REMOVAL OF NITROGEN COMPOUNDS IN SLAUGHTERHOUSE WASTEWATER BY USING ANAEROBIC AMMONIUM OXIDATION PROCESS

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Abstract: *According to the planning of cattle and poultry slaughterhouse and processing systemup towards 2020, Hanoi city approvedwith 10 planned industrial slaughterhouse sites and 34 planned semi-industrial slaughterhouse sites. The amount of slaughterhouse wastewater is calculated of about 2,300-6,100 m^3/day, excluding wastewater from small and uncontrolled slaughterhouses. This research was implemented in the experimental lab-scale to evaluate ammonium removal capacity in slaughterhouse wastewater by combined process of partial nitritation and anaerobic ammonium oxidation (anammox). The real slaughterhouse wastewater was collected from ThinhAn slaughterhouse and organic matter as COD was removed by previous AnMBR. The influent NH_4^+ concentration was changed from 80 to 160 mg N/L. T-N loading rate of 0.1 to 0.25 kgT-N/m^3/day with HRT was controlled from 36hrs to 10 hrs.The effluent NH_4^+-N concentration was always less than 10 mg N/L which satisfied the Column B of QCVN 40:2011/BTNMT - National Technical Regulation on Industrial Wastewater.*

Keywords: *anammox; biomass carrier,slaughterhouse wastewater; NH_4^+-N; NO_2^-N.*

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1. Introduction

According to the Decision No. 5791/QD-UBND issued by People's Committee of Hanoi city dated in Dec. 12th, 2012 to approve the planning of cattle and poultry slaughterhouse and processing system in Hanoi city up towards 2020, there will be 10 planned industrial slaughterhouse sites which will produce 54 tons of buffalo meat/day, 405 tons of pork/day and 144 tons of poultry meat/day. In addition, 34 planned semi-industrial slaughterhouse sites will produce 63 tons of buffalo meat/day, 187 tons of pork/day, 93 tons of poultry meat/day [1]. Therefore, capacity of slaughtering pigs is expected to be 592 tons/day. However, according to the Decision No. 5003/QD-UBND, issued by People's Committee of Hanoi city dated in Jul. 28th, 2017 to amend and supplement the planning of cattle and poultry slaughtering and processing system, Hanoi amended and supplemented 16 semi-industrial sites with higher slaughtering pigs capacity up to 763 tons/day [2].

Meanwhile, the amount of water demand forpork meat processing is about 3-8 m^3/ton depending on the slaughtering technology [3,4]. With thiswater demand, the amount of slaughterhouse wastewater is calculated of about 2,300-6,100 m^3/day, excluding wastewater from small and uncontrolled slaughterhouses. Based on the survey data, the concentration of organic matter as COD and ammonium nitrogen were ranged of 700-1,300 mg/L and 100-250 mg N/L, respectively [5]. The discharge of such kind of wastewater without any treatment will cause the environmental pollution.

In Vietnam, treatment of ammonium nitrogen in slaughterhouse wastewater by anammox process has been investigated but its publications still limited. In this study, A technology based on the combination of partial nitritation and anammox processes was developed to treat the ammonium nitrogen in slaughterhouse wastewater by a single reactor using poly acrylic and and bath ball as biomass carriers. Experimental results showed that ammonium removal efficiency reaching 92% and 87.8% at NH_4^+-Nloading rate of 0.04 kgN/m^3/d and 0.14kgN/m^3/d, respectively [6].

With these above reasons,this research was implementedin the experimental lab-scale to evaluatethe removal capacity ofammonium nitrogen in slaughterhouse wastewater by combined process of partial nitritation and anaerobic ammonium oxidation (anammox).The real slaughterhouse wastewater was collected from ThinhAn slaughterhouse.

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Within the scope of this research, organic matter of this wastewater was treated previously by anaerobic membrane bioreactor (AnMBR) in lab-scalewith a controlled COD parameter below 150 mg/L.

