PARTIAL NITRITATION OF SYNTHETIC LANDFILL LEACHATE IN AN ATTACHED IMMOBILIZED REACTOR WITH ACRYL FIBER BIOMASS CARRIER

Pham Khac Lieu*, Hiroyuki Tokitoh* and Kenji Furukawa**

** Graduate School of Science and Technology, Kumamoto University Kurokami 2-39-1, Kumamoto 860-855, Japan,*
*** Department of Civil Engineering and Architecture, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-855, Japan*

ABSTRACT

As the first step in intended nitrogen removal by combination of nitritation and ANAMMOX process, the partial nitritation of simulated leachate was studied in lab-scale reactor using acryl resin fiber as the biomass carrier. The influent had ammonium concentration up to 240 mgN/L, TOC/NH_4-N ratio of about 0.1 and quite high concentration of inorganic ions (Ca^{2+}, Mg^{2+}, Fe^{2+}, Cl^-, SO_4^{2-},...) . After start-up time, the reactor was put into operation at HRT of 6 h, volumetric loading rate up to 1.0 kg NH_4-N/m^3.d. The effects of operating factors (e.g. temperature, pH and air flowrate) on responses including ammonium conversion percentage, effluent NO_2-N/NH_4-N ratio and effluent NO_3-N were assessed by statistical screening experimental design. The preliminary results showed that in the experimental circumstance, air flowrate was the most significant factor affecting to the targets and it could get a controllability of partial nitritation. The ammonium conversion of 52-54%, effluent NO_2-N/NH_4-N ratio of about 1.0 and effluent nitrate fraction of about 10% were obtained. These results are well expected for next step of ANAMMOX process.

KEYWORDS

acryl resin fiber, landfill leachate, partial nitritation

INTRODUCTION

In sanitary landfill practices, leachate is either recycled many times to the landfill or collected and sent away for treatment. Although being removed partly during secondary treatment together with organics, ammonium nitrogen is still required further treatment. For biological removal of nitrogen from leachate, conventional nitrification-denitrification with suspended growth, attached growth or combined mode were studied and applied (Kettunen et al., 1996, Pelkonen et al., 1999, Hoilijoki et al., 2000, Jokela et al., 2002, Wellander et al., 1997, Jeong-hoon Im, 2001).

Recently, the development of ANAMMOX process has opened up a new pathway for nitrogen removal from wastewater (Jetten et al., 2001, Schmidt et al, 2003). Partial nitritation, i.e. conversion of a half of ammonium into nitrite, is required as a preceding step for ANAMMOX application. Combination of partial nitritation and ANAMMOX was applied to the treatment of ammonia-rich wastewaters, such as sludge digester liquor (van Dongen et al., 2001, Fux et al., 2002, Twachtmann). Landfill leachate was suggested as a potential object for combined partial nitritation-ANAMMOX treatment.

Partial nitritation so far has been studied as an intermediate step in CANON process (Sliekers, 2002), combined SHARON-ANAMMOX process, or separate step (Ruiz et al., 2003). The process was carried out by suspended growth mode (activated sludge or SBR reactor) for high ammonia influents, or by attached growth mode for low ammonia influents, and almost the studied influents were low or without organic contents. In general, partial nitritation could be achieved by selective inhibition of nitrite oxidizers and making ammonium oxidizers favorable. The way to do this included carrying out the process at high temperature, low dissolved oxygen and short HRT (Ruiz et al, 2003, So-Hyun J. et al., 2000).

Acryl resin fiber has been used successfully as attaching material for nitrification of groundwater at the Environmental Sanitary Engineering Laboratory of Kumamoto University (Furukawa, 2003).

This paper presents some first results of investigation on the partial nitritation stage of synthetic landfill leachate using acryl resin as biomass carrier.

MATERIALS AND METHODS

Reactor system

The nitritation process was studied using a reactor system controllable in influent flow, air flow, pH and temperature. The system's scheme is shown in Fig.1. The reactor is made from acryl resin, has a total volume of 5.0 L and an liquid volume of 4.65 L (Fig.2, left). The biomass carrier is acryl resin fiber, being prepared in form of a net (Fig.2, right). Two pieces of net were used and each of them has the size of 28 cm x 40 cm. and the weight of 27 g.

