LAB-SCALE APPLICATION OF COMBINED PARTIAL NITRITATION -ANAMMOX PROCESS FOR NITROGEN REMOVAL FROM LANDFILL LEACHATE

ỨNG DỤNG QUÁ TRÌNH KẾT HỢP NITRIT HÓA BÁN PHẦN VÀ ANAMMOX XỬ LÝ LOẠI NITƠ TRONG NƯỚC RỈ RÁC Ở QUY MÔ PHÒNG THÍ NGHIỆM

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ABSTRACT

It is well known that the novel treatment processes combining partial nitritation and anammox (anaerobic ammonium oxidation) are suitable for the removal of nitrogen from ammonium-rich and BOD-low wastewaters such as "old" landfill leachate or secondarily pretreated leachate. Lower oxygen supply, without organic carbon addition and lower CO_2 emission are typical advantages of a novel process over the conventional nitrification-denitrification. In this study, a single-stage nitrogen removal using partial nitritation and anammox (SNAP) process was developed and applied for treatment of leachate from the Thuyphuong Sanitary Landfill in Hue. A 5-L fix-bed type reactor was used. The reactor was seeded with activated sludge and an anammox-enriched sludge. After about 200 days of process start-up, process performance at different nitrogen loading rates (0.04 to 0.32 kg-N/m^3/d) was investigated on synthetic feeding medium. Then, the treatment performance was studied on diluted leachate having COD of about 200 mg/L and NH_4-N of 140 mg/L. At an HRT of 24 h, aeration rate of 0.1 vvm, room temperature (30-32^{o}C) and pH 7.5, the SNAP process achieved stable performance with ammonium conversion rate of 92% and total nitrogen removal rate of 81%, gave the effluent NH_4-N concentration less than 25 mg/L.

Keywords: anammox, landfill leachate, nitrogen removal, SNAP

TÓM TẮT

Các quá trình xử lý nitơ mới kết hợp nitrit hóa bán phần và anammox (oxy hóa kỵ khí amoni) thích hợp đối với các loại nước thải có nồng độ amoni cao và BOD thấp như nước rỉ rác "già" hay nước rỉ rác đã qua xử lý bậc hai. Nhu cầu cấp khí thấp hơn, không cần phải bổ sung carbon hữu cơ và phát thải CO_2 thấp hơn là những ưu điểm của các quá trình xử lý mới so với phương pháp nitrat hóa-khử nitrat truyền thống. Trong nghiên cứu này, một quá trình kết hợp nitrit hóa bán phần và anammox chỉ trong một bể phản ứng (viết tắt là SNAP) đã được phát triển và áp dụng vào xử lý nước rỉ rác từ bãi chôn lấp chất thải rắn Thủy Phương ở Huế. Bể phản ứng dung tích 5-L kiểu lớp đệm cố định được sử dụng. Bùn hoạt tính và bùn đã được làm giàu vi khuẩn anammox được nạp vào bể lúc đầu. Sau hơn 200 ngày khởi động, sự vận hành của bể xử lý ở các tải trọng nitơ khác nhau (từ 0,04 đến 0,32 kg-N/m^3/ngày) đã được khảo sát trên nước thải tổng hợp. Sau đó, sự vận hành của bể trên nước rỉ rác thật pha loãng đến COD khoảng 200 mg/L và có NH_4-N = 140 mg/L đã được nghiên cứu. Ở các điều kiện HRT = 24 giờ, tốc độ sục khí = 0,1 vvm, nhiệt độ phòng (30-32^{o}C) và pH 7,5; quá trình SNAP đã vận hành khá ổn định với hiệu suất chuyển hóa amoni đạt 92% và hiệu suất loại tổng nitơ đạt 81%, cho đầu ra có nồng độ NH_4-N dưới 25 mg/L.

Từ khóa: anammox, nước rỉ rác, SNAP, xử lý nitơ

1. Introduction

Leachate from municipal solid waste landfill contains nitrogenous compounds at very high concentrations. Ammonium is the dominant nitrogen form in leachate because it is not oxidized under anaerobic condition inside landfill cells. Ammonium concentration of leachate varies greatly depending on the aging phases of landfill. So far, major targets of landfill leachate treatment in Vietnam have been organic and color removals, even though the national regulation for leachate discharge (QCVN 25:2009/BTNMT) includes ammonium and total nitrogen limits.