2. Materials and methods

2.1 Laboratory-scale reactor of combined process of partial nitritation (PN) and anammox (AX) (Fig.1)

2.2 Operational procedure of the partial nitritation and anammoxlab-scale reactor (hereafter called as PN/AX reactor)

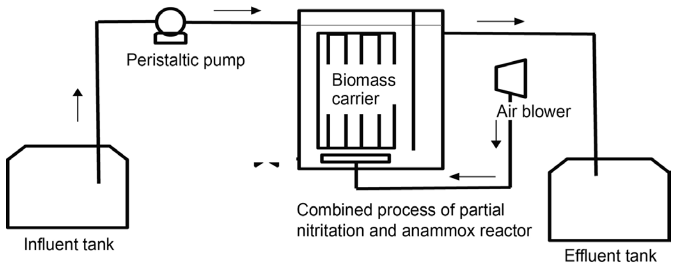

Figure 1. *Schematic diagram of combined process of partial nitritation and anammox*

2.2.1 Bacteria and seed sludge loading procedure

- Placetomycetes bacteria: 100 mL pure Placetomycetes bacteria were attached on the surface biomass carrier material as shown in Fig.2a. This bacteria were supplied by Meidensa Company, Nagoya, Japan.

- Nitrosomonas bacteria were attached on the surface material with a mass of 100g (109 CFU/g). Bacteria were enriched and supplied by the Institute of Tropical Biology, Academy of Science and Technology of Vietnam.

a) Seed sludge loading procedure

Step 1: 100 mL of Placetomycetes bacteria were poured into the reactor with fixed biomass carrier material and slaughterhouse wastewater effluent from AnMBR. After adding the seed sludge,the reactor was aerated to maintain the dissolved oxygen (DO) in the range of 0.5-1.0 mg/L (condition for Placetomycetes bacteria to survive) and mixing well for attachement of bacteria on the surface of material as shown in Figs. 2a and 2b. show the attached sludge on the surface of the carrier material after about 24 h of aeration.

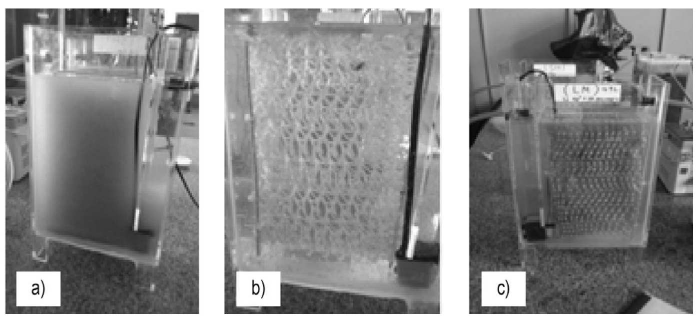

Figure 2. *Seed sludge loading procedure*
a, b) The attachement of Placetomycetes bacteria on the surface biomass carrier material; c) The attachement of Nitrosomonasbacteria on the surface biomass carrier material.

Step 2: Dissolved about 100 g of dry sludge in water for forming solution. Pour this solution into the reactor and using the air blower for mixing well and made good condition for Nitrosomonascan attach on the outer layer of the carrier material. Also after about 24 h, Nitrosomonas sludge was observed attached on the surface of material as shown in Fig. 2c.

Step 3: The system was operated in continuous conditions with a hydraulic retention time of 36h.

b) Wastewater

Slaughterhouse wastewater was taken from effluent slaughterhouse wastewater of AnMBR which organic matter as COD parameter was treated and controlled less than 150 mg/L.

c) Operational conditions and regime

Influent was fed in up-flow mode using a peristaltic pump (Eyela Co., Ltd., Tokyo). The reactor temperature was maintained at $33^{o}C$ to $35^{o}C$, controlled by the thermal stability equipment of the aquarium. Light is known to have a negative effect (30-50% rate reduction) on ammonium removal rate; consequently, dark conditions were maintained using black vinyl sheet enclosures.

Within 183 days of operation from Jannuary to July, 2015, the reactor was operated with different operating regimes of hydraulic retention time (HRT) and total nitrogen loading rate (TNLR) to evaluate the efficiency of ammonium removal in slaughterhouse wastewater as well as stability of the system. The operating parameters of the model are shown in Table 1. Theslaughterhouse wastewater after AnMBR is pumped from the influent tank to the PN/AX reactor with the different concentration of nitrogen compounds varying belong to the real wastewater.

