DENITIRIFICATION TREATMENT OF NITRIFIED HANOI GROUNDWATER USING SWIM BED TECHNOLOGY

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ABSTACT

An attached-growth denitrifying swim-bed reactor using thread type acrylic resin biomass carrier (Biofringe:BF) was shown to be effective for achieving high nitrogen removal performances. Very low effluent TN levels of less than 2 mg N/*l* were obtained even at a high volumetric loading rate (VLR) of 0.72 kg/m^3/d, corresponding to an HRT of only 1 hour with an influent of 30 mg/*l* NO_3-N. Even at an extremely high VLR of 1.44 kg/m^3/d, high denitrification efficiencies of 80~90% were obtained with effluent TN concentration of about 3~6 mg/*l*, which are below the maximum allowable level for nitrogen in drinking water. The BF biomass carrier also offered a big advantage with respect to sludge retention capacity, which was demonstrated in low effluent SS levels even at an HRT as short as one~half hour.

No reduction in denitrification efficiencies were observed at high bulk DO levels of up to 1.5 mg/*l* as well as low temperature of 12°C. Slight decrease in denitrification efficiencies occurred when the VLR was sharply increased. This demonstrated that denitrifying bacteria in the swim-bed reactor were in sufficient number and quickly adapted to a sharp increase in VLR. The result obtained in this study demonstrates that denitrification in swim-bed reactor is less sensitive in comparison to other. This process can reduce sensitivity to the change of operational conditions.

KEY WORDS

Groundwater contamination, denitrification, nitirification, Hanoi groundwater, Swim bed, Biofringe

INTRODUCTION

Nitrate is considered to be relatively nontoxic for adults but it can cause health problems for infants. Nitrate can easily be converted to nitrite in the environment by bacteria. In infants, nitrite interacts with the hemoglobin in red blood cells, which causes an oxygen deficiency resulting in methemoglobinemia, commonly known as "blue baby syndrome". The Would Health Organization (WHO) has set maximum allowable concentrations of NO_3^--N and NO_2^--N to be 11.3 mg/*l* and 0.9 mg/*l*, respectively, in drinking water. [1)]In order to meet the WHO standard, nitrogen removal treatment must be applied. Nitrification of ammonium-contaminated Hanoi Groundwater was conducted in previous studies[2),3)]

In this research, biological nitrate removal (denitrification) was experimentally studied. In heterotrophic denitrification process, nitrate acts as the electron acceptor and organic

substrate is electron donor. Ethanol was selected as organic carbon source for denitrification in this study.

The swim-bed attached growth technology applied in this study offered many advantages for heterotrophic denitrification process such as a long sludge retention time, low effluent suspended solids concentration and turbidity, reduced sensitivity to toxic loads, high treatment efficiency and no need for sludge recycle. [4]It also eliminates head losses with absence of clogging and channeling, which cannot be easily avoided in fix-bed processes. This swim-bed technology was firstly applied for the treatment of nitrified Hanoi groundwater and its denitrifying capabilities were evaluated experimentally in bench-scale experiments.

MATERIALS AND METHODS

Experimental system

Figure. 1 shows a schematic diagram of the experimental system used in this study. The reactor used in this study was made from acryl resin and had a diameter of 210 mm and the height to the outlet port was 390 mm with a total volume of 14 *l*. The reactor had two main parts, the central column of 50 mm in diameter and 365 mm in height served as a