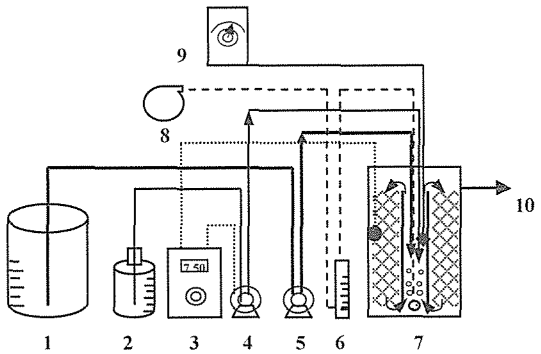

Fig. 1. Scheme of nitritation reactor system
(1) Influent tank (2) $NaHCO_3$ solution (3) pH controller
(4) $NaHCO_3$ pump (5) Influent pump (6) Airflow meter
(7) Reactor (8) Air pump (9) Heater (10) Effluent

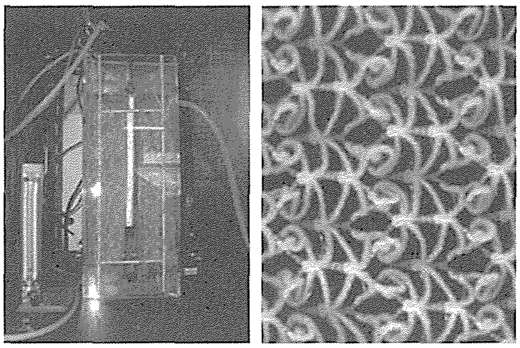

Fig.2. Photos of nitritation reactor (left) and biomass carrier (right)

Influent composition and analysis

Landfill leachate is generally characterized by high concentration of organic, nutrient and inorganic constituents (Tchobanoglous, 1993). Regarding to organic and nitrogen contents, leachate from mature landfill or after secondary anaerobic treatment contains relatively low degradable organic matter but still high ammonia concentration (Hoilijoki et al., 2000). However, it is difficult to give a representative range of ammonium. For example, leachate from an 8 year-age landfill in Ammassuo, Finland contained 110~160 mg NH_4-N/L (Jokelaa et al., 2002); an anaerobically pretreated landfill leachate also in Finland had 53~270 mg NH_4-N/L (Hoilijoki et al., 2000). A 6 month-survey at Nam Son landfill in Vietnam gave an ammonium concentration range of leachate after three treatment ponds of 107 ~ 630 mg-N/L (Hung et al., 2003).

In this study, a synthetic leachate which simulates mature or anaerobically pre-treated leachate was used as influent. The desired composition parameters are shown in Table 1. All chemicals were pure grade and made available as stock solutions. Influents were prepared by diluting with tap water.

Parameters being monitored daily for influent and effluent included pH, NH_4-N, NO_2-N, NO_3-N and alkalinity. Parameters such as TOC and DO were determined irregularly. Analytical methods for parameters were followed the Standard Methods (APHA, 1995). pH was measured with Mettler 320 pH meter (TOLEDO). Nitrogen compounds were determined spectrophotometrically using U-2010 Spectrophotometer (HITACHI). Measuring TOC was performed on TOC-5050 Analyzer (SHIMADZU) and DO was measured with OM-51 DO meter (HORIBA).

Design of experiment (DOE) methodology

To evaluate effects of operational conditions on partial nitritation process, the methodology from DOE was adopted. Temperature (T), pH and air flowrate (AirQ) were factors; and ammonium conversion rate, effluent NO_2-N/NH_4-N ratio and effluent NO_3-N percentage were responses for DOE. The experimental matrix for screening DOE which is in random order and includes 11 runs is presented in Table 2. Each run was designed in a period of 4~5 days or 16~20 HRTs.

Table 1. Composition of synthetic leachate

Component	Concentration, mg/L
1. NH_4Cl	916
2. KH_2PO_4	43.4
3. $NaHCO_3$	420
4. $KHCO_3$	500
5. $C_8H_5O_4K$ (*)	37.5
6. $FeSO_4.7H_2O$	16
7. Na_2.EDTA	16
8. $CaCl_2.2H_2O$	235.2
9. $MgSO_4.7H_2O$	328