Table 1. *Operational parameters of the PN/AX reactor for ammonium removal in slaughterhouse and processing wastewater*

Operational phase	Time (Days)	Wastewater flowrate (L/day)	HRT (h)	Average T-NLR (kgT-N/m^3/day)
1	0-29 (29 days)	2.5	36	0.1±0.01 (n = 9)
2	30-56 (27 days)	3.75	24	0.12±0.03 (n = 9)
3	57-89 (33 days)	5.0	18	0.14±0.01 (n = 10)
4	90-127 (38 days)	7.5	12	0.25±0.05 (n = 9)
5	128-183 (56 days)	9	10	0.25±0.01 (n = 18)

2.3 Chemical analyses

The experiment was conducted in the laboratory of Water Supply and Sanitation Division, Faculty of Environmental Engineering, National University of Civil Engineering. Parameters of influent and effluent stream were analyzed 2-3 times per week. Ammonium concentrations were measured by colorimetic method with Nessler reagent at wavelength of 420nm. In accordance with Standard Methods [7], nitrite concentrations were estimated by the colorimetric method (4500-NO_2^-B) and nitrate by the UV spectrophotometric screening method (4500-NO_3^-B). Nitrite was determined to have an interfering response in the nitrate UV screening method of 25% of the nitrate response on a nitrogen weight basis, thus the results were corrected by calculation. Levels of pH were measured by using a MettlerToledo-320 pH meter and DO was measured by using a DO meter (D-55, Horiba).

3. Results and discussion

3.1 Efficiencies of ammonium removal in PN/AX reactor

The reactor was operated with different HRT. When the NH_4^+-N concentration in the effluent reduced to about 10 mg N/L, the HRT is shortened to increase the NH_4^+-N removal load rate. The systemwas divided into five operating phases as described in Fig. 3. As shown in Fig. 3, the influent concentrations of NO_2^--N and NO_3^--N were less than 1 mg N/L.

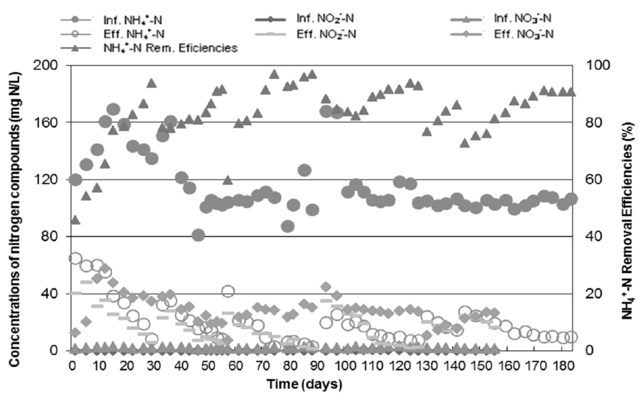

Figure 3. *Relationship between influent/effluent concentrations of nitrogen compounds and NH_4^+-N removal efficiencies*

Phase 1 was the start-up phase with a 29-day of operation and a HRT was maintained at 36h. The influent NH_4^+-N concentration was keeped as 144.5±15 mg N/L, and the average NH_4^+-N removal efficiency was achieved of 71.4±15.4%. In this phase, the influent NH_4^+-N concentrationwas quite high in compared to the later phases. On the other hand, it is the adaptation stage of Nitrosomonas bacteria and Planctomycetes bacteria (attached on the surface carrier material before operation), the microbial activitieswere still limited, evensometimes the sludge color changed from light brown to black. This phenomenon occurs because the influent NH_4^+-N concentrationwas quite high for the reactor start-up phase whichaffected to the bacteria shocking, not adapted to the new condition. It was found that in the first 20 days of this phase, the effluent NH_4^+-N concentration was relatively high with 38-65 mg N/L. However, about 10 days later the reactor was operated more stable. In the day of 29th, when influent NH_4^+-N concentration was 134.9 mg N/L, effluent NH_4^+-N concentration was only 8.2 mg N/L. This result shows that treatment efficiency of NH_4^+-N is quite high with 93.9%. It should also be noted that with the high NH_4^+-N treatment effect, such as Nitrosomonas and some other bacteria such as nitrobacter, are more actively than anammox bacteria at this time, NH_4^+-N was converted to NO_2^-- N and NO_3^--N as shown in Fig. 3. Therefore, the effluent concentration of NO_3^--N was quite high of more than 40 mg N/L in this phase.