Conventional biological nitrogen removal from wastewater is based on the combination of nitrification and denitrification. High oxygen consumption in nitrification stage and addition of organic carbon source in denitrification stage make this treatment approach costly. Denitrification stage also emits CO_2 and N_2O.

In 1995, a new nitrogen metabolic pathway namely anammox (anaerobic ammonium oxidation) was discovered [1]. In this reaction, as described in equation 1 [2], ammonium is oxidized to nitrogen gas by nitrite under anaerobic condition.

$$NH_4^+ + 1.32\,NO_2^- + 0.066\,HCO_3^- + 0.13\,H^+ \rightarrow 1.02\,N_2 + 0.26\,NO_3^- + 0.066\,CH_2O_{0.5}N_{0.15} + 2.03\,H_2O \quad (1)$$

Once ammonium is partially oxidized to nitrite, it is favorable for the subsequent application of anammox to remove nitrogen. Novel nitrogen removal process based on the combination of partial nitritation and anammox has been recognized as a promising alternative for ammonium-rich and COD-low wastewaters such as supernatant of sludge digester, pre-treated landfill leachate. Reduction of oxygen supply and elimination of organic carbon addition are two typical advantages of the novel process. In addition, there is no CO_2 and N_2O emission in the novel process. Practically, nitritation and anammox steps can be implemented in separate or single-stage systems. A single-stage process named SNAP (Single-stage Nitrogen removal using Anammox and Partial nitritation) was developed and tested for synthetic landfill leachate [3], [4]. This paper introduces our study on application of the developed SNAP process for ammonium removal from a local landfill leachate.

2. Materials and Methods

2.1. Leachate

Leachate used for study was from the Thuy Phuong Sanitary Landfill in Thua Thien Hue province. Leachate from both closed and active sites is collected into a mixing tank and treated through a pond system. Leachate samples were taken at the mixing tank from March to July 2010. Some characteristics of leachate in this study include: pH = 7.6 – 8.6, COD = 633 – 1175 mg/L, BOD_5 = 90 – 295 mg/L, BOD_5/COD ratio = 0.14 – 0.26 and NH_4-N = 98 – 310 mg/L.

2.2. Experimental setup

Reactor system used is a submerged aerated fixed bed (SAFB) type, as shown in figure 1. The reactor's liquid volume is 5 L. A net-type acryl-resin fiber material (BX, NET Co. Ltd., Japan) was used as biomass carrier. For starting-up, the reactor was co-seeded with activated and anammox sludges. Activated sludge, originated from wastewater treatment system of Hue Beer Company, had been cultured in laboratory for long time. Anammox sludge was enriched from sludge of an UASB reactor treating swine wastewater [5]. The start-up phase lasted about 200 days by feeding a medium containing ammonium as the sole nitrogen substrate (see table 1). After starting-up, the reactor was fed with the same medium for investigating SNAP performance under different nitrogen loading rates (NLR). Operational conditions included temperature: 30 – 32°C, pH: 7.2 – 7.5 and aeration rate: 0.01 vvm. Leachate then was applied for investigating the nitrogen removal under different pH levels and COD concentrations. Raw leachate was diluted to 120 – 200 mg COD/L to serve as leachate matrix and $(NH_4)_2SO_4$ was added to adjust ammonium concentration.

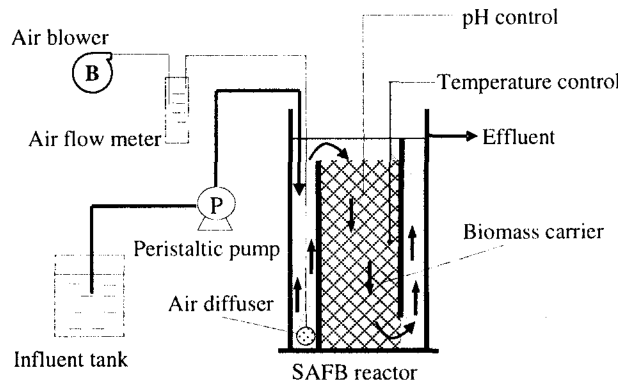

***Figure 1**. Schematic diagram of reactor system.*

2.3. Analytical methods

Influent and effluent samples were taken and analyzed for NH_4-N, NO_2-N, NO_3-N and COD. COD, NO_2-N and NO_3-N were determined in accordance with Standard Methods [6]. A modification of standard phenate method was applied for NH_4-N [7].