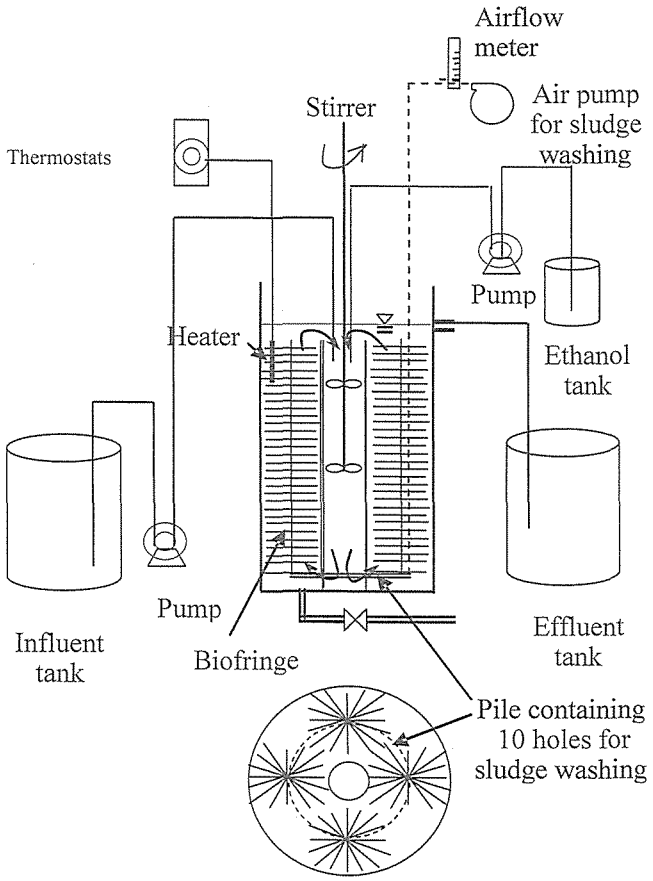

Fig. 1-Schematic diagram of denitrification reactor using biofringe (DNBF)

mixing zone and downdraft section. The mechanical stirrer (FBLM 575 W-A, 3000 rpm) was placed in this zone for mixing as well as providing circulation throughout the reactor. Influent and ethanol-phosphate solutions were introduced within the downdraft section of the mixing zone using peristaltic pumps. The operational temperature of the reactor was maintained at 25°C. The biological zone in the updraft section contained four double-yarns of acrylic fiber biomass carrier (Biofringe: BF, NET Co. Ltd.) as biomass carriers. The support filament of 325 mm in length contained 103 fringe yarns for each BF carrier. The total volume packing ratios and specific surface areas of the BF carrier were 0.69 % and 12.5 m^2/m^3, respectively. A pipe of 9 mm in diameter connected to an air pump containing 10 holes of 0.1 mm in diameter was placed in the bottom of the reactor for back washing. The DNBF reactor was initially seeded with laboratory activated sludge cultivated by fill and draw cultivation method using synthetic wastewater made of peptone and meat extract. The denitrification activity of this seed sludge was determined to be 2.5 mg-N/g-VSS/h

Experimental procedures

For startup of the reactor, 28 g of seed activated sludge was inoculated in the DNBF reactor. After the attachment stage of seed sludge, denitrification treatment was started. Synthetic influent containing 30 mg NO_3-N/*l* was introduced for the DNBF reactor. HRT of 10 hours was maintained for an initial NO_3^- VLR of 0.072 kg-N/m^3/d. Then, the NO_3^- VLRs were increased in a stepwise manner by decreasing the HRT to evaluate the denitrification capacity of the DNBF reactor. The influent NO_3^- concentration was increased to 50~90 mg-N/L from day 148 to examine denitrification efficiency of the DNBF reactor at a higher NO_3^- contaminated level.

Synthetic influents

Tap water supplemented with 30 mg NO_3^--N/*l* was used as synthetic influent for DNBF in order to investigate the nitrogen removal performance of the DNBF reactor. An ethanol-phosphate solution was fed separately using a peristaltic pump at C/N ratios in the range of 2.5 to 1. Phosphate was fed as nutrient for biomass growth at P/N ratios of 0.04.

Analytical methods

Influent and effluent NO_3^-, NO_2^- and NH_4^+ were analyzed almost daily. NO_3^- was determined by the colorimetric brucine method using the UV spectrophotometer in this sub-study instead of UV spectrophotometer screening method (Standard Method[5]). Effluent Total-N was determined by the persulfate method. COD, NO_2^-, NH_4^+, DO, pH, SS, MLSS and VSS were measured according to Standard Methods.