(*) *Potassium hydrogen phthalate*

Table 2. Experimental design matrix

Run #	X_1	X_2	X_3	T, °C	pH	AirQ, L/min
1	0	0	0	32.5	7.5	0.3
2	-1	1	-1	30	7.8	0.1
3	1	1	-1	35	7.8	0.1
4	-1	-1	1	30	7.2	0.5
5	0	0	0	32.5	7.5	0.3
6	1	1	1	35	7.8	0.5
7	1	-1	1	35	7.2	0.5
8	-1	1	1	30	7.8	0.5
9	0	0	0	32.5	7.5	0.3
10	1	-1	-1	35	7.2	0.1
11	-1	-1	-1	30	7.2	0.1

Data were treated statistically using STATGRAPHICS Plus 5.1. Two regression models were used to evaluate effects of factors. One is DOE defined model which does not contain three-factor interaction (Eq.1), and the other includes three-factor interaction (Eq.2):

$$Y_i = b_0 + b_1 \times X_1 + b_2 \times X_2 + b_3 \times X_3 + b_{12} \times X_1 \times X_2 + b_{13} \times X_1 \times X_3 + b_{23} \times X_2 \times X_3 \quad \text{(Eq.1)}$$

$$Y_i = b_0 + b_1 \times X_1 + b_2 \times X_2 + b_3 \times X_3 + b_{12} \times X_1 \times X_2 + b_{13} \times X_1 \times X_3 + b_{23} \times X_2 \times X_3 + b_{123} \times X_1 \times X_2 \times X_3 \quad \text{(Eq.2)}$$

Where,

Y_1: NH_4 conversion rate (%); Y_2: NO_2-N/NH_4-N ratio; Y_3: effluent NO_3-N/total-N (%)

X_1, X_2, X_3: coded values for factors T, pH and AirQ, respectively (X_i=-1 for low level, X_i=0 for center point, and X_i=+1 for high level)

Batch experiment

After run#11, a portion of sludge was detached from the reactor and used for a batch experiment to evaluate its nitritation capacity. The medium used for batch experiment contained 381.7 mg/L NH_4Cl (or 100 mg-N/L); 88 mg/L KH_2PO_4 (or 20 mg-P/L); 15 mM $KHCO_3$, 15 mM $NaHCO_3$; and 1mL/L trace element solution. The volume of medium was 1L, the initial MLVSS was 2,700 mg/L, the temperature was kept at 30°C and the aeration was done with excess amount of oxygen. Samples were taken after starting aeration and after 1,2,3,4, and 6 hours. Parameters including alkalinity, NH_4-N, NO_2-N, and NO_3-N were analyzed. The Monod kinetic model was applied for treatment of data.

RESULTS AND DISCUSSION

Reactor start up

The reactor was seeded with activated sludge which had been cultured by fill-and-draw method for long-time in our laboratory. The sludge was originally rich in both heterotrophic bacteria as well as nitrifiers. Total amount of seed sludge was 14 g based on MLSS.

The influent was introduced at starting flowrate of 0.2 L/h (i.e. HRT ~ 24 h) and ammonium concentration of 20 mg-N/L. Then the nitrogen load (volumetric loading rate, VLR) was increased step-wise by both increases in ammonium concentration and in flowrate. The start-up profile of VLR and ammonium conversion rate is shown in Fig. 3.

When the VLR was around 0.8 kgN/m^3.d, the reactor was quite "steady" at ammonium conversion rate of about 60%. Influent flowrate of 0.78 L/h was selected corresponding to HRT of 6 h and a VLR around 1 kgN/m^3.d.

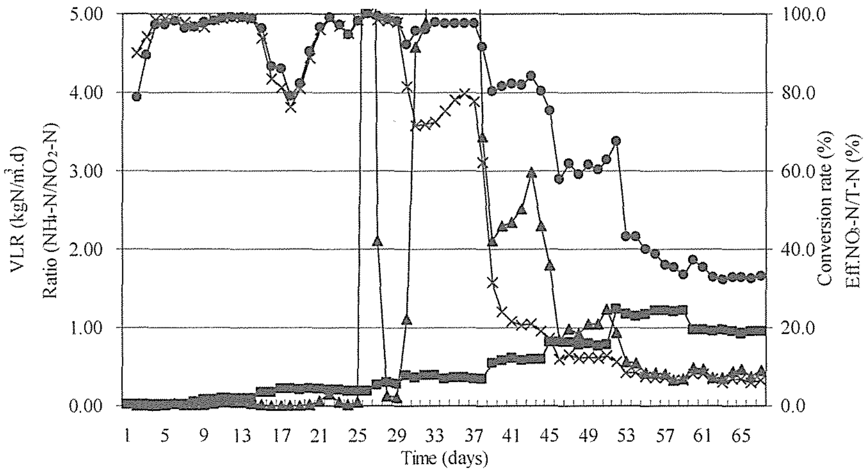

Fig.3. VLR, NH_4 conversion rate, effluent NO_2-N/NH_4-N ratio and effluent NO_3-N profile during start-up phase

