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CONTROL STRATEGIES OF NITRITE ACCUMULATION IN A SUBMERGED BIOFILTER

Abstract: *Short-cut nitrification under various Nitrogen Loading Rate (NLR), dissolved oxygen (DO) concentrations and pHs at a constant temperature of 25 ±1 0C was investigated in a submerged biofilter reactor. The lowest NO_2-N/NO_x-N ratio was observed when the NLR was up to 160 g/m^3·day. Further increase the NLR resulted in incomplete oxidation of ammonium and the effluent NH_4-N and NO_2-N concentration increased. Although the highest NO_2-N/NO_x-N ratio of 0.61 was achieved, the NH_4-N removal efficiency was drastically dropped to 48% at the NLR of 294 g NH_4-N/m^3.day. The highest NO_2-N/NOx-N ratio of 0.68 was achieved at the pH of 9.0 and 1.0 mg O_2/l. However, NN_4-N removal efficiency and the NO_2-N/NO_x-N ratio were sharply dropped to 33% and 0.55 by getting the NLR to 381 g NH_4-N/m^3·day at the DO concentrations of 2.0 mg/l.*

Key words: partial nitrification, NO2-N/NOx-N ratio.

INTRODUCTION

In order to eliminate ammonium in the wastewater, biological method is widely applied because; the low cost and the nitrogen compounds are converted to the biomass and nitrogen gas. A recirculated supernatant generated from the wastewater treatment plants (WWTP) with anaerobic sludge digestion, contributes to 15-20% of the influent nitrogen load [1]. Currently, many municipal wastewater treatment plants encounter the problem of overload of NH_4-N, which makes it difficult to be biologically nitrified generated in side-stream wastewaters such as nitrified municipal sludge decants. This high level of ammonium makes it difficult to be biologically nitrified due to the ammonia toxicity to nitrifiers and the extensive oxygen requirement for nitrification. Therefore it is desirable to treat ammonium rich supernatant before returning to the head of wastewater treatment plant [2]. In the partial nitrification processes, since NO_2-N and NO_3-N are intermediary compounds in nitrification and denitrification, a partial nitrification to NO_2-N and denitrification from accumulated NO_2-N, instead from NO_3-N, would be feasible [3]. In recent years, partial nitrification process has been great attention for nitrogen compounds removal because of the low operational cost of this process considering the DO and organic carbon requirements [4-8]. Accumulation of NO_2-N in the effluent water could be achieved by operating the experimental set-up under high pH, low DO concentrations, short sludge retention time, etc.

In this study, the environmental factors such as DO concentrations and pH affects on the NH_4-N removal efficiency and NO_2-N/NO_x-N ratio were investigated at various nitrogen loading rate (NLR).

The experiments were carried out at constant temperature of 25^0C in the submerged biofilter.

2. MATERIALS AND METHODS

2.1. FEED WASTEWATER

The synthetic wastewater, which was contained trace metals and vitamins necessary to maintain bacterial growth, was used in the experimental study. The synthetic wastewater constituents was presented in the Table 1 [2].

2.2. REACTOR SET-UP AND OPERATION

The PNBR had a liquid volume of 2.6 liter and was filled with plastic coils which was provided 0.5 m^2 resulting in 188.5 m^2 surface area/m^3 for bacterial growth and completely submerged. The influent wastewater was pumped continuously to the bottom of PNBR using peristaltic pump and discharged from the top of reactor to an effluent tank. The PNBR was operated at the temperature of 25^0C ± 1 and an air diffuser was installed directly at the bottom and the DO concentration was measured periodically at the top of reactor by using a DO meter (YSI 5100). The schematic diagram of experimental set-up was presented in the Figure 1.

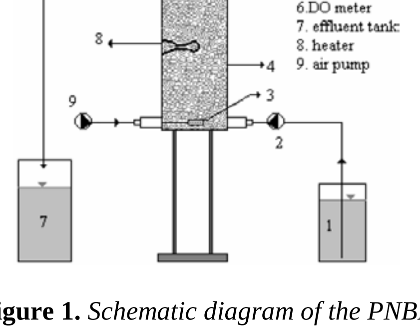

Figure 1. *Schematic diagram of the PNBR*

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The partial nitrification bioreactor (PNBR) was inoculated with microorganisms taken from the nitrification batch reactor in the laboratory of Environmental Engineering Department.

