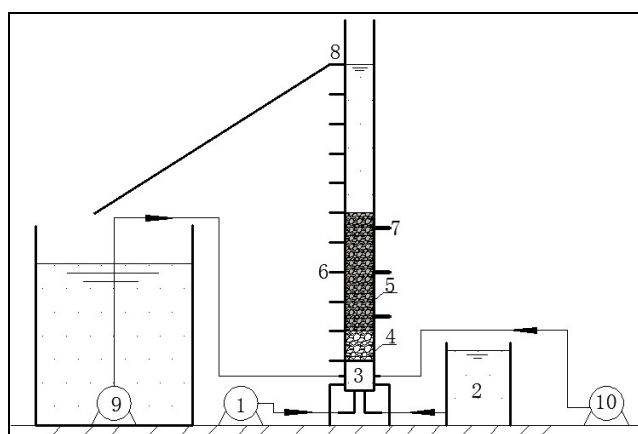
reactor volume is required and a high capital cost will be induced. On the other hand, a low EBRT induces a high hydraulic flushing leading to biofilm detachment or sloughing and affects the system performance. In addition, a low EBRT also increases the backwashing frequency and results in an increased operating cost.

In this paper, two tertiary DNBFs were operated under different EBRTs. Long-term performance of the two DNBFs, nutrient removal along the biofilter depth and performance of biofilters within a backwashing cycle were investigated so as to clarify the denitrification performance for tertiary nitrogen removal.

## 2. Materials and Methods

The two tertiary DNBFs were made from plexiglass column with a diameter of 10 cm and a height of 125 cm, and the schematic diagram of the experimental system is shown in Figure 1. One biofilter was packed with quartz sand with sizes between 2 and 4 mm (DNBF<sub>S</sub>), and the other with sizes of 4–6 mm (DNBF<sub>S</sub>). The packed depth of quartz sand was 50 cm with a support gravel stone layer of 10 cm at the bottom. The biofilters were backwashed every 24 h for 15 min with combined air and water. During the backwashing, the water flow rate was 5 L/min and the air flow rate was 13 L/min.

**Figure 1.** Schematic diagram of the experimental system. 1: Influent pump; 2: Methanol stock tank; 3: Premixing zone; 4: Gravel support layer; 5: Quartz sand layer; 6: Water sampling port; 7: Sand sampling port; 8: Effluent; 9: Backwashing water pump; 10: Backwashing air pump.



The secondary effluent in the 7th wastewater treatment plant, Kunming, was used as the feeding and methanol was dosed as the external organic carbon with the carbon to nitrogen ratio of 3.42. During the study period, the influent chemical oxygen demand (COD) concentration was 20 mg/L, ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) was 2.2 mg/L, nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ ) was 7.65 mg/L, nitrite nitrogen ( $\text{NO}_2^-\text{-N}$ ) was 0.1 mg/L, pH was 6.9 and the wastewater temperature was around 22 °C.

The two tertiary DNBFs were operated under EBRTs of 30 min, 15 min and 7.5 min, respectively. The EBRT was 30 min during the start-up period, after the system reached steady state and adequate data were collected, and it was then decreased to 15 min and 7.5 min sequentially to examine the effect of EBRT on the system performance. During the long-term operation, parameters such as nitrate and nitrite *etc.*, were tested daily to examine dynamics of nutrient removal in both biofilters. Under steady

state at each EBRT, samples were taken every 10 cm along the biofilter depth, and concentrations of typical parameters ( $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N, COD, NTU, pH and DO) were tested so as to investigate denitrify biokinetics of each biofilter. In addition, performance of denitrify biofilters within a backwashing cycle was examined for each EBRT at steady state to evaluate the performance stability of the system. Samples were taken at intervals (hours 0, 0.5, 1, 2, 4, 6, 8, 12 and 24) starting from the end of each backwashing to the beginning of the next backwashing, and parameters of  $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N, COD,  $\text{NH}_4^+$ -N, NTU, pH and DO were tested.

COD,  $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N,  $\text{NH}_4^+$ -N, MLSS and NTU were determined according to standard methods [15]. The pH and DO were measured using probes of pH3110 and OXI315i (WTW, Munich, Germany), respectively.

