COD AND NITROGEN REMOVAL OF AEROBIC GRANULAR SLUDGE IN SEAFOOD PROCESSING WASTEWATER TREATMENT

Phuoc-Dan Nguyen, Xuan-Thanh Bui*, and Trong-Luc Nguyen

Faculty of Environment, Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam,
e-mail: bxthanh@hcmut.edu.vn

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Abstract

Aerobic granule was formed and stably in the sequencing batch airlift reactor with the seafood-processing wastewater at different organic loading rates (OLR) and nitrogen loading rates (NLR). At the N/COD ratio of 0.1, the COD removal efficiency was ranging from 94 to 96 % for OLR of 2.6 – 7.2 kg COD/m^3.d. The TKN removal efficiency was 93, 94 and 79 %, respectively. At the varied N/COD ratios, the TKN removal efficiency was approximately 95 % for the NLR of 0.3 and 0.6 kg N/m^3.d (N/COD of 0.1-0.2). The TKN removal efficiency reduced to 66% at the NLR of 0.9 kg N/m^3.d. In general, nitrification process occurred completely at the OLR less than 4.8 kg COD/m^3.d and the NLR less than 0.6 kg N/m^3.d. The simultaneous organic and nitrogen removal was effective at the OLR of 2.6-4.8 kg COD/m^3.d and the NLRs of 0.3 - 0.6 kg N/m^3.d.

Keywords: Aerobic granule, N/COD ratio, Nitrogen loading rate, Nitrogen removal, Organic loading rate, Seafood-processing wastewater

Introduction

The seafood processing industry consumes a large amount of water with the rate of 40-114 m^3 per ton of products [1]. This is one of the water pollution sources in Ho Chi Minh City, Vietnam. This type of wastewater contains high concentrations of organic and nitrogenous compounds. The high strength wastewater was suitable to treat by granular sludge technology. Aerobic granule shows advantageous in terms of high settling ability, simultaneous organic and nitrogen removal, high biomass retention, etc. Depends on the feeding wastewater, the biodiversity of microorganisms in these biogranules coexists in the structure of granule including bacteria such as acidifying, nitrifying, denitrifying, autotrophs, phosphorus accumulating species, etc. [2,3]. The components and quantity of microorganisms depend on the subtrate, organic loading rate (OLR), COD/N ratio, etc. *Nitrosomonas* and *nitrobacter* exist in the depth of 70-100 µm from the granule surface. The denitrifying bacteria (*Bacteroides spp.)* appears as deep as 800-1000 µm from the granule surface. Thus, the large granule contains both aerobic and anaerobic zones in the structure.

The OLR was found to have certain impact on the time of granule formation. The suitable OLR range was from 2.5-15 kg COD/m^3.d for synthetic wastewater. When the OLR increased from 3-9 kgCOD/m^3.d, the granule size also increased from 1.6-1.9 mm [4,5]. The OLR did not influence on the granule morphology but density, biomass retention, and settling ability. An increase in OLR led to the biomass growth which could weaken the granule structure [5]. Thus, it is necessary to maintain a certain OLR to supply enough food for microorganisms in whole granules. However at the high OLR, it is worth to take into account the inhibition of microbial growth, oxygen diffusion, mixing condition, and granule stability. Tay et al. [6] reports that the higher OLR the larger granule size and better settling ability. The physico-chemical characteristics were different at various operated OLRs. The biodiversity is low at the higher OLR and vice versa [7]. The high OLR stimulated the granule formation and produced large granule size with weak structure while it was opposite for the low range. Therefore, the OLR can be a factor, stimulating granule size and increasing biomass in system. It was similar for the NLR. Thus, both organic and nitrogen loading rates influenced the structure, strength, and stability of granules.

According to Jin et al. [8] the N/COD ratio reduced, the growth of autotrophs was inhibited. The nitrification could not occur at the ratio of N/COD less than 0.1. The growth of nitrite- and ammonia-oxidizing bacteria increased at which heterotrophs reduced. The nitrification took place at the ratio of N/COD of 0.1–0.3 but it did not occur at the ratio lower than 0.05.