Table 1. *Synthetic wastewater constituents [2]*

Chemicals	Concent. (mg/l)	Chemicals	Concent. (mg/l)
NH_4Cl	100–400	$CoCl_2{\cdot}6H_2O$	0,0119
Na_2EDTA	4,83	$Na_2MoO_4.{\cdot}2H_2O$	0,066
$CuSO_4$	0,0046	$MgSO_4{\cdot}7H_2O$	36,97
$ZnSO_4{\cdot}7H_2O$	0,023	$NaHCO_3$	226
$CaCl_2{\cdot}2H_2O$	36,74	$FeCl_3{\cdot}6H_2O$	0,316
H_3BO_3	1,0	KH_2PO_4	1920

The initial pH value of feeding wastewater was adjusted to be 7.5, 8.0, 8.5, and 9.0 at the DO concentration of 1.0±0.2 mg/l. The DO concentration affects on the NO_2-N accumulation and NH_4-N oxidation was also tested for 1.0±0.2 and 2.0±0.2 mg/l at constant pH value. The NLR was increased gradually by varying the influent NH_4-N concentration of PNBR.

2.3. ANALYTICAL METHODS

The PNBR effluents were collected daily and filtered using 0.45 µm, white, 47 mm radius filters to remove impurities. The concentrations of NH_4-N, NO_3-N and NO_2-N were tested by using analytical kits; NH_4-N (14752), NO_2-N (14776) and NO_3-N (14773) with the Merck photometer (Nova 60 Model). The analysis of samples was carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. START-UP PERIOD

The main goal of start-up period was to promote nitrification organisms growth to obtain attachment and biofilm formation onto the filling materials. The PNBR was operated in a batch mode with water recycling. The influent wastewater pH and DO concentrations at the top of PNBR was adjusted to 7.5 and 2.0 mg/l, respectively. The NH_4-N removal efficiency of 80% achieved during the first two weeks operation. During the start-up periods NO_2-N was not detected and nitrification was quickly completed to nitrate. After the start-up period, the PBNR was operated in a continuous mode and the NH_4-N concentration in the influent water was increased gradually.

The PNBR was operated at various pH values, DO concentrations, and NLRs to determine optimal operational condition to achieve the highest NO_2-N/NO_x-N ratio and NH_4-N removal efficiency.

3.2. THE NLR EFFECTS ON THE NO_2-N/NO_X-N RATIO

Variation of the NLR was provided with changing influent NH_4-N concentrations and flow rate of water between 50-260 mg NH_4-N/l and 3.3-5.0 l/day (hydraulic retention time (HRT) was between 12.2 and 18.5 hour), respectively.

The NLR was gradually increased from about 100 to 160 g/m^3·day by varying the influent NH_4-N concentration in the feeding wastewater. This change resulted in complete oxidation of NH_4-N, the NH_4-N removal efficiency was increased from 88 to about 98% and the NO_2-N concentration slightly increased to 5.0 mg/l in the effluent water. The lowest NO_2-N/NO_x-N ratio was observed when the NLR was up to 160 g/m3·day. Further increase the NLR caused partial nitrification and resulted in incomplete oxidation of ammonium and the effluent NH_4-N and NO_2-N concentration increased. The NO_2-N accumulated in effluent water and the NO_2-N/NO_x-N ratio was increased to 0.293 at the NLR of 196 g NH_4-N/m^3.day. Although the highest NO_2-N/NO_x-N ratio of 0.61 was achieved, the NH_4-N removal efficiency was drastically dropped to 48% at the NLR of 294 g NH_4-N/m^3.day (Figure 2). As shown in Figure 2, it was evident that the PNBR was unable to provide high NH_4-N oxidation when the NLR was higher than 196g NH_4-N/m^3·day under experimental conditions. During the NLR experimental studies, free ammonia (FA) concentrations were between 1.0-3.2 mg/l and the free nitric acid (FNA) (HNO_2) concentrations were lower than the inhibition level.