The biomass yield coefficient was calculated based on the following equations:

$$Y_{COD} = 1 - \frac{r_{COD}}{q_{ME} \times i_{COD,ME}} \quad (1)$$

$$q_{ME} = \frac{Q_{ME}}{V_f} \quad (2)$$

$$r_{COD} = r_{O_2} + r_{den,COD} = \frac{Q_{in} [O_{2,in} + 2.86(NO_{3,in} - NO_{3,out}) + 1.72(NO_{2,in} - NO_{2,out})]}{V_f} \quad (3)$$

where,  $r_{COD}$  is the volumetric removal rate of substrate based on the COD equivalent ( $\text{kg}/\text{m}^3 \cdot \text{d}$ );  $Q_{in}$  is the influent flow rate ( $\text{m}^3/\text{d}$ );  $O_{2,in}$  is the influent DO concentration ( $\text{kg}/\text{m}^3$ );  $NO_{3,in}$  is the influent  $\text{NO}_3^-$ -N concentration ( $\text{kg}/\text{m}^3$ );  $NO_{3,out}$  is the effluent  $\text{NO}_3^-$ -N concentration ( $\text{kg}/\text{m}^3$ );  $NO_{2,in}$  is the influent  $\text{NO}_2^-$ -N concentration ( $\text{kg}/\text{m}^3$ );  $NO_{2,out}$  is the effluent  $\text{NO}_2^-$ -N concentration ( $\text{kg}/\text{m}^3$ );  $V_f$  is the reactor volume ( $\text{m}^3$ );  $q_{ME}$  is the volumetric rate of methanol dosage ( $\text{kg}/\text{m}^3 \cdot \text{d}$ ); and  $i_{COD,ME}$  is the COD equivalent coefficient of methanol.

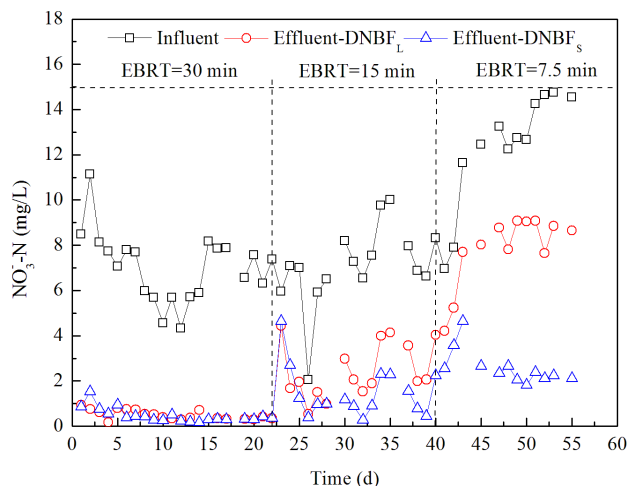
### 3. Results and Discussion

#### 3.1. Long-Term Performance under Different EBRTs

Both biofilters were started with the EBRT of 30 min and the dosed carbon to nitrogen ratio of 3.42, and after a period of stable operation, the EBRT was then decreased to 15 min and 7.5 min. The performance of the two biofilters during the long-term operation at EBRTs of 30 min, 15 min and 7.5 min are given in Figure 2 and Table 1.

The two biofilters reached steady state after 15 days operation, which was similar to previous results. For example, with the influent  $\text{NO}_3^-$ -N concentration of 15 mg/L and methanol as the carbon source, 18 days were used to start-up an up-flow denitrification filter at 23 °C [16]. At the EBRT of 20 min and methanol as the organic carbon, a denitrification filter reached steady state after about 25 days operation [17].

**Figure 2.** Long-term dynamics of the influent and effluent  $\text{NO}_3^-$ -N concentrations in both biofilters under different empty bed retention times (EBRTs).