In this study, the performance of aerobic granular sludge in terms of organic and nitrogen removal at various N/COD for seafood processing wastewater was investigated.

Materials and Methods

Reactor Set-up

Aerobic granules were cultured in a sequencing batch airlift reactor (SBAR) with the working volume of 2.4 L, the diameter and length of down-comer was 6.5 cm and 104 cm. Those of riser were 4.5 cm and 90 cm respectively. The riser tube was positioned 2 cm above the bottom of the SBAR. Air was supplied through a porous stone diffuser at the superficial air velocity of 2.1 cm/s. Every batch, 1.3 L of supernatant was removed, equal to the volume exchange ratio of 54 %. The SBAR was operated at 3 hour cycles, including 6 minutes of feeding, 346 minutes of aeration, 3 minutes of settling and 5 minutes of supernatant drainage.

Seed Sludge and Support Media

Seed sludge was taken from an activated sludge plant. Initially, the seed sludge (MLSS of 4000 mg/L, SVI_{30} of 200 mL/g) was operated with glucose-based synthetic wastewater for granule formation. The wastewater components was similar to Thanh et al. [4]. The shell carrier with the size of 50–200 μm with amount of 20 g/L was added as a support for granule formation. After 5 months of operation with synthetic glucose-based wastewater, granule started failure with filamentous and fungus microorganims on the surface. Then, synthetic seafood-processing wastewater (400 mL granules, MLSS of 3875 mg/L, SVI_{30} of 65 mL/g) was replaced.

Wastewater Characteristics

Synthetic seafood – processing wastewater was made by mixing 200 g of anchovy fish without heads and bonds into 10 L of water. The characteristics are expressed in term of mg/L: COD (4800-5600), BOD_5 (2380-2850), N-NH_3 (31.5), TKN (300-400), N-NO_2 (0.025), N-NO_3 (0.086), total phosphorus (133-205), SS (273-590), and alkalinity (450-670). Wastewater pH was adjusted in the range of 7.2 ± 0.2 by $NaHCO_3$. The wastewater was diluted to acchieve the required OLR.

In this study, the granule characteristics, organic and nitrogen removal were investigated through the two following experiments. The first experiment, it was operated at the varied OLRs (2.6, 4.8 and 7.2 kg COD/m^3.d) at the contant N/COD ratio of 0.1. In the second experiment, the N/COD ratios varied (0.1; 0.2 and 0.3) which corresponds to the NLR of 0.3; 0.6 and 0.9 kg N/m^3.d. To achieve the certain NLR, the NH_4Cl was added into the wastewater.

Analytical Methods

Granule characteristics and treatment performance were investigated through physico-chemical parameters such as pH, DO, MLVSS, MLSS, granule size, and SVI. The nitrogen removal were investigated through parameters such as TKN, $N-NH_3$, $N-NO_2$, and $N-NO_3$. The methods for all analysis were followed acording to standard methods [9].

Results and Discussion

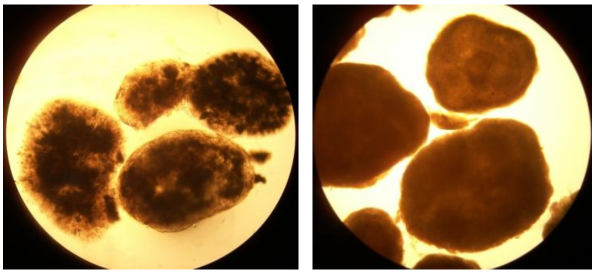
Effect of OLR on Granule Characteristics and Nitrogen Removal at Fixed N/COD Ratio

Granule Characteristics

The morphohology of granules cultured from synthetic glucose-based wastewater was diversified at later stage such as spherical, elipsoit with filaments on surface and loosen structure. However, the surface of granules appeared smooth without filaments and fungus after two weeks of operation with synthetic seafood wastewater (Figure 1). The granule structure was stable and stronger from the third week. The granule color appeared dark yellow. The size increased gradually with OLRs and was stable around 1-3 mm. During this period, it is observed that the soft structure granules broken down. The light sludge fraction (suspended solids) drained out of the system. This explains for the reduction of sludge concentration during the starting period. At higher OLR, the larger granule formed dominantly (2-3 mm). Compared to glucose-fed granules, the seafood wastewater-fed granules were more stable and stronger. This could be explained that seafood wastewater contained sufficient certain minerals, metals and nutrients which are components in the sludge matrix [10].