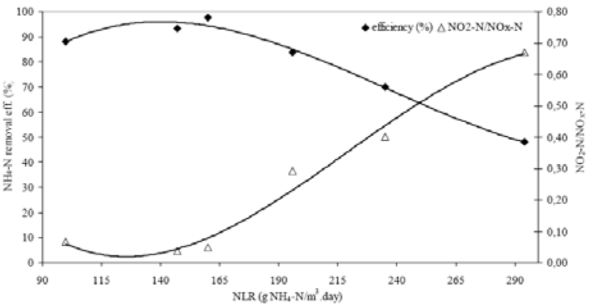

Figure 2. *NO_2-N/NO_x-N ratio and removal efficiency variation at different NLR*

3.3. EFFECTS OF pH VARIATION ON THE NO2-N/NOX-N RATIO

The pH and DO concentration effects on the NO_2-N accumulation were investigated to achieve the highest NO_2-N/NO_x-N ratio under operational conditions. The ammonium-oxidizing bacteria (AOB) and the nitrite oxidizing bacteria (NOB) were inhibited 10-150 mg/l and 0.1-1.0 mg/l of free ammonia (FA), respectively and all nitrifying bacteria were inhibited above 0.2 mg/l of free nitric acid (FNA) (HNO_2) [9]. The equation 1 and 2 are used for the calculations of FA and (FNA) concentrations [9]. Since the NO_2-N accumulation is achieved by FA, the feeding solutions of pHs was varying between 7.5 and 9.0 at DO concentrations of 1.0 and 2.0 mg/l, respectively.

$$FA(mg/l) = \frac{17}{14}\frac{\sum NH_4 - N(mg/l)\cdot 10^{pH}}{e^{6344/(273+T)} + 10^{pH}} \quad (1)$$

$$HNO_2(mg/l) = \frac{47}{14}\frac{\sum NO_2 - N(mg/l)}{e^{-(2300/273+T)}\cdot 10^{pH}} \quad (2)$$

Effect of operational conditions on the NO_2-N/NO_x-N ratio was presented in the Figure 3. Under the operational conditions, the PNBR was operated at higher NLR for the DO concentration of 2.0 mg/l than 1.0 mg/l. The pH affects the NOB and the NO_2-N/NO_x-N ratio in the effluent water was increased by increasing the pH value to 9.0 in the feeding wastewater for both DO concentrations. The highest NO_2-N/NO_x-N ratio of 0.68 and 0.55 were achieved for the DO concentrations of 1.0 and 2.0 mg /l at the applied NLR for the 325 and 381 g/m^3·day, respectively. Increasing DO concentration from 1.0 to 2.0 mg/l decreased the NO_2-N accumulation and NH_4-N removal efficiency.

The results indicated that pH had a clear effect on the NLR and NO_2-N/NO_x-N ratio even at DO concentration as high as 2.0 mg/l. Although the ratio of NO_2-N/NO_x-N was 0.6 at the pH of 7.5, increasing the pH value from 7.5 to 8.0, the removal efficiency was slightly decreased from 48 to 38 % at the NLR of 292 NH_4-N/m^3·day. In order to increase the NH_4-N removal efficiency, the NLR of 282 g NH_4-N/m^3·day was tested at the pH of 8.5. The NH_4-N removal efficiency and NO_2-N oxidation increased to 54% and 0.57, respectively. The highest NO_2-N/NO_x-N ratio of 0.68 was achieved at the pH of 9.0 and NLR of 325 g NH_4-N/m^3·day. However, the NH_4-N removal efficiency decreased slightly to 52%. Anthonisen et al. (1976) reported that the NOB is more sensitive than the AOB to the FA. The activity of NOB was inhibited at high pH due to the FA concentration increases with increase in pH value.

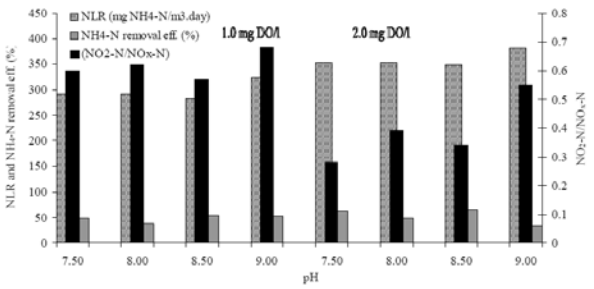

Figure 3. *Variations of the NO_2-N-NO_x-N ratio at various DO, pH and NLR*

The experimental studies confirmed that NO_2-N accumulation could be achieved by regulating pH to control FA concentration. But the threshold inhibition concentrations of FA found in the literature were different [10] and Kim et al [11] reported that the NO_2-N accumulation can not be provided for a long time by using only pH for control strategies.