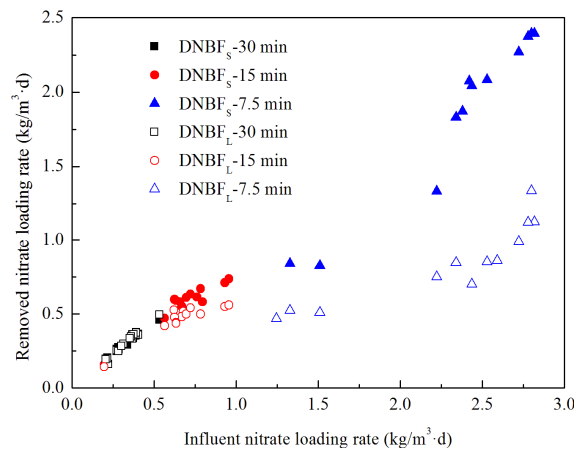
**Table 1.** Performance of the two biofilters during the long-term operation.

EBRT		DNBF <sub>s</sub>			DNBF <sub>L</sub>		
		30 min	15 min	7.5 min	30 min	15 min	7.5 min
COD	Influent	125.02 ± 21.67	125.06 ± 9.26	120.33 ± 9.87	123.22 ± 16.48	126.87 ± 8.90	115.60 ± 8.82
	Effluent	82.85 ± 19.64	77.31 ± 16.85	53.44 ± 8.63	88.94 ± 18.32	83.25 ± 15.82	82.20 ± 10.14
	Removal	33% ± 12%	38% ± 12%	55% ± 7%	29% ± 10%	34% ± 12%	28% ± 5%
$\text{NO}_3^-$ -N	Influent	7.02 ± 1.49	7.10 ± 1.74	13.5 ± 0.97	7.02 ± 1.49	7.10 ± 1.74	13.5 ± 0.97
	Effluent	0.47 ± 0.31	1.27 ± 1.08	2.26 ± 0.26	0.49 ± 0.21	2.45 ± 1.18	7.82 ± 1.58
	Removal	93% ± 3%	82% ± 8%	83% ± 2%	92% ± 2%	68 ± 8%	36% ± 5%
$\text{NO}_2^-$ -N	Influent	0.10 ± 0.12	0.07 ± 0.04	0.06 ± 0.05	0.10 ± 0.12	0.07 ± 0.04	0.06 ± 0.05
	Effluent	0.12 ± 0.18	0.42 ± 0.21	0.62 ± 0.16	0.22 ± 0.21	0.42 ± 0.19	0.68 ± 0.11
$\text{NH}_4^+$ -N	Influent	2.51 ± 1.78	1.85 ± 1.96	0.66 ± 0.56	2.51 ± 1.78	1.85 ± 1.96	0.66 ± 0.56
	Effluent	1.76 ± 1.96	1.45 ± 1.81	0.49 ± 0.39	1.28 ± 1.79	1.39 ± 1.84	0.54 ± 0.39
	Removal	47% ± 27%	27% ± 19%	36% ± 11%	45% ± 29%	22% ± 15%	17% ± 12%
Turbidity	Influent	3.78 ± 0.71	4.21 ± 0.93	4.38 ± 1.09	3.78 ± 0.71	4.21 ± 0.93	4.38 ± 1.09
	Effluent	1.10 ± 0.11	1.63 ± 0.29	2.01 ± 0.26	1.21 ± 0.25	1.71 ± 0.25	2.13 ± 0.21
	Removal	69% ± 6%	59% ± 9%	51% ± 11%	66% ± 8%	58% ± 7%	49% ± 9%

At EBRTs of 30 min, 15 min and 7.5 min, with respect to the influent  $\text{NO}_3^-$ -N concentration of  $7.0 \pm 1.5$  mg/L,  $7.1 \pm 1.7$  mg/L,  $13.5 \pm 1.0$  mg/L, its removal percentage was 93%, 82% and 83% in DNBF<sub>s</sub> and was 92%, 68% and 36% in DNBF<sub>L</sub>, respectively. Therefore, with decreasing EBRTs, the  $\text{NO}_3^-$ -N removal percentage decreased. For the EBRT of 30 min, the two biofilters had similar performance in the removal of  $\text{NO}_3^-$ -N; for the EBRT of 15 min and 7.5 min, the effluent  $\text{NO}_3^-$ -N concentration of DNBF<sub>s</sub> was lower than that of DNBF<sub>L</sub>, indicating that the small media size sand benefited denitrification. In the study of Farabegoli *et al.* [16], with the influent  $\text{NO}_3^-$ -N concentration of 15 mg/L, EBRT of 7 min and the silica sand size of 0.5–1.5 mm, the  $\text{NO}_3^-$ -N removal percentage was 55% in an up-flow denitrification filter at 23 °C with methanol as the organic carbon source. With the influent  $\text{NO}_3^-$ -N concentration of 15 mg/L, EBRT of 30 min and the media size of 2 mm, Koch and Siegrist [18] obtained the  $\text{NO}_3^-$ -N removal percentage was 87% at 15 °C.