At the steady state of the OLR of 2.6 kg $COD/m^3.d$, the MLVSS mainatined at 2300 mg/L and the MLVSS/MLSS ratio was as high as 0.9. Especially, filamentous and fungus granules (*white granules*) vanished completely and replaced by dark yellow granules with smooth and spherical structure. The granule size was in the range of 0.5-2.0 mm. The settling ability improved through the reduction in SVI value. When the OLR increased, the settling ability slightly reduced, but much better compared to activated sludge. The SVI were 50; 54 and 70 mL/g at the OLR of 2.6; 4.8 and 7.2 kg $COD/m^3.d$ respectively. The OLR increased, the activity of microorganisms increased to degrade the available organic substrates. This process produces more EPS, thus increase the viscosity of bulk liquid [11].

It shows that the seafood processing wastewater can improve stability and structure of aerobic granules. According to Liu et al. [11], the stability of granule can be observed with the presence of nitrifying microorganisms by increasing the N/COD ratio. Nitrifying microorganisms developed slower compared to heterotrophs and the structure of nitrifying biofilm was stronger than that of heterotrophs [8].



(a) (b)

Figure 1. Granule morphology (a) cultured by glucose-based wastewater with filaments and fungus on the granule surface; (b) after 24 days operated by seafood-based wastewater

COD and Nitrogen Removal

Figure 2 presents that from day 17-35, the SBAR was operated at OLR of 2.6-4.8 kgCOD/m^3.d (F/M = 0.8-0.9 kg COD/kg VSS.d). The MLVSS increased from 2300 mg/L to 6300 mg/L. The SRT reduced from 15 days (day 20) to 4 days (day 33) because of an increase in excess sludge drained through the effluent valve. The MLVSS in effluent increased from 70 mg/L to 786 mg/L. From day 35 to 51, the reactor was operated at OLR of 7.2 kg COD/m^3.d (F/M = 1.23-1.86 kg COD/kg VSS.d). The biomass concentration reduced from 5240 mg/L (day 37) to 4050 mg/L (day 51). The high OLR caused the serious washout of suspended solids due to the sharp increase in substrate concentration. At this operating conditions, the SRT fluctuated in the range of 2.5–4.5 days. MLVSS and SRT reduced at OLR of 7.2 kg COD/m^3.d. This was due to the production of viscous biofilm which was origin from EPS. The viscous biofilm covered the granule surface and lessen its settling ability. The washed out biomass was as high as 1320 mg/L. This makes the SRT and sludge concentration in reactor low.