(■)VLR (▲)NO_2-N/NH_4-N ratio (•)conversion rate (×) NO_3-N percentage

During start-up time, DO inside reactor decreased stepwise and then narrowly varied from 1.0 to 2.5 mg/L at the end. This DO variation was inversely related to the applied nitrogen load. The alkalinity consumptions during the start-up phase (data not shown) were found to be closed to the theoretical value.

Effects of operating conditions on responses

After success in start-up, the reactor was put into experimental design plan in order to investigate the effects of operating conditions on responses. The Fig.4 shows responses of 11 runs and the Table 3 shows regression coefficients and some other major statistical parameters

From the calculated data, it can be seen the most significant effect was of air flowrate while pH and temperature seemed to have minor effects.

Significant value of b_{123}, decrease in errors and increase in R-squared values when the regression includes 3-factor term confirm that three factors have interactive effects to the responses.

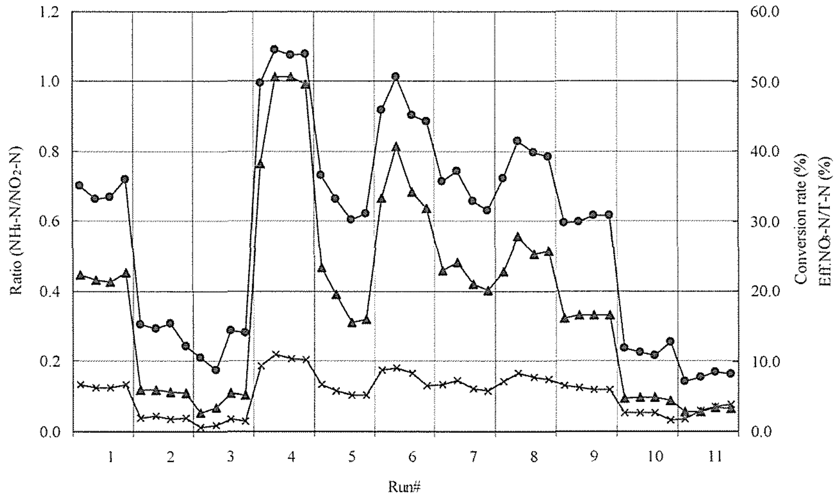

Fig.4. NH_4 conversion rate, effluent NO_2-N/NH_4-N ratio and effluent NO_3-N profile during DOE phase

(▲) NO_2-N/NH_4-N ratio (•) conversion rate (×) NO_3-N percentage

Table 3. Regression parameters for two types of model

Term	Y_1		Y_2		Y_3	
	Model (Eq.1)	Model (Eq.2)	Model (Eq.1)	Model (Eq.2)	Model (Eq.1)	Model (Eq.2)
b_0	28.82 ± 2.13	28.82 ± 1.40	0.37 ± 0.04	0.37 ± 0.01	5.39 ± 0.33	5.39 ± 0.27
b_1	-1.32 ± 2.50	-1.32 ± 1.65	-0.04 ± 0.05	-0.04 ± 0.02	-0.59 ± 0.39	-0.59 ± 0.32
b_2	0.71 ± 2.50	0.71 ± 1.65	-0.02 ± 0.05	-0.02 ± 0.02	-0.39 ± 0.39	0.39 ± 0.32
b_3	15.83 ± 2.50	15.83 ± 1.65	0.28 ± 0.05	0.28 ± 0.02	2.98 ± 0.39	2.98 ± 0.32
b_{12}	2.39 ± 2.50	2.39 ± 1.65	0.08 ± 0.05	0.08 ± 0.02	0.52 ± 0.39	0.52 ± 0.32
b_{13}	-1.52 ± 2.50	-1.52 ± 1.65	-0.04 ± 0.05	-0.04 ± 0.02	-0.24 ± 0.39	-0.24 ± 0.32
b_{23}	-1.12 ± 2.50	-1.12 ± 1.65	-0.03 ± 0.05	-0.03 ± 0.02	0.20 ± 0.39	0.20 ± 0.32
b_{123}	N.A	4.11 ± 1.65	N.A	0.10 ± 0.02	N.A	0.54 ± 0.32
R-squared	91.28	97.17	90.19	99.19	94.29	97.10
Standard error	7.08	4.66	0.14	0.05	1.09	0.89
Mean abs.error	3.99	2.02	0.08	0.01	0.59	0.39

Factors affecting the nitrite accumulation during nitrification were discussed by many authors. The core of influence, in fact, was in the inhibition of bacteria by free ammonia.