The relationship between the influent nitrate loading rate and the removed nitrate loading rate is shown in Figure 3. In both biofilters, with increasing influent nitrate loading rates, the removed nitrate loading rate also linearly increased, indicating that both systems were mainly substrate-limited rather than biomass-limited. However, for DNBFL, at the high influent nitrate loading rate, it seemed that the removed nitrate loading rate was not increased any more, indicating that a biomass-limited condition came to occur. Under EBRTs of 30 min, 15 min and 7.5 min, the influent nitrate loading rate were 0.32 kg/(m<sup>3</sup>·d), 0.67 kg/(m<sup>3</sup>·d) and 2.28 kg/(m<sup>3</sup>·d), respectively. The removed nitrate loading rates were 0.31 kg/(m<sup>3</sup>·d), 0.56 kg/(m<sup>3</sup>·d) and 2.15 kg/(m<sup>3</sup>·d) in DNBFS, and were 0.31 kg/(m<sup>3</sup>·d), 0.45 kg/(m<sup>3</sup>·d) and 1.08 kg/(m<sup>3</sup>·d) in DNBFL, respectively. In a denitrification sand filter with sand sizes between 2 and 4 mm, Aesory *et al.* [19] obtained the removed nitrate loading rate between 1 and 2.5 kg/(m<sup>3</sup>·d); Holloway *et al.* [20] obtained that with the influent nitrate loading rate between 0.7 and 2.1 kg/(m<sup>3</sup>·d), the removed nitrate loading rate increased with increasing influent nitrate loading rates.

**Figure 3.** The relationship between the removed NO<sub>3</sub><sup>-</sup>-N loading rate and the influent NO<sub>3</sub><sup>-</sup>-N loading rate.



At EBRTs of 30 min, 15 min and 7.5 min, the consumed COD to the removed N ratios were 5.11, 5.27 and 4.11 in DNBFS, and were 5.28, 5.40 and 3.73 in DNBFL, respectively. The COD/N ratio reduced with decreasing EBRTs, and the possible reason could be that under high EBRT conditions, more carbon source was degraded through other processes besides denitrification, resulting in increased consumption of carbon source. DeBarbadillo *et al.* [21] reviewed that when methanol was dosed for denitrification, the COD/N ratio was between 4.79 and 5.2. Purtschert *et al.* [22] obtained the COD/N ratio was 6–6.75 with the NO<sub>3</sub><sup>-</sup>-N concentration of 10 mg/L and methanol as the carbon source. Koch and Siegrist [18] obtained the COD/N ratio was 4.8 with methanol as the carbon source and the NO<sub>3</sub><sup>-</sup>-N loading rate of 2.0 kg/(m<sup>3</sup>·d). By calculation, the cost for methanol dosage was 0.06–0.08 yuan/m<sup>3</sup> for DNBFS and 0.04–0.05 yuan/m<sup>3</sup> for DNBFL depending on the consumed COD to the removed N ratio and the current price of methanol.

At EBRTs of 30 min, 15 min and 7.5 min, the COD based biomass yield coefficient was 0.37, 0.40 and 0.26 kg/kg in DNBFS, and was 0.39, 0.41 and 0.15 kg/kg in DNBFL. It could be seen that the biomass yield coefficient at the EBRT of 7.5 min was obviously lower than those at the other conditions. This might be due to that at a low EBRT, the contact time between denitrifiers and substrate was too short, leading to a slow metabolism. The biomass yield coefficients obtained under