3.4. DO CONCENTRATIONS EFFECTS ON THE NO2-N/NOX-N RATIO

Effects of DO on the NO_2-N accumulation were tested for concentrations of 1.0 and 2.0±0.2 mg O_2/l at constant pH of 9.0. The growth rate of NOB at low DO concentration was lower than the AOB, which will result in NO_2-N accumulation [6]. It is known from the Figure 2 that, 48 % NH_4-N removal efficiency and 0.67 NO_2-N/NO_x-N ratios was obtained at the NLR of 294 g NH_4-N/m^3·day. The biofilter was operated at the NLR of 325 and 381 at the DO concentrations of 1.0 and 2.0 mg/l, respectively (Figure 4). The highest NO_2-N/NO_x-N ratio of 0.68 was achieved at the pH of 9.0 and 1.0 mg O_2/l. However, N_4-N removal efficiency and the NO_2-N/NO_x-N ratio were drastically dropped to 33% and 0.55 by getting the NLR to 381 g NH_4-N/m^3·day.

Low concentrations of DO, inhibited the NOB and the NO_2-N/NOx-N ratio was ascending by accumulating the NO_2-N concentrations in the effluent water, the previous experimental study carried out at the biofilm system was confirmed this results [1, 12]. The accumulation of NO_2-N in the effluent water could be controlled also by varying the biological reaction time by the HRT and NLR.

The previous experimental study indicated that the HRT positively affects the NO_2-N/NOx-N ratio by decreasing the HRT [13 and 14]. This change resulted in incomplete oxidation of NH_4-N and the effluent NH4-N concentration increased. Although, the NO_2-N accumulation was greater at the short reaction time compared to longer one, the NH_4-N oxidation was limited and the NH_4-N concentrations were increased in the effluent water. As a result it could be determined that the HRT and NLR have significant effect on the NO_2-N/NO_x-N ratio in the PNBR. A convenient HRT and NLR should be applied to achieve partial nitrification. Due to the DO half-saturation coefficients of AOB is lower than the NOB, low DO concentration is more restrictive for the growth of NOB than AOB, which will result in nitrite accumulation [15].

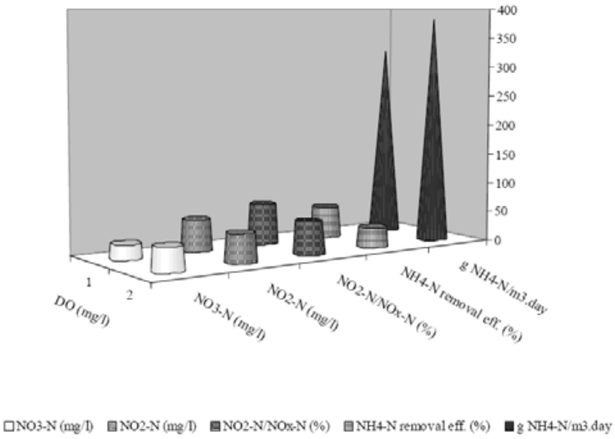

Figure 4. *DO effects on the oxidation of NH_4-N and NO_2-N/NO_x-N ratio*

CONCLUSION

The PNBR was operated at various pH, DO, and NLR at constant temperature to determine the highest NH_4-N oxidation and NO_2-N/NO_x-N ratio. The AOB grow faster than the NOB at elevated temperatures (>15 0C). Although the PNBR was operated at low temperature considering the optimal temperature for the NOB, considerable NO_2-N accumulation was obtained by using submerged biofilter at the temperature of 25^0C. The highest NO_2-N/NO_x-N ratios was achieved at the pH and DO concentrations 9.0 and 1.0 mg/l, respectively. However, the PNBR could be operated at high NLR by ascending the DO concentrations to 2.0 mg/l. The effluent water of PNBR can be used for the Anommox processes which needs about 1/1 NH_4-N/NO_2-N ratio.

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