In the phase 2, the reactor was operated for 27 days with a shortened HRT down to 24h when the effluent NH_4^+-N concentration in the first phase was decreased significantly. The influent NH_4^+-N concentration was lower than the first phase, fluctuating in the range of 115.6±23.9 mgN / L. The average NH_4^+-N treatment efficiency increased from the previous phase of 83.4%±5%. This may be due to the lower influent NH_4^+-N concentration as well as the adaptability and viability of the two types of bacteria even at shorter HRT. In this phase, the effluent NH_4^+-N in the first 15 days was quite high of 21.5-35.2 mg N/L in compared with the end of this phase of 8.4 mgN/L. This can be explained that the shortening of HRT also means increasing the NH_4^+-N loading rate, it is take time for adapting of bacteria, especially the Planctomycetes bacteria.This also explain that why the effluent concentrations of NO_2^-N and NO_3^--N was quite lowabout 10 mg N/L and 20 mg N/L, respectively at the end of this phase. In the last 3 phases, the effluent concentrations of NO_2^-N and NO_3^--N also low of 20 mg N/L and 30 mg N/L.

Phase 3 was operated for the next 33 days with reduction of HRT to 18h. The influent NH4+-N concentration was lower than that of the previous phase and ranged of about 105.8±9.5 mg N/L. The average NH_4^+-N treatment efficiency also increased in compared with the previous phase of 87.1±11.1%. This shows that the operation of the system has been more stable than previous phases. At the end of this phase, the influent and effluent NH_4^+-N concentrations of 98.8 mg N/L and 3 mg N/L, respectively and corresponding to removal efficiency of 97%.

In phase 4, HRT was reduced to 12 hours for 38 days. The influent NH_4^+-N concentration was higher than in the previous phase with 121±22.5 mg N/L. However, the average NH_4^+-N removal efficiency did not significantly change in compared with the previous phase of 88.4%±3.8%. On the day 127th, with the influent NH_4^+-N of 104 mg N/L, the removal efficiency was 92.9%. Although the operating time at this stage was longer than previous phases, the effluent NH_4^+-N concentration also reached 7.4 mg N/L which was satisfiedthe value of column B, QCVN 40:2011/BTNMT for National Technical Regulation on Industrial Wastewater [8].

Phase 5 was taken longer operational time of 56 days with short HRT of 10h. It was difficult for adapting of bacteria due to the short HRT. Therefore, the effluent NH_4^+-N concentration was reached to value of the column B, QCVN 40:2011/ BTNMT in the last 10 days eventhe influent NH^+-N concentrations were lower than in the previous phaseof 104.1±2.6 mg N/L. However, the removal efficiency of NH_4^+-N decreased slightly of 84±6%. By the end of the operational time, on the day 173th, with influent NH_4^+-N concentration of 108.6 mg N/L, the removal efficiency of 91.1% and effluent NH_4^+-N concentration reduced initially to 9.6 mg N/L. Although the effluent concentration of NH_4^+-N has met the allowed standard, but the operational time of this phase is longer than the previous phases. Therefore, depending on the the discharge demand, it can be considered to operate the system with a HRT of 12h or 10h.

The removal efficiency of NH_4^+-N in slaughterhouse wastewater in this study was similar to removal efficiency of NH_4^+-N in another research report of 92% and 87.8% [6].