EBRTs of 30 min and 15 min were consistent with previous results: Koch and Siegrist [18] obtained the coefficient was  $0.4 \text{ kg}_{\text{COD-X}}/\text{kg}_{\text{COD}}$  with methanol as the carbon source and the  $\text{NO}_3^-$ -N loading rate of  $2.0 \text{ kg}/(\text{m}^3 \cdot \text{d})$ ; Farabegoli *et al.* [16] obtained the coefficient was  $0.3 \text{ kg}_{\text{COD-X}}/\text{kg}_{\text{COD}}$  in an up-flow denitrification filter at the EBRT of 7 min with the silica sand size of 0.5–1.5 mm. Through literature review, deBarbadillo *et al.* [21] and Ledwell *et al.* [4] found the coefficients was  $0.4 \text{ kg}_{\text{COD-X}}/\text{kg}_{\text{COD}}$  and  $0.39 \text{ kg}_{\text{COD-X}}/\text{kg}_{\text{COD}}$ , respectively.

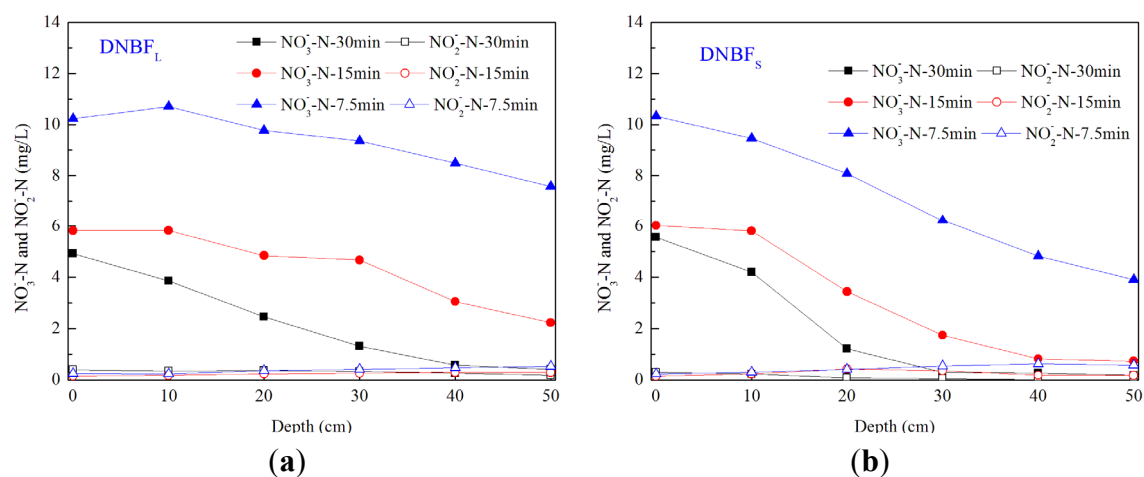
Under EBRTs of 30 min, 15 min and 7.5 min, the influent  $\text{NO}_2^-$ -N concentration was 0.10 mg/L, 0.07 mg/L and 0.06 mg/L, respectively; the effluent  $\text{NO}_2^-$ -N concentration was 0.12 mg/L, 0.42 mg/L and 0.62 mg/L in  $\text{DNBF}_S$ , and was 0.22 mg/L, 0.42 mg/L and 0.68 mg/L in  $\text{DNBF}_L$ . With decreasing EBRTs, the effluent  $\text{NO}_2^-$ -N concentration in both biofilters increased but with concentrations always below 1 mg/L. In the study of Gomez *et al.* [23],  $\text{NO}_2^-$ -N was accumulated with the concentration of around 5 mg/L with glucose as the carbon source, while it was less than 1 mg/L with methanol or ethanol as the carbon source. Foglar and Briski [24] obtained that the accumulated  $\text{NO}_2^-$ -N concentration was 1.2 mg/L with methanol as the carbon source.

Under EBRTs of 30 min, 15 min and 7.5 min, the influent turbidity was 3.78, 4.21 and 4.38 NTU, respectively, the effluent turbidity was 1.10, 1.63 and 2.01 NTU in  $\text{DNBF}_S$ , and was 1.21, 1.71 and 2.13 NTU in  $\text{DNBF}_L$ . With decreasing EBRTs, the effluent turbidity of both biofilters gradually increased, and the turbidity of  $\text{DNBF}_S$  was slightly lower than that of  $\text{DNBF}_L$ . In the study of Jimenez and Buitron [25], the influent turbidity was 5.1–8.8 NTU and the effluent turbidity was 1.8–2.9 NTU with the tertiary filter media size of 5.5 mm. With the media size between 6.3 and 12 mm, the turbidity was removed from 8.41 NTU to 0.71–0.81 NTU in a denitrify biofilter [26].