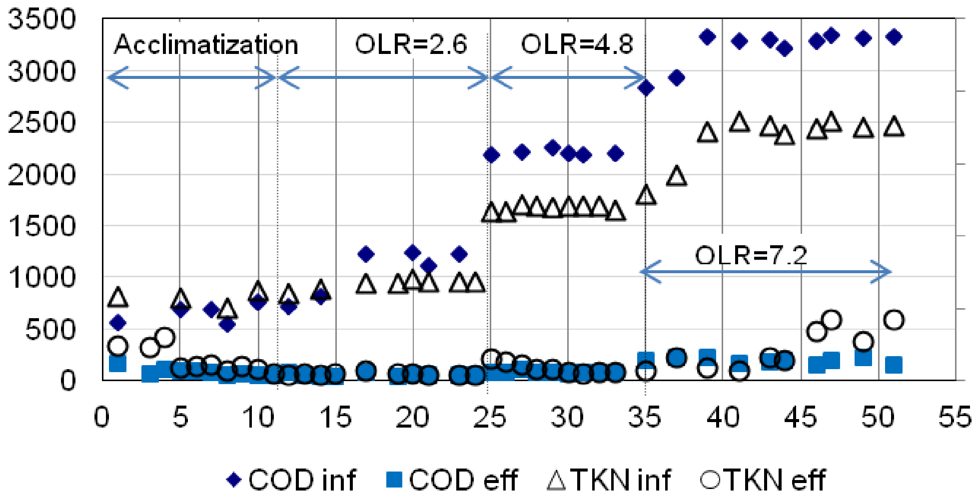


Figure 2. Removal efficiency of COD and TKN at various OLRs

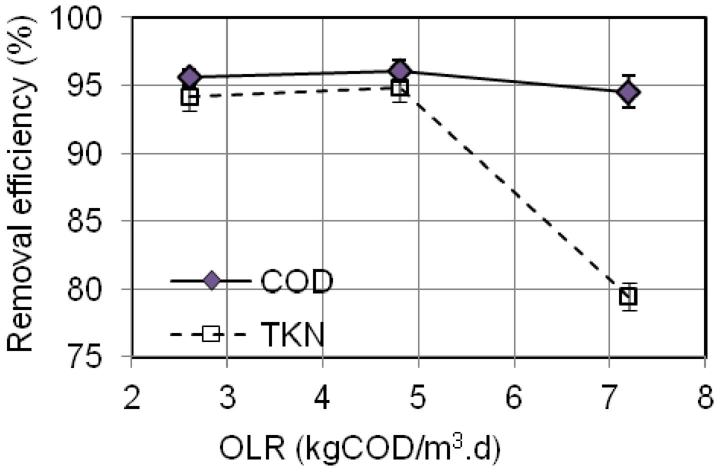


Figure 3. Removal efficiency of COD and TKN at different organic loading rates

Figure 3 indicates the removal efficiency of COD was ranging from 94 to 96% at three OLRs. Effluent concentrations of COD was 56 ± 12, 82 ± 7 and 186 ± 23 mg/L at the OLR of 2.6, 4.8 and 7.2 kgCOD/m^3.d, respectively. While the average removal efficiency of

TKN was 93, 94, and 79%, respectively. The respective effluent concentrations of TKN reached 6.4, 12.4, 84.0 mg/L. It indicates that at the same N/COD ratio, an increase in the applied organic loading rate makes the nitrification process weaken. The dominance of heterotrophs inhibits the growth of nitrifying microorganisms. It is observed that the simultaneous removal of organic and TKN was highest at the OLR of 4.8 kgCOD/m^3.d at the N/COD of 0.1.

Effect of OLR on the Nitrification of Granules at the Constant N/COD Ratio

Figure 4 shows that at the OLR of 2.6 kg COD/m^3.d (NLR of 0.3 kg N/m^3.d), the effluent concentration of N-NH_3 always lower than 2 mg/L while the concentration of N-NO_3 increased and reached the maximum concentration of 119 mg/L (influent TKN of 136 mg/L). It indicates that the organic nitrogen was transformed into nitrate nitrogen. At this stage the granule size varied from 0.5-2.0 mm. According to De Kreuk et al. [12], the smaller size the better nitrification. The smaller size had better contact with oxygen and substrate. The ease of oxygen diffusion enhanced nitrification into NO_x, mostly nitrate nitrogen form. The optimum size of granule for nitrogen removal was 1.2-1.4 mm. The concentration of N-NO_3 always higher than that of N-NO_2 which was opposite which the result of authors [4,13]. This notices the complete nitrification occured in the granular sludge system at OLR as low as 2.6 kg COD/m^3.d.

At the OLR of 4.8 kg COD/m^3.d (NLR of 0.52 kg N/m^3.d), the effluent concentration of N-NH_3 was 2.4 mg/L. The concentration of N-NO_2 was less than 1 mg/L while that of N-NO_3 varied in the range of 152-169 mg/L (influent TKN of 240 mg/L). At this loading rate, the SRT fluctuated in the range of 3.5-5.6 day but the nitrification still occured. It shows that the granule was retained longer in reactor and contained nitrifying microorganisms in the inner core of granule. At this stage, granule size was in the range of 1.0-3.0 mm. The large size granule limited the oxygen diffusion. Li et al. [7] reported that DO concentration in granule reduced gradually from the surface to the core. It reached zero at the depth of 1.6 mm from the granule surface. The anaerobic zone existed in the deeper zone, thus the denitrification could occur in the inner core of granule. The removal of nitrate nitrogen depends on the granule size.