If showing data obtained in this study on the graph developed by Anthonisen et al., which is widely used to identify the inhibitory possibility of free ammonia (FA) and free nitrous acid (FNA) from in-reactor concentrations of ammonium and nitrite (Buyng-Ho H. et al., 2000), almost data fell into the Zone 2 (Fig.5). This means that FNA did not inhibit nitrifying bacteria but FA concentrations were in the range of inhibition of Nitrobacter.

All three mentioned factors in this study have direct or indirect relation to the free ammonia formation.

High pH leads to the high free-ammonia concentration in equilibrium with ammonium. Low aeration creates bad circulation and too high aeration creates excess oxygen supply which is favorable to nitrite oxidizers. The enough aeration also support the removal of free ammonia, hence reduces its inhibition. Temperature, in a hand, affects the microbiological reaction rate (the higher temperature the higher reaction rate), another hand, contributes to the equilibrium NH_3-NH_4^+ (the higher temperature the higher free ammonia).

The main purpose of DOE application in this study was to evaluate the effects of operational factors rather than to optimize responses. However, the most suitable results for next ANAMMOX step were observed in the run#4. This run gave an average ammonium conversion rate of 53.0%, effluent NO_2-N/NH_4-N ratio of 0.99 and effluent NO_3-N percentage of 10.1%.

From the responses of effluent nitrate vs. airflow (in run# 1,4,6,7,8), it was clearly that an increase in aeration would lead to an increase in nitrate. However, high nitrate is not expected in this study.

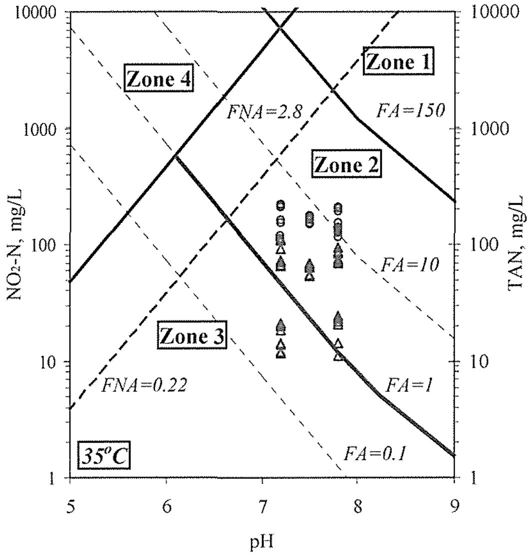

Fig. 5. Anthonisen graph of nitrification inhibition by FA and FNA

Zone 1: inhibition of Nitrobacter and Nitrosomonas by FA; Zone 2: inhibition of Nitrobacter by FA; Zone 3: complete nitrification; Zone 4: inhibition of Nitrobacter by FNA.

O: NH_4-N, Δ: NO_2-N

About the parameter AirQ/N-Load

During the DOE phase, DO inside reactor varied irregularly, even under the same aeration rates. DO profile is shown in Fig.6. Generally, DO for nitritation process was as low as 1.0 ~ 2.0 mg/L.

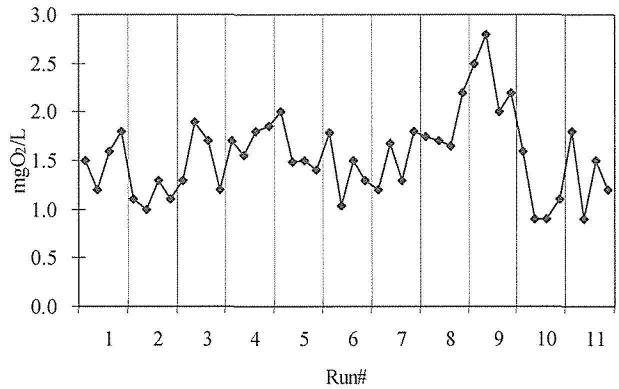

Fig 6. DO profile during DOE phase

The oxygen measurement by DO meter normally is subjected to sensitively variation. To control a constant DO in reactor, even under the same conditions of nitrogen load and aeration rate, is a very difficult task. Therefore, it is not easy to use DO as an operational factor in lab experiment as well as in practice. The superficial air velocity was used in some studies as an operational factor instead of DO. The ratio of air flowrate to applied ammonium load (AirQ/N-Load) may be a good factor. This ratio reflects the aeration requirement (not oxygen supply only) for nitrification based on unit nitrogen load, and is comparable. At certain nitrogen load, only control of air flowrate is required and this control is simple and can be done exactly.