### 3.2. Dynamics of Oxidized Nitrogen along the Biofilter Depth

Samples were taken every 10 cm along the biofilter depth, and dynamics of nitrite and nitrate are shown in Figure 4.

**Figure 4.** Dynamics of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N concentrations in both biofilters along the biofilter depth. (a)  $\text{DNBF}_L$  with large sand size; (b)  $\text{DNBF}_S$  with small sand size.



The dynamics along the biofilter depth was also converted to dynamics with time and was then regressed by the linear equation. Under EBRTs of 30 min, 15 min and 7.5 min, in  $\text{DNBF}_S$ , the

reduction rates of  $\text{NO}_3^-$ -N to  $\text{NO}_2^-$ -N were 0.38 mg/(L·min), 0.82 mg/(L·min) and 1.93 mg/(L·min), and the reduction rates of  $\text{NO}_2^-$ -N to  $\text{N}_2$  were 0.36 mg/(L·min), 0.81 mg/(L·min) and 1.82 mg/(L·min); in  $\text{DNBF}_L$ , the reduction rates of  $\text{NO}_3^-$ -N to  $\text{NO}_2^-$ -N were 0.32 mg/(L·min), 0.50 mg/(L·min) and 0.86 mg/(L·min), and the reduction rates of  $\text{NO}_2^-$ -N to  $\text{N}_2$  were 0.31 mg/(L·min), 0.47 mg/(L·min) and 0.77 mg/(L·min). With decreasing EBRTs, the denitrification rate increased in both biofilters, and the denitrification rate in  $\text{DNBF}_S$  was higher than that in  $\text{DNBF}_L$ . In addition, the reduction rate of  $\text{NO}_3^-$ -N to  $\text{NO}_2^-$ -N was higher than that of  $\text{NO}_2^-$ -N to  $\text{N}_2$  in both biofilters, which could be used to explain why  $\text{NO}_2^-$ -N was accumulated.

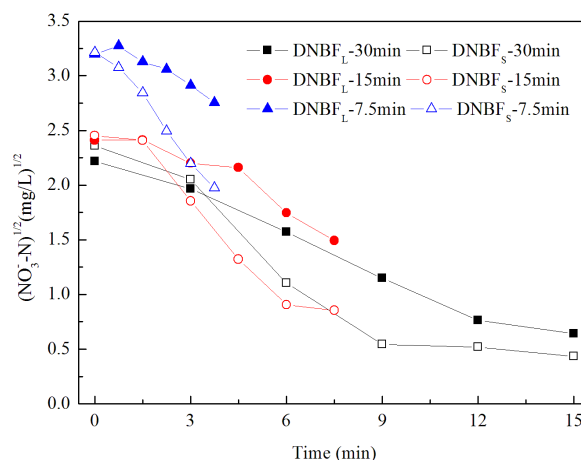
Wastewater flow along the biofilter depth could be considered as a plug flow, and denitrification could be described with a half-order reaction as follows [27].

$$C = C_i \left(1 - \frac{1}{2} \frac{k_{1/2v} HA}{C_i^{1/2} Q}\right)^{1/2} \tag{4}$$

where,  $C$  is the  $\text{NO}_3^-$ -N concentration at different biofilm depths (mg/L);  $C_i$  is the initial  $\text{NO}_3^-$ -N concentration at the inlet of biofilter (mg/L);  $k_{1/2v}$  is the half-order coefficient ((mg/L)<sup>1/2</sup>/min);  $H$  is the biofilter depth from the inlet (dm);  $A$  is the area of biofilter (dm<sup>2</sup>) and  $Q$  is the flow rate (L/min).