At the OLR of 7.2 kg COD/m^3.d (NLR of 0.76 kg N/m^3.d), the effluent concentrations of N-NH_3 and TKN increased. This reveals the limit of nitrification of system at high OLR. The concentration of N-NO_3 decreased from 160 mg/L to 27 mg/L. At this operating condition, the nitrate nitrogen concentration reduced significantly and organic nitrogen was not converted into nitrite and nitrate completely.

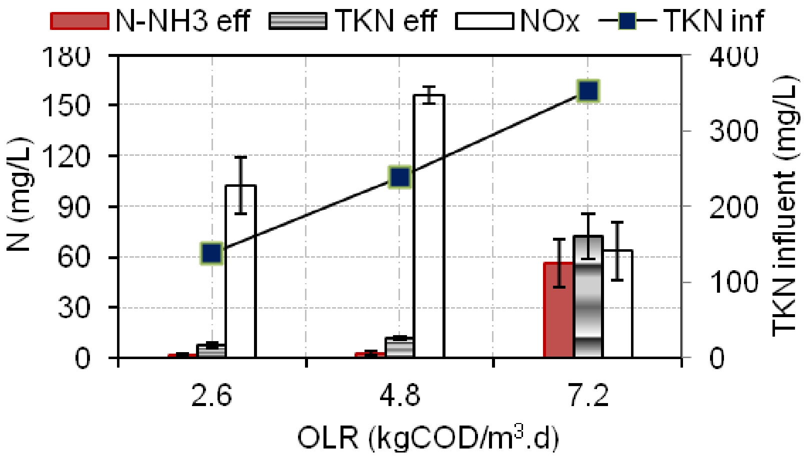


Figure 4. Change of nitrogen species with OLR

Figure 4 shows that at the OLRs of 2.4-4.8 kg COD/m^3.d, the nitrification occured completely at these loading rates. At the OLR of 7.2 kg COD/m^3.d, the nitrification process reduced. The nitrification occured started after 90 minutes at the OLR of 2.6 and 4.8 kg COD/m^3.d while at the OLR of 7.2 kg COD/m^3.d, it happened after 270 minutes.

In activated sludge process, the nitrification happened at the SRT of 10-15 days. According to Liu and Tay [14] the simultaneous organic and nitrogen removal occured in the granular sludge system at the SRT higher than 4 days. In this study, the proces could occur at SRT of less than 5 days. This indicates the calculated SRT of granular sludge reactor was not similar to that of activated sludge process. These results are as same as [4]. This can be explained through the special structure of granules that made granule maintained in the reactor as long as its disintegration or washout.

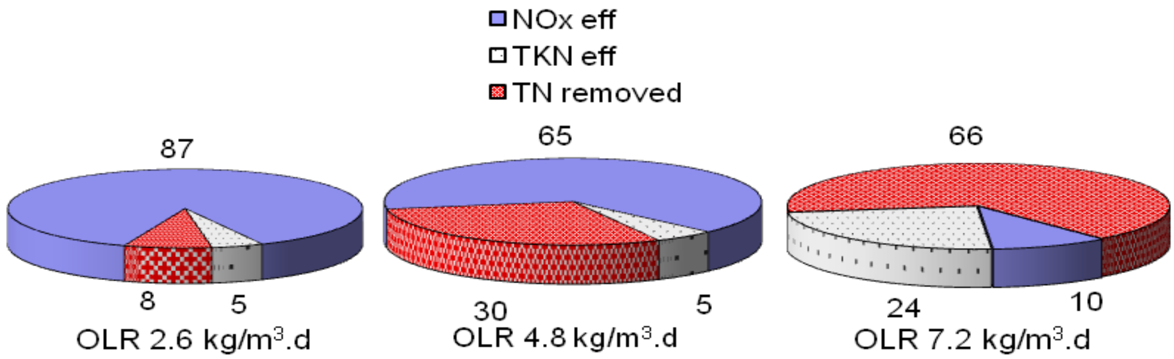


Figure 5. Nitrogen balance at various OLRs (N/COD = 0.1)

Figure 5 presents that the nitrogen removal through cell systhesis and denitrification was 8, 30 and 66% for the OLR of 2.4, 4.8 and 7.2 kg COD/m^3.d. At the first two OLRs, the TKN mostly converted into N-NO_3. However at the OLR of 7.2 kg COD/m^3.d, the nitrification occured incompletely and the effluent TKN concentration was still high (24% of influent TKN). Similarly, the concentrations of NO_x increased with the first two OLRs and reduced at the highest OLR.