RESULTS AND DISCUSSION

Kinetic analysis

Batch experiments were conducted to determine the kinetic parameters of the denitrifying sludge. Two sludge samples were taken from DNBF reactor on days 5 and 45. The Michaelis-Menten kinetic model was applied. **Fig. 2** shows the Lineweaver-Burk's plots used for the determination of the kinetic constants. From these plots, the specific maximum denitrification rate (v_m) and saturation constant (K_m) were determined to be:

V_m= 0.44 mg-N/mg VSS/d and K_m= 25.1 mg NO_3-N/*l* for the sludge sample of day 5
V_m= 0.76 mg-N/mg VSS/d and K_m= 4.06 mg NO_3-N/*l* for the sludge sample of day 45

A much higher maximum denitrification rate and lower saturation constant were obtained for the denitrifying sludge which had a longer acclimation time in the swim-bed DNBF reactor, thus demonstrating a higher affinity of the DNBF sludge for the substrate.

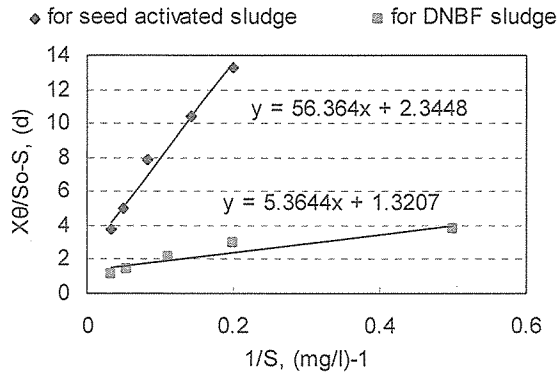

Fig. 2- Lineweaver-Burk's plots for determination of kinetic constant for seed and DNBF sludge

Denitrification performances

Operational conditions for the DNBF process are shown in **Table 1**. **Fig. 3** shows the changes in HRT, VLR, influent and effluent nitrogen concentrations, and denitrification efficiencies during Runs A-G.

In Run A, the DNBF reactor was fed nitrified effluent from nitrified BF reactor (NBF). In this period, the NBF reactor was operated at a short HRT of 5 hours. Nitrification efficiencies of about 80 and 90% and high effluent NH_4^+ concentrations of 2~4.3 mg/*l* were obtained for the NBF reactor in this period. The NBF process influent contained 23-26.5 mg NO_3-N/*l* and 2.5~6 mg (NO_2+NH_4)-N/*l*. Influent DO and pH levels were in range of 4~6 mg/*l* and 6.8~7.4, respectively. The stirrer speed was set at 1,500 rpm and the observed bulk DO concentrations were 1.2~1.5 mg/*l* for the DNBF reactor during this run. The results showed that effluent NO_2-N, NO_3-N, NH_4-N and TN for the DNBF process were close to zero during this run demonstrating that nitrogen was effectively removed and both nitrification and denitrification occurred in the DNBF reactor.

From day 30, the NBF and DNBF reactors were separated, and a medium consisting of 30 mg NO_3^--N/*l* was used as influent for the DNBF reactor. Influent DO and pH levels were in the ranges of 7.0~8.5 mg/*l* and 7.1~7.6, respectively. The DNBF reactor obtained high denitrification efficiencies of 98-100% in Run B. From day 36 the stirrer speed was increased to 2,000 rpm to improve circulation of water through the biological zone (Run C). Bulk DO concentrations in the biological zone increased to 4.0~5.2 mg/*l* during this run. Denitrification efficiencies decreased sharply during this Run and dropped to zero at days 44-48. From these results, it was found that denitrification was inhibited at DO concentration of 4 mg/*l* and stopped when DO concentrations reach to 5 mg/*l* in the swim-bed reactor. At stirrer speed of 1,500 rpm and 2,000rpm, water flow velocities in BF zone were bout 12 cm/s and 22 cm/s, respectively. When the stirrer speed was reduced again to about 1,500 rpm from day 50, the bulk DO concentration decreased to less than