***Table 1**. Composition of feeding medium for starting-up and developing SNAP process*

Component	Concentration	*Micronutrient solution I*	
$(NH_4)_2SO_4$	Subject to change*	EDTA	5 g/L
$KHCO_3 + NaHCO_3$ (1:1)	752 mg/L	$FeSO_4$	5 g/L
KH_2PO_4	44 mg/L (10 mg-HPO_4/L)	*Micronutrient solution II*	
$CaCl_2.2H_2O$	89 mg/L (32 mg-Ca/L)	EDTA	12 g/L
$MgSO_4$	165 mg/L (16 mg-Mg/L)	$ZnSO_4$	0.43 g/L
Micronutrient solution I	1 ml/L	$CoCl_2.6H_2O$	0.24 g/L
Micronutrient solution II	1 ml/L	$MnCl_2.4H_2O$	0.99 g/L
		$CuSO_4.5H_2O$	0.25 g/L

Start-up phase: 15 mg-N/L Developing phase: 40 to 240 mg-N/L		$NaMoO_4.2H_2O$	0.22 g/L
		$NiCl_2.6H_2O$	0.19 g/L
		$NaSeO_4.10H_2O$	0.21 g/L
		H_3BO_4	0.014 g/L

2.4. Calculations

Ammonium conversion efficiency (ACE) was calculated from influent and effluent NH_4-N concentrations while nitrogen removal efficiency (NRE) was calculated from influent and effluent T-N concentrations, as shown in equations 2 and 3 respectively. T-N is defined as sum of three nitrogen forms: NH_4-N, NO_2-N and NO_3-N.

$$ACE = \frac{Inf.NH_4\text{-}N - Eff.NH_4\text{-}N}{Inf.NH_4\text{-}N} \times 100 \quad (2); \qquad NRE = \frac{Inf.T\text{-}N - Eff.T\text{-}N}{Inf.T\text{-}N} \times 100 \quad (3)$$

Experimental stoichiometric coefficients of SNAP process were estimated using nitrogen balance. Two sets of coefficient were calculated, one is based on 1 mol NH_4^+ applied (equation 4) and another is based on 1 mol NH_4^+ removed (equation 5).

$$1\ NH_4^+ \rightarrow a\ NH_4^+\ (\text{residual}) + b\ NO_2^- + c\ NO_3^- + d\ N_2 \quad (4)$$

$$1\ NH_4^+ \rightarrow b'\ NO_2^- + c'\ NO_3^- + d'\ N_2 \quad (5)$$

(Theoretical values: a = 0.167; d = 0.340; b'= 0.06 and d' = 0.408).

3. Results and discussions

3.1. SNAP treatment performance on synthetic medium at different NLRs

Data on SNAP performance in seven steps with different NLRs are summarized in table 2. At the same HRT of 24 h, ACE and NRE showed a general decreasing trend when NLR was increased. The decrease in ACE was more significant than that in NRE, which is reflected also through the increase in coefficient of NH_4^+ and decrease in coefficient of N_2 in (a) rows.

Table 2. *SNAP treatment performance on synthetic medium at different NLRs*

HRT (h)	NLR ($kg\text{-}N/m^3/d$)	ACE (%)	NRE (%)	Eff.NO_2-N (mg/L)	Eff.NO_3-N) (mg/L)	Stoichiometric coefficients				
							NH_4^+	NO_2^-	NO_3^-	N_2
24	0.04	78.5 ± 7.0	59.8 ± 6.8	0.8 ± 0.8	6.9 ± 1.4	(a)	0.215	0.020	0.167	0.299
						(b)		0.026	0.213	0.381
24	0.08	76.6 ± 3.3	54.9 ± 6.3	2.6 ± 0.8	14.8 ± 2.0	(a)	0.233	0.032	0.185	0.275
						(b)		0.042	0.242	0.358

