Optimum Carbon/Nitrogen Ratio for upgrading single-stage activated sludge process in the Frozen Seafood Industry

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Abstract

The study aimed to upgrade the nitrogen removal efficiency in the existing activated sludge process for treating the effluent from anaerobic treatment units in the frozen seafood industry. The experiments provided simultaneous nitrification-denitrification in the single-stage activated sludge process without major changes being made in the civil engineering system. Under very low operating oxygen concentration, with oxidation-reduction potential for aeration control, The carbon/nitrogen ratio was proved to be the main factor for high nitrogen removal efficiency in the process. COD:TKN in this study was 10:1. It can provide for both satisfactory simultaneous carbon and nitrogen removal.

Keyword: *COD:TKN ratio, Frozen seafood industry, Simultaneous nitrification-denitrification*

1. Introduction

The frozen seafood industry is one of Thailand's top export performers. Most expansion has taken place in southern Thailand. The wastewater from these factories contains high organic carbon and nutrient levels. Nowadays, the Activated Sludge Process (ASP) is applied to these factories in order to reduce the land required for treatment plants and to increase treatability. However, due to high carbon concentrations in their wastewater, applying only the ASP has led to high operation costs, including the cost of electricity for aeration. Therefore, anaerobic treatment units, such as Upflow Anaerobic Sludge Blanket (UASB), was introduced to reduce organic loads.

Combining biological processes for nitrification, denitrification, anaerobic, and aerobic removal of carbonaceous nutrients to affect nitrogen removal provides a considerable number of different process possibilities. These feature various configurations of separate-stage and combined processes. A high nitrogen removal rate can generally be achieved in a separate sludge system in which the effluent from the nitrification stage is fed to a separate anoxic reactor for denitrification.

It was noted that the influent wastewater from the frozen seafood factory contained high concentrations of nitrogen. The influent nitrogen concentrations normally exceeded the desirable level. Their treatment systems required a nitrogen removal process. The organic carbon level had the greatest impact on the efficiency of the denitrification process. But, in fact, a process which combines the ASP and UASB can not treat nitrogen properly. The effect was caused by the reduction of the carbon source by methane production in the UASB reactor and less degradable carbon was available for denitrification in the ASP with nitrogen removal units. Their carbon:nitrogen (C:N) ratio was not applicable, and therefore, an external carbon source was required.

Zhang and Zhou [1] reported that a C:N ratio in wastewater of 10 and Dissolved Oxygen (DO) at 0.5 mg/L can treat organic carbon, organic nitrogen, and ammonia-nitrogen at the highest capacities: 89.5, 43.0, and 98.5 percent, respectively. However, they also