Effect of the N/COD Ratios on Nitrification Process at the Constant OLR

Granule Characteristics, COD and TKN Removal

In this study, the influent COD was maintained at OLR of 2.6 kgCOD/m^3.d while the NLR varied from 0.3, 0.6 and 0.9 kg TKN/m^3.d (N/COD ratio of 0.1, 0.2 and 0.3). At the begining, the granule size varied from 1.5-3.0 mm. The settling ability of granule was found to be better at higher NLR. The SVI reduced from 72 to 49 mL/g when the NLR increased.

Figure 6 shows the removal efficiency of TKN was about 95% for the NLR of 0.3 and 0.6 kg N/m^3.d. The effluent concentration of TKN was 5.9 and 12.8 mg/L respectively. At the NLR of 0.9 kg N/m^3.d, the removal efficiency reduced to 66%, with the effluent concentration of TKN of 140 mg/L. It is observed that the nitrification capacity of granular sludge system was twice compared to that of activated sludge process. The nitrification capacity of activated sludge was approximately 0.32 kg N/m^3.d [15].

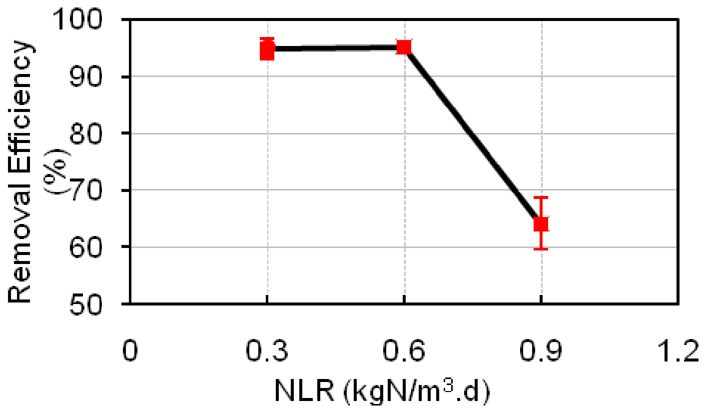


Figure 6. Comparison of nitrogen removal at various NLRs

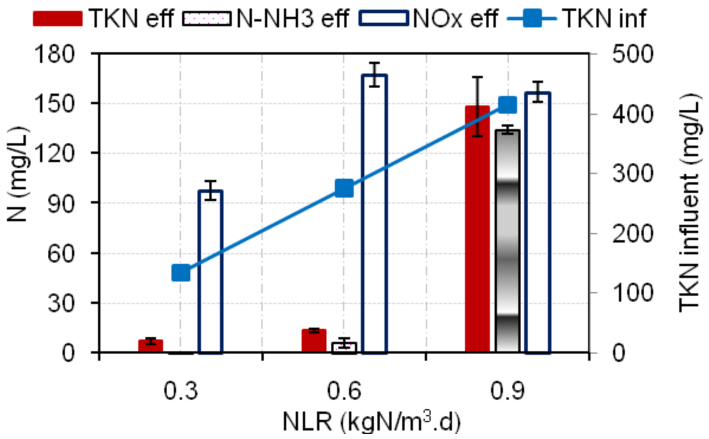


Figure 7. Change of nitrogen species at various NLRs

At the NLR of 0.3 kg N/m^3.d (N/COD = 0.1), concentration of ammonia in effluent was not detected while the concentration of nitrate increased and reached highest value of 88.7-99.8 mg/L. The nitrate nitrogen concentration was lower compared to that in the previous experiment (119 mg/L), even at the same operating conditions (OLR of 2.6 kg COD/m^3.d, NLR of 0.3 kg N/m^3.d). The reason was due to the difference in the size of granules in the two experiments. In the second experiment, the granule size was 2-3 mm (82%) while it was as small as 0.5-1.5 (86%) in the first experiment. The larger size granules enabled the better complete nitrogen removal through simultaneous nitrification denitrification.