1.2 mg/*l* in Run D and nitrogen removal efficiencies increased sharply to 99% at day 56. Then, VLRs were increased stepwise to 0.72 kg-N/m^3/d corresponding to an HRT as short as one hour (Runs E, F and G). High denitrification efficiencies of 90~100% were obtained in these Runs. The decrease in denitrification efficiencies occurred when the VLR was increased sharply. This demonstrated that denitrifying bacteria in the reactor were in sufficient number and quickly adapted to a sharp increase in VLR.

Denitrification efficiencies decreased to 80~90% in Run H when the VLR was increased to an extremely high level of 1.44 kg-N/m^3/d (HRT was 0.5 hour), which resulted in higher effluent TN levels of 3~6 mg/*l*, but these values were still below the maximal acceptable nitrogen concentration for drinking water[3].

Table 1 - Operational conditions for DNBF reactor (averages)

Run	Days of operation (d)	Inf. NO_3-N conc. (mg/L)	HRT (h)	VLR* (kg NO_3-N/m^3/d)	Stirrer speed (rpm)	Reactor bulk DO (mg/L)	C/N ratio
A	(1-29)	23-29	10	0.072	1600	1.2~1.5	2~2.5
B	(30-35)	30	10	0.072	1600	1.2~1.5	2~2.5
C	(36-49)	30	10	0.072	2000	4.0~5.2	2~2.5
D	(50-59)	30	10	0.072	1600	0.2~1.2	2~2.5
E	(60-78)	30	7-3	0.10-0.24	1600	0.2~1.2	2
F	(79-119)	30	3-1.5	0.24-0.48	1000	0~0.5	2
G	(120-133)	30	1	0.72	1000	0~0.5	2
H	(134-147)	30	0.5	1.44	1000	0~0.5	2
I	(148-155)	50	1	1.2	1000	0~0.5	2
K	(156-160)	60	1	1.44	1000	0.3~0.7	2
L	(161-165)	90	1	2.16	1000	0.3~0.7	2
M	(166-170)	30	1	0.72	1000	0.3~0.7	1
N	(171-173)	30	1	0.72	1000	0.3~0.7	0.8

* VLR: Volumetric loading rate

In order to examine the adaptation of DNBF reactor for the treating higher NO_3^- contaminated groundwater, the HRT was kept at 1 hour and influent NO_3^- concentration was increased to 50~90 mg-N/*l* (Run I, K, L) from day 148. High denitrification efficiencies of 90~95% at VLR of 1.2 kg-N/m^3/d were achieved during Run I. During Run K (VLR: 1.44 kg-N/m^3/d), denitrification efficiencies of 88-90% were achieved. These results demonstrated that for the same loading rate of 1.44 kg/m^3/d, a higher influent NO_3-