In our study, with influent ammonium concentration of 240 mg/L, HRT of 6 h; the ratios would be 160, 96 and 32 L-air/g-N for airflow of 0.5, 0.3 and 0.1 L/min, respectively. Similar ratios can be calculated as 198~1632 L-air/g-N in a biofilm nitrification with nitrite accumulation of 500 mgNH_4-N/L influent (Ho-Joon and Dong-Jin, 2003); 360 L-air/g-N in biofilm airlift reactor nitrification of 196 mgNH_4-N/L influent (Garrido J.M. et al., 1997).

Batch experiment

Data from batch experiment are shown in the Fig.7. The Lineweaver –Burk plot that is linearized from Monod kinetics for these data is depicted in Fig.8.

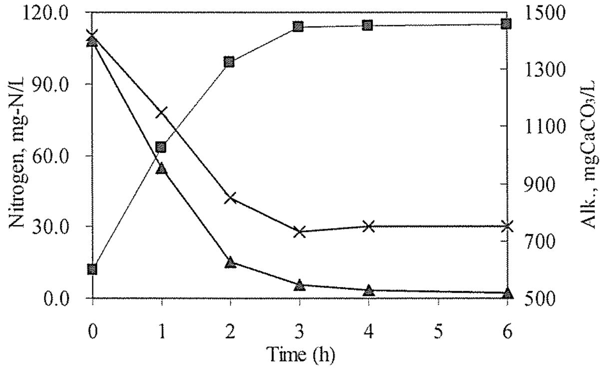

Fig.7. Profile of batch experiment
(▲) NH_4-N (■) NO_x-N (×) Alkalinity

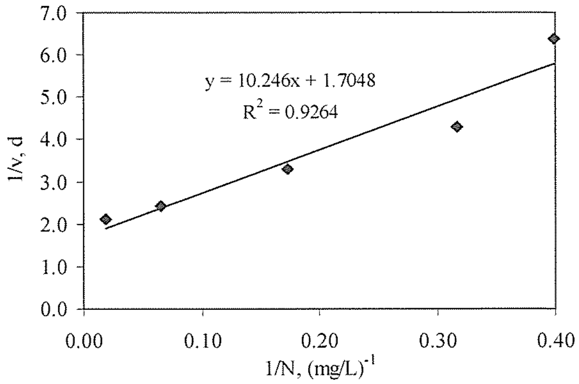

Fig.8. Lineweaver –Burk plot for nitrification

From the last figure, following values were found:

$$v_{max} = 0.587 \text{ mgNH}_4\text{-N/mgVSS.d}^{-1} \text{ and } K_N = 6.01 \text{ mgNH}_4\text{-N/L}.$$

where, v_{max} is maximum nitrification rate, and K_N is saturation constant. Both values of v_{max} and K_N are in the typical ranges for nitrifiers cited by various textbooks. The obtained v_{max} was higher than those of nitrification of high ammonium wastewater as in Table 4.

Specially, the high nitrite fraction in effluent NO_x (final NO_2-N : NO_3-N = 27 : 1) indicates that the ammonium oxidizing bacteria might be selectively predominant in the nitrifiers.

Table 4. Maximum nitrification rates in systems for treating high-strength ammonium wastewater

System	T (°C)	Nitrification rate (mgNH$_4$-N/mgVSS.d)	Reference
Nitrifying biofilm	28–32	0.18–0.21	Arnold, 2000
Nitrifying sludge	28–32	0.14–0.18	Arnold, 2000
Nitrifying sludge	25	0.37	Carrera, 2003

CONCLUSIONS

1. Partial nitritation of synthetic leachate can be achieved with a fixed film reactor using acryl resin fiber as attaching material. The short HRT (6h) is an advantage of the process.
2. Statistical tool showed that operational factors such as temperature, pH and air flowrate had interactive effects to the nitritation process; and among them, air flowrate was major factor in experimental conditions. At temperature of 30°C, pH 7.2 and air flowrate of 0.5 L/min (or air-to-nitrogen load of 160 L-air/g-N), the effluent can be suitable for next ANAMMOX process.
3. The sludge from nitritation reactor had a high nitrifying activity, in general, and nitritation activity, in particular.
4. Further studies are going on to get the long-term stability of the system, the better effluent as well as the treatability of higher influent ammonium concentration.