24	0.12	69.6 ± 2.5	54.5 ± 1.7	6.6 ± 0.7	11.4 ± 1.3	(a)	0.304	0.055	0.096	0.272
						(b)		0.080	0.137	0.392
24	0.24	60.7 ± 1.7	52.3 ± 2.2	13.4 ± 1.6	6.7 ± 1.0	(a)	0.393	0.056	0.028	0.262
						(b)		0.092	0.046	0.431
12	0.24	56.7 ± 9.6	55.4 ± 7.7	3.9 ± 1.8	9.9 ± 3.9	(a)	0.435	0.032	0.081	0.226
						(b)		0.056	0.143	0.400
12	0.32	66.8 ± 2.0	58.1 ± 2.2	4.5 ± 1.5	9.6 ± 2.2	(a)	0.332	0.028	0.059	0.291
						(b)		0.042	0.089	0.435
24	0.12	82.1 ± 3.8	63.9 ± 7.0	9.0 ± 6.6	13.9 ± 1.8	(a)	0.178	0.071	0.109	0.321
						(b)		0.086	0.133	0.390

Eff.NO_2-N, Eff.NO_3-N: concentrations of effluent nitrite and nitrate.

(a). Based on 1 mol NH_4^+ applied, (b).Based on 1 mol NH_4^+ removed.

This means AOB are inhibited much more than anammox bacteria at higher ammonium concentration. *Nitrosomonas* bacteria are found to be inhibited at ammonia concentration from 10 to 150 mg/L [8], while anammox bacteria are stated to be not inhibited at up to 100 mM ammonia [9].

Data from two steps with the same NLR of 0.24 kg-N/m^3/d indicate that HRT affect significantly ACE and NRE: the longer HRT was the better treatment performance was. At the last step, experimental coefficients were quite close to theoretical values, which means the conversion occured in reactor had approached the desired process. Longer operational time would enhance the stable co-growth of AOB and anammox bacteria populations, hence the performance of SNAP process in the last step was better than in the 3rd step, even both steps have same NLR of 0.12 kg-N/m^3/d.

3.2. SNAP treatment performance on leachate at different pH and COD levels

3.2.1. At different pH values

From days 537 to 554, the treatment performance under three pH levels of 7.0, 7.5 and 8.0 was investigated. Leachate, diluted to COD lower than 150 mg/L and

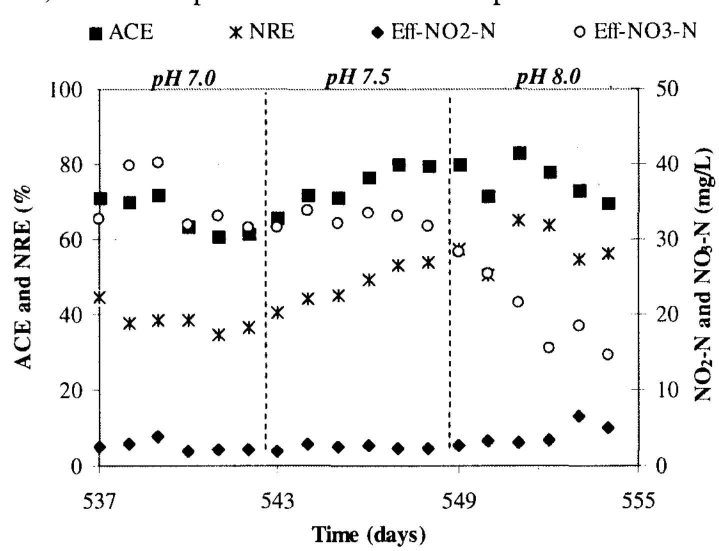

Figure 2. Changes in ACE, NRE, effluent NO_2-N and NO_3-N at three pH levels.

adjusted to ammonium concentration of 120 to 140 mg-N/L, was used as the influent. Main experimental results are shown in figure 2. In general, there was an increase in NRE (from 38.4% to 57.9%) when pH was increased from 7.0 to 8.0. ACE was observed to increase only when pH was increased from 7.0 to 7.5. At pH 8.0, some abnormal changes in NRE and ACE were found. Also, effluent NO_3-N was decreased quickly from about 30 mg/L to 20 mg/L. Stoichiometric coefficients calculated for three pH levels were not much deviated from theoretical values. This indicates the conversion of nitrogen in leachate in the reactor still followed SNAP mechanism. In order to minimize free ammonia in reactor and save bicarbonate solution used for pH controlling, pH 7.5 was recognized as the best value for operation of SNAP process in this study.

3.2.2. At different COD concentrations

From days 555 to 580, influent COD concentration was increased gradually by decreasing dilution factor of original leachate. Influent ammonium concentration was around 140 mg-N/L. Reactor's pH was maintained at 7.5. Data on treatment performance under three COD concentrations of 100, 150 and 200 mg/L are presented in figure 3.