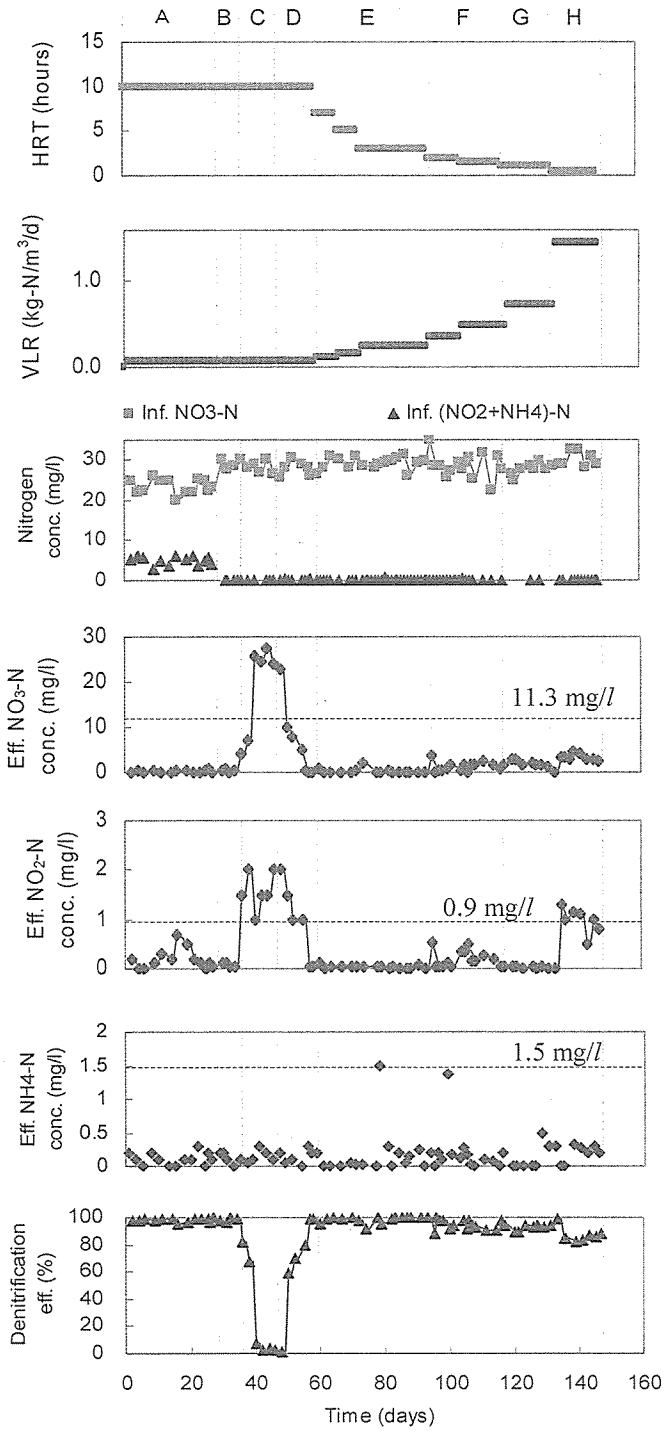

Fig. 3- Change in HRT, VLR, influent and effluent nitrogen concentrations and denitrification efficiencies for DNBF during Runs A-H

N concentration and longer HRT did not have much influence on denitrification efficiency. At a high loading rate of 2.16 kg-N/m^3/d during Run L, denitrification efficiencies decreased to 82~86%, resulting on high effluent TN levels of up to 11.6~16.0 mg-N/*l*. Higher nitrogen removal rates of 1.73~1.84 kg-N/m^3/d were achieved in this Run, but effluent TN concentrations exceed the maximum contaminated limit for TN in drinking water.

DO influence

DO concentration in reactor affected denitrification rates. The denitrification rate decreased sharply with the increase of DO to 4~5.2 mg/L during Run C. At DO of 1.2~1.5 mg/*l* during Run A, B, D, E and 0.3~0.7 mg/*l* during Run H~L, effective denitrification could be achieved with high denitrification efficiencies under high nitrate loading rates up to 1.44 kg-N/m^3/d. At low DO concentrations of closed to zero during Run F, anaerobic reaction occurred resulting in the production of hydrogen sulfide smell and increases in effluent NH_4^+ and COD consumption.

Effect of temperature

The reactor temperature was kept at 25°C throughout the study. During Runs K, L, M and N, at high VLRs of 1.44~2.16 kg-N/m^3/d, the reactor temperature was reduced to 12~13°C due to cold whether even though the heater was set at 25-30°C. No decreases in denitrification efficiencies were observed. High denitrification efficiencies of 90% were still achieved during Runs K, M and N.