The result regressed by the half-order equation is shown in Figure 5. Good linear relationships between the half-order  $\text{NO}_3^-$ -N concentration and the EBRT were obtained in both biofilters under all EBRTs. Under EBRTs of 30 min, 15 min and 7.5 min, the half-order coefficients were 0.42, 0.48 and 0.70 (mg/L)<sup>1/2</sup>/min in  $\text{DNBF}_S$ , and were 0.22, 0.24 and 0.25 (mg/L)<sup>1/2</sup>/min in  $\text{DNBF}_L$ , respectively. With decreasing EBRTs, the half-order coefficient increased significantly in  $\text{DNBF}_S$ , while there was only a slight increase in  $\text{DNBF}_L$ . Hanning *et al.* [28] obtained the half-order coefficient of 0.18 (mg/L)<sup>1/2</sup>/min in a denitrification filter with media sizes of about 5–6 mm and the influent  $\text{NO}_3^-$ -N concentration of 5–6 mg/L, which was similar to that obtained in  $\text{DNBF}_L$  in this study. In addition, Hanning *et al.* [28] found that the half-order coefficient increased with increasing the initial nitrate concentrations. This might be one of the reasons responsible for the increased half-order coefficient at the EBRT of 7.5 min in  $\text{DNBF}_S$ , where the initial nitrate concentration was relatively high. In addition, the high flow rate at the low EBRT might be another reason for the increased half-order coefficient. For example, in fluidized bed biofilters with good hydraulic conditions, this value could be as high as 12 (mg/L)<sup>1/2</sup>/min [27].

**Figure 5.** The half order nitrate concentration as a function of the residence time in both biofilters under different empty bed retention times (EBRTs).