3.2 NH_4^+-N removal loading rate in PN/AX reactor

Fig. 4 describes the variation in NH_4^+-N removal loading rate in the PN/AX reactor. Results of this study show that the NH_4^+-N removal loading rate increases gradually during each operational phase. During the 5 operational phases, the NH_4^+-N removal loading rates increased from 0.07±0.02 kg N/m^3/day in phase 1 to 0.1±0.02 kg N/m^3/day in phase 2 and from 0.12±0.02 kg N/m^3/day in phase 3 increased up to 0.21±0.04 kg N/m^3/day.In phase 5, the NH_4^+-N removal loading rate reached to 0.21±0.02 kg N/m^3/day which is similar to the phase 4 but it was taken rather long operational time for 56 days.

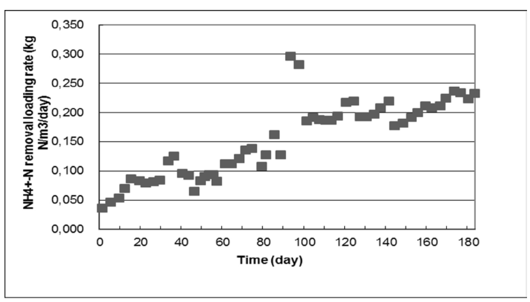

Figure 4. *Changes of NH_4^+-N removal loading rate*

However, at the day 93th, when HRT reduced from 18 hrs to 12 hrs and influent NH_4^+-N concentration increased to 166 mg N/L, NH_4^+-N removal loading rate increasedsuddenly up to 0.3 kg N/m^3/day. If Planctomycetes bacteria was exposed to wastewater with high NH_4^+-N concentration at the same time of HRT reduction for a long time, bacteria may not be adapted immediately and it will be inhibited. It may caused the reduction of removal efficiency. Forturnately, the influent NH_4^+-N concentration decreased sharply to 111.6 mg N/L, so the NH_4^+-N removal loading rate was reduced accordingly to 0.19 kg N/m^3/day and bacteria also was adapted in this circumstance.

The operational results of this reactor show that the application of the PN/AX is very promisingand practical. With HRTs of 18h, 12h and 10h, effluent NH_4^+-N concentration was 3 mg N/L, 7.4 mg N/L and 9.8 mg N/L, respectively. These values meet the Column B of QCVN 40:2011/BTNMT. However, with the HRT of 10h, the operational time should be longer to ensure that the effluent NH_4^+-N concentration also meets in stablelythe Column B, QCVN 40: 2011/BTNMT.

3.3 Attached biomass observation

After 183 days of operation, seed sludge was adapted and attached on the surface of biomass carrier material in slaughterhouse wastewater as shown in Fig. 5.

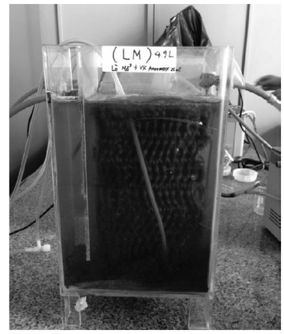

Figure 5. *Attached biomass observation after 183 days*

4. Conclusions

In the operational phases of PN/AX reactor with real slaughterhouse wastewater after AnMBR, with HRTs of 18h, 12h and 10h, the influent NH_4^+-N concentration was fluctuated from 100 mg N/L to 160 mg N/L, the effluent NH_4^+-N concentration was always less than 10 mg N/L. This value meets the Column B of QCVN 40:2011/BTNMT. In addition, the NH_4^+-N removal loading rate increases gradually from 0.07 ± 0.02 kg N/m^3/day in phase 1 to 0.21 ± 0.02 kg N/m^3/day in phase 5.

This showed that the nitrogen compound in slaughterhouse wastewater can be removed by the PN/AX reactor. However, the fluctuation of influent NH_4^+-N concentration may inhibited to Planctomycetes and lead to the shocking of bacteria

The above results proved that this technology is applicable for treatment of wastewater containinghigh nitrogen concentration such as slaughterhouse wastewater, rejected wastewater from sludge treatment process, the effluent from septic tanks, etc. However, this study should be implemented in pilot scale to confirm the appropriate technology for nitrogen removal from wastewater containing high nitrogen concentration.

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