Carbon to nitrogen (C/N) ratio and COD consumption

C/N ratio was maintained at a high value of 2~2.5 throughout the experiment to ensure that organic substrate was always available. Changes in influent and effluent NO_3-N and COD concentrations and the changes in removal ratio of COD/NO_3-N and DO concentration were shown in **Fig. 4** and **5**, respectively. 60~90% of COD removals were observed during Runs A, B, and D, with mg COD consumption per mg of NO_3-N denitrified to nitrogen gas were calculated to be 5.0 to 6.8, and the C_{used}/N ratios ranging from 1.41 to 1.64 were estimated during these Runs (1 mg C was approximately 3.9 mg COD). These values were

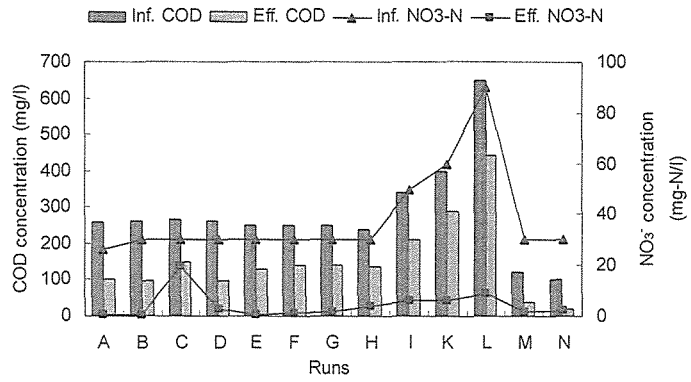

Fig. 4 - Changes in influent and effluent COD and NO_3-N during DNBF experiments

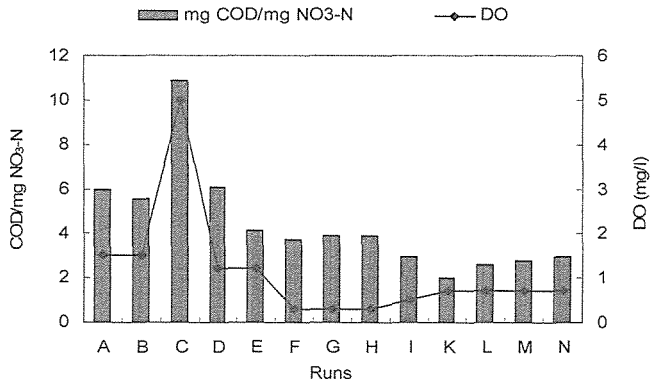

Fig. 5- Changes in removal ratio of COD/NO_3-N and DO concentration during DNBF experiments

high in comparison with the calculated value from the stoichiometry of the denitrificationreaction using ethanol as H-donor for denitrification. (1.05 mg-C/mg NO_3-N). Lower C/N ratio of 1 and 0.8 were applied during Runs M and N for determining the lowest acceptable C/N ratio in continuous denitrification experiment for treating nitrified Hanoi groundwater. The influent contained 30 mg NO_3-N/*l* and HRT was 1 hour during these Runs. Denitrification efficiencies of about 91 and 88% were observed for Runs M and N, respectively. The effluent NO_3^- and NO_2^- concentrations of about 2.7~3.3 and 0.01~0.15 mg-N/*l*, respectively, during these runs, were still much lower in comparison to the maximum allowable level set by WHO, so the applied C/N ratio could be more reduced.

Alkalinity production and pH

For each mg of nitrate nitrogen reduced during biological denitrification about 3.5 mg of alkalinity are produced. Influent alkalinity levels were in a range of 20-90 mg-$CaCO_3$/*l* and effluent alkalinities were between 90 and 190 mg-$CaCO_3$/*l* and the reactor pH levels changed from 7.1 to 8.1 during Runs A~H, which is within the optimum range for denitrification. Adjustment of pH was not requited for efficient denitrification in this study. High NO_3^- influent concentrations of 60~90 mg/*l* resulted on high effluent alkalinity ranging from 250 to 280 mg/*l* during Runs K and L, respectively. Reactor pH levels increased up to 9.1 during these runs. No significant reduction on nitrogen removal rates during these runs.