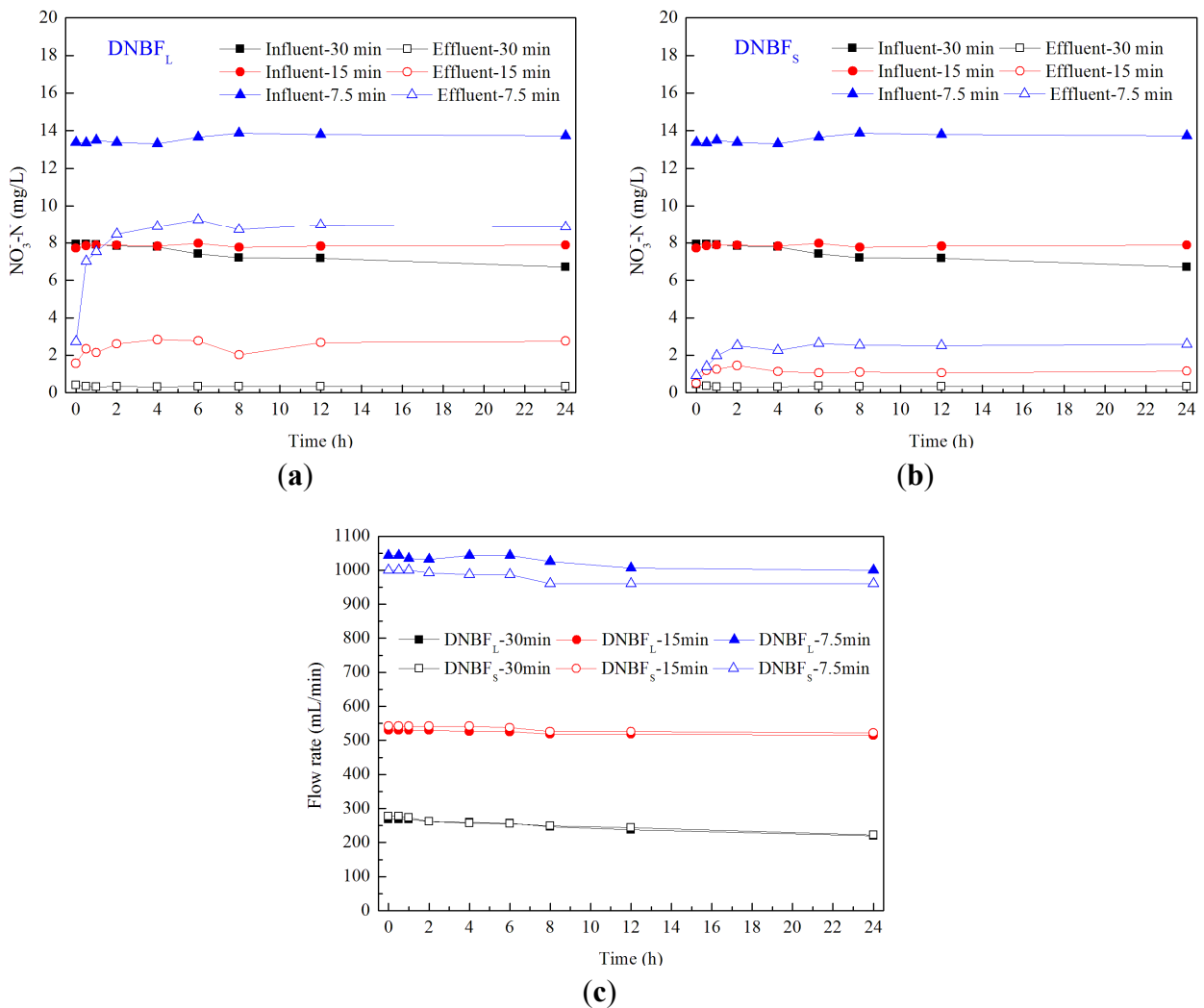




3.3. Performance of Biofilters within a Backwashing Cycle

Samples were taken at intervals starting from the end of the backwashing to the beginning of the next backwashing, and the results are given in Figure 6. During the backwashing, the performance of both biofilters was stable, with the removal percentage of  $\text{NO}_3^-$ -N fluctuated within 5%. While the flow rate was slightly decreased in both biofilters during the backwashing cycle. Under EBRTs of 30 min, 15 min and 7.5 min, the flow rate decreased to 80%, 96% and 96% of the initial flow rate after 24 h operation in  $\text{DNBF}_S$ , while to 82%, 97% and 97% in  $\text{DNBF}_L$ , respectively. With decreasing EBRTs, the decreased percentage of the flow rate reduced gradually. In addition, due to the higher head loss in  $\text{DNBF}_S$  with small size sands, its flow rate decreased slightly higher than that in  $\text{DNBF}_L$  with large size sands. Under the inlet flow rate of 0.3 L/min, 0.4 L/min, 0.5 L/min and 0.6 L/min, when compared to the large particle size sand filter, Moore *et al.* [6] found that the flow rate was reduced by 66%, 70%, 37% and 38% during a backwashing cycle in the small particle size sand filter.

**Figure 6.** Dynamics of  $\text{NO}_3^-$ -N and flow rate within one backwashing cycle in both biofilters under different EBRTs. (a) Dynamics of  $\text{NO}_3^-$ -N in  $\text{DNBF}_L$ ; (b) Dynamics of  $\text{NO}_3^-$ -N in  $\text{DNBF}_S$ ; (c) Dynamics of flow rates in  $\text{DNBF}_L$  and  $\text{DNBF}_S$ .



#### 4. Conclusions

(1) At EBRTs of 30 min, 15 min and 7.5 min, the  $\text{NO}_3^-$ -N removal percentage was 93%, 82% and 83% in DNBF<sub>S</sub> with sand size of 2–4 mm, and was 92%, 68% and 36% in DNBF<sub>L</sub> with sand size of 4–6 mm, respectively.

(2) With the influent  $\text{NO}_3^-$ -N loading rate ranged from 0.32 kg/(m<sup>3</sup>·d) to 2.28 kg/(m<sup>3</sup>·d), the removed  $\text{NO}_3^-$ -N loading rate increased with increasing the influent  $\text{NO}_3^-$ -N loading rate.

(3) Under EBRTs of 30 min, 15 min and 7.5 min, the half-order coefficients were 0.42, 0.48 and 0.70 (mg/L)<sup>1/2</sup>/min in DNBF<sub>S</sub>, and were 0.22, 0.24 and 0.25 (mg/L)<sup>1/2</sup>/min in DNBF<sub>L</sub>, respectively.

(4) During the backwashing cycle, the performance of both biofilters was stable, and the removal percentage of  $\text{NO}_3^-$ -N fluctuated within 5%.

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#### Author Contributions

Nan Wei and Yunhong Shi carried out the experiment and prepared the first edition of the manuscript. Guangxue Wu and Hongying Hu took charge of the whole framework of this work. Yihui Wu and Hui Wen contributed to the collection and analysis of the experiment data.

#### Conflicts of Interest

The authors declare no conflict of interest.

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