At the NLR of 0.6 kg N/m^3.d (N/COD = 0.2), the concentration of N-NH_3 in effluent reduced and reached 4.5 mg/L on day 73. At the end of batch, most of organic nitrogen converted into ammonia nitrogen form (Figure 8). The nitrate concentration gradually increased and reached 150 mg/L (influent TKN of 276 mg/L). At this stage, the concentration of N-NO_3 was equal to that of NLR of 0.52 kg N/m^3.d (OLR = 4.8 kg COD/m^3.d) but higher than that of NLR of 0.3 kg N/m^3.d in the first experiment.

At the NLR of 0.9 kg N/m^3.d (N/COD = 0.3), the concentration of N-NH_3 in effluent varied in the range of 131-137 mg/L. The concentration of N-NO_3 gradually reduced and stabilized in the range of 148-167 mg/L (influent TKN of 414 mg/L). At this operating condition, the nitrification was not complete even at the SRT of 18 days.

Figure 7 shows that the nitrification was complete at the NLR of 0.3-0.6 kg N/m^3.d (N/COD = 0.1-0.2) while it was not at 0.9 kg N/m^3.d (N/COD = 0.3). This result was found to be similar to that of Yang et al [16].

Nitrogen Balance at Different NLRs

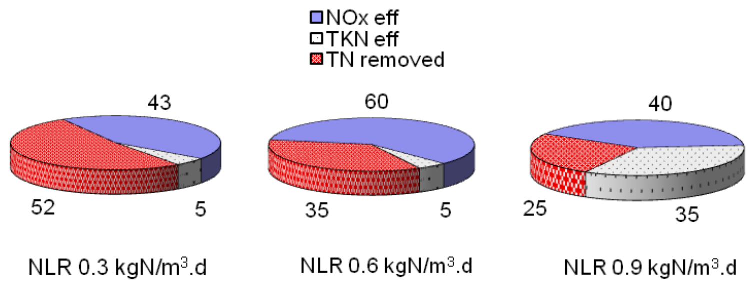


Figure 8. Nitrogen balance at different NLRs

Figure 8 shows that the TN removal from biomass yield and denitrification was 52, 35 and 25% for the NLR of 0.3, 0.6 and 0.9 kgN/m^3.d, respectively. The effluent concentration of NO_x at the NLR of 0.6 kg N/m^3.d increased up to 60%. The ammonia stripping was neglegible due to pH lower than 8.5 so the nitrogen loss was for the major of the denitrification process and biomass yield. The effluent TKN concentration was as low as 5% for the NLR of 0.3-0.6 kg N/m^3.d while it was 35% for the remaining NLR. This indicates that the nitrogen removal was acchieved effectively at the NLR lower than 0.6 kg N/m^3.d.

Conclusions

Granules was unstable with glucose-fed wastewater after a period of operation. However, they recovered with sea-food processing wastewater after 3 weeks of operation. The fungus and filamentous granules disappeared and the clear, strong outer surface granules formed in the seafood processing wastewater. The granules were more stable with the real wastewater.

The removal efficiency of COD was more than 96% at the F/M ratio of 0.80-1.86 kg COD/kgVSS.d at the constant N/COD ratio. At the OLR lower than 4.8 kg COD/m^3.d the nitrification was complete while it was not for the OLR of 7.2 kg COD/m^3.d. The activity of nitrifying microorganism worsen at the high OLR. The removal efficiency of TKN at the OLR of 7.2 kg COD/m^3.d and NLR of 0.76 kg N/m^3.d reduced to 76%.

At the fixed OLR of 2.6 kg COD/m^3.d, the nitrification process increased with the N/COD ranging from 0.1-0.2. It reduced at the ratio of 0.3.

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