REFERENCES

APHA, AWWA and WEF (1995). Standard methods for the examination of water and wastewater. 19th edition. *American Public Health Association*, Washington DC.

Arnold E, B.Ohm B, Wilderer PA (2000). Application of activated sludge and biofilm sequencing batch reactor technology to treat reject water from sludge dewatering systems: a comparison. *Water Sci Technol*, **41(1)**, 115–22.

Carrera J., et al. (2003). Biological nitrogen removal of high-strength ammonium industrial wastewater with two-sludge system. *Water Research*, **37**, 4211–4221.

Furukawa K. et al. (2003). Nitrification of groundwater contaminated with NH_4^+ using a novel acryl resin fiber for biomass attachment. *Proceeding of 4th General seminar of the Core University Program*. JSPS (Japan) and NCST (Vietnam), Osaka, **July 2003**.

Fux C. et al. (2002). Biological treatment of ammonium-rich wastewater by partial nitritation and subsequent anaerobic ammonium oxidation in a pilot plant. *J. of Biotechnology*, **99**, 295-306.

Garrido J.M. et al. (1997). Influence of dissolved oxygen concentration on nitrite accumulation in a biofilm airlift suspension reactor. *Biotechnology and Bioengineering*, **53**, 168-178.

Hoilijoki TH, Kettunen RH, Rintala JA. (2000). Nitrification of anaerobically pretreated municipal landfill leachate at low temperature. *Water Research*, **34**, 1435–46.

Hung, Trinh Le at al. (2003). Study on leachate treatment system of Namson (Hanoi) landfill. *Proceeding of International Workshop on Technology of MSW Treatment – Experiences and Challenges*. Co-organized by HNU (Vietnam) and DUT (Germany). Hanoi, **March 2003**.

Jeong-hoon Im, et al. (2001). Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system. *Water Research*, **35** (10), 2403–2410.

Jetten M.SM. et al. (2001). Microbiology and application of the anaerobic ammonium oxidation ('ANAMMOX') process. *Current Opinion in Biotechnology*, **12**, 283–288.

Jokelaa J.P.Y., et al. (2002). Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. *Water Research*, **36**, 4079–4087.

Kettunen R.H. et al. (1996). Anaerobic and sequential anaerobic-aerobic treatment of municipal landfill leachate at low temperatures. *Bioresource Technology*, **58**, 31-40.

Pelkonen M, Kotro M, Rintala J (1999). Biological nitrogen removal from landfill leachate: a pilot scale study. *Waste Management & Research*, **17**, 493-497.

Ruiz G. et al. (2003). Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration. *Water Research*, **37**, 1371–1377.

Schmidt I. et al. (2003). New concepts of microbial treatment processes for the nitrogen removal in wastewater. *FEMS Microbiology Reviews*, **27**, 481-492.

Sliekers A.O. et al. (2002). Completely autotrophic nitrogen removal over nitrite in one single reactor. Water Research, **36**, 2475–2482.

So-Hyun J. et al. (2000). Partial nitrification in an upflow biological aerated filter by O_2 limitation. *Biotechnology Letters*, **22**, 937-940.

Tchobanoglous G., H. Theisen, and S. Vigil (1993). *Integrated Solid Waste Management: Engineering Principles and Management Issues*. McGraw-Hill, Inc. New York, New York.

Twachtmann U. et al. A novel concept for the treatment of the effluent from anaerobic sludge digestion with trickling filters. *Project report* **02WA926/2**, http://www.uni-stuttgart.de/

van Dongen U. et al. (2001). The SHARON®-ANAMMOX® process for treatment of ammonium rich wastewater. *Water Science & Technology*, **44 (1)**,153-160.

Wellander U, Henrysson T. and Wellander T. (1998). Biological nitrogen removal from municipal landfill leachate in a pilot scale suspended carrier biofilm process. *Water Research* **32(5)**, 1564-1570.