Effluent SS, sludge yield, and sludge withdrawal

Clear effluent with low SS concentrations of 0~5 mg/*l* were obtained with nitrate VLRs up to 0.48 kg-N/m^3/d. Effluent SS levels increased slightly to 10 and 15 mg/*l* at VLRs of 0.72 and 1.44 kg-N/m^3/d, respectively during Runs G and H. These results demonstrated that the BF biomass carrier could retain high amounts of sludge. The end product of nitrogen gas escaped as gas bubbles, which bound to the suspended sludge and caused sludge to rise to the surface of the reactor. This sludge was estimated to be 0~5 mg per litter of influent and needed to be removed frequently only during Runs F, G and H.

After a long operational period of 140 days, the effluent SS levels decreased to less than 5 mg/*l* event at high VLRs of 1.44 kg-N/m^3/d and short HRT of one hour. A total sludge amount in the DNBF reactor of 148 g was estimated at day 180 and the observed sludge yield (Y_{obs}) of 0.29 g VSS/g NO_3-N removed was estimated for the first 180 days.

Comparison of treatment capability of DNBF reactor with another denitrification reactor

Table 2 shows the comparison of treatment capability of denitrification treatment process for drinking water treatment. As evident from this comparison, our developed swim bed denitrification process showed the extremely high NO_3-N removal rate of 1.26 kg NO_3-N/m^3/d under temperature of 25 ℃. This value is 2 to 3 times higher compared with the removal rates for another reactor. Comparing with another reported denitrification process, our developed process has big advantages of easy and stable operation without clogging problem which is the big obstacle for fixed bed and membrane reactors. Also, our developed process can produce clear effluent without suspended solids. This treatment performance is important of considering the following purification process after biologic al nitrogen removal process.

Table 2- Comparison of denitrification performance for drinking water production in different systems

System	Electron donor	Removal rate (kg NO_3-N/m^3/d)	Temp. (°C)	Reference
Fluidized-bed Bioreactor	Hydrogen	0.34	18-23	6
Fixed-bed Bioreactor	Ethanol	0.75	12	7
Fixed-bed Bio-electrochemical reactor	Hydrogen	0.25	25	8
Immobilized Bioreactor	Starch	0.46		9
Membrane Bioreactor	Ethanol	0.30	25	49
Swim-bed DNBF reactor	**Ethanol**	**1.84***	**13**	**This study**
	Ethanol	**1.26**	**25**	**This study**

*influent NO_3-N: 90 mg N/*l*

CONCLUSION

An attached-growth DNBF swim-bed reactor was shown to be effective for achieving high nitrogen removal performances. Low effluent TN levels of less than 2 mg N/*l* were obtained even at a high VLR of 0.72 kg/m^3/d, corresponding to an HRT of only 1 hour with an influent of 30 mg/*l* NO_3-N. Even at an extremely high VLR of 1.44 kg/m^3/d, high denitrification efficiencies of 80~90% were obtained with effluent TN concentration of about 3~6 mg/*l*, which are well below the maximum allowable level for nitrogen in drinking water. The BF biomass carrier also offered a big advantage with respect to sludge retention capacity, which was demonstrated in low effluent SS levels even at an HRT as short as one-half hour.

The obtained results showing that no reduction of denitrification efficiency was observed at high bulk DO levels of up to 1.5 mg/*l* during Runs A, B, D and E as well as low temperature of 12°C during Runs K-N. Slight decrease in denitrification efficiencies occurred when the VLR was sharply increased. This demonstrated that DNBF denitrifying bacteria were in sufficient number and quickly adapted to a sharp increase in VLR. The result obtained in this study demonstrating that denitrification in the DNBF reactor is less sensitive in comparison to other. This process can reduce sensitivity to the change of operational conditions.

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