It can be seen that ACE and NRE were not influenced by the increase in COD up to 200 mg/L. Even nitrogen removal was better at COD of 200 mg/L than at 150 and 100 mg/L. The effluent NH_4-N in all cases was lower than limit values in QCVN 25:2009/BTNMT class B1. There may be two explanations for the increase in nitrogen removal at high influent COD: (1)-contribution of denitrification and (2)-organic carbon metabolism by anammox bacteria. Recently, new species of anammox bacteria were found to be able to oxidize organic acids in the presence of ammonium, nitrite and nitrate [10], [11].

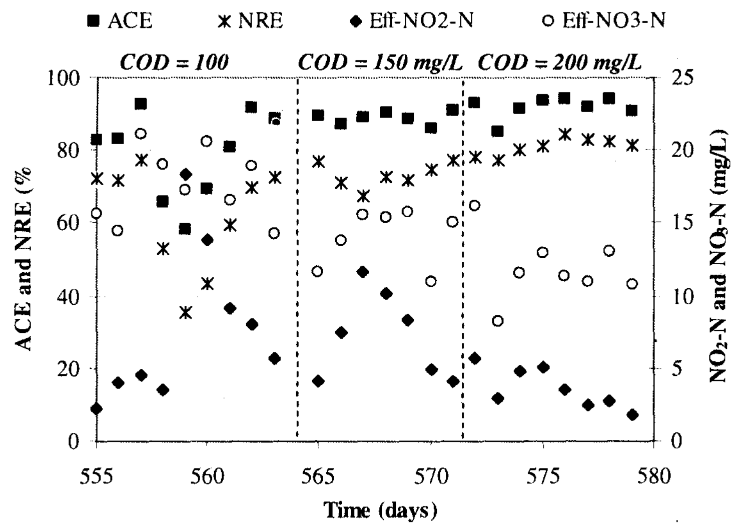

***Figure 3.** Changes in ACE, NRE, effluent NO_2-N and NO_3-N at three COD concentrations.*

Table 3 presents the stoichiometric coefficients calculated in three experimental steps. High values of coefficient for N_2 indicate the high nitrogen removal under the existence of organic carbon. It is assumed from data obtained that nitrogen removal could be improved at higher COD concentrations. This is the further target of our study, in order to find the highest COD that limit the nitrogen removal by SNAP process.

4. Conclusions

Using synthetic medium with ammonium as the sole substrate, the SNAP process was able to convert 67% of influent ammonium and remove 58% of total nitrogen at NLR of 0.32 kg-N/m^3/d (influent ammonium concentration of 160 mg-N/L). Higher nitrogen removal of 64% was achieved at NLR of 0.12 kg-N/m^3/d. Data on stoichiometric coefficients showed a gradual approach to the theoretical process during experiment.

Table 3. *Stoichiometric coefficients of SNAP process at three COD concentrations*

COD, mg/L	Stoichiometric equation
100	$1\ NH_4^+ \rightarrow 0.120\ NH_4^+ + 0.034\ NO_2^- + 0.114\ NO_3^- + 0.366\ N_2$ $1\ NH_4^+ \rightarrow 0.039\ NO_2^- + 0.129\ NO_3^- + 0.416\ N_2$
150	$1\ NH_4^+ \rightarrow 0.108\ NH_4^+ + 0.055\ NO_2^- + 0.106\ NO_3^- + 0.366\ N_2$ $1\ NH_4^+ \rightarrow 0.061\ NO_2^- + 0.119\ NO_3^- + 0.410\ N_2$
200	$1\ NH_4^+ \rightarrow 0.850\ NH_4^+ + 0.024\ NO_2^- + 0.080\ NO_3^- + 0.406\ N_2$ $1\ NH_4^+ \rightarrow 0.026\ NO_2^- + 0.087\ NO_3^- + 0.444\ N_2$

Application of SNAP process to the treatment of diluted landfill containing 120 - 140 mg-N/L and 100 - 200 mg-COD/L gave a good treatment performance. It was able to stably convert 92% of influent ammonium and remove 81% of total nitrogen by the process, even at influent COD of 200 mg/L. Effluent ammonium and total nitrogen concentrations were lower than the limit values in national discharge regulation for landfill leachate (QCVN 25:2009/BTNMT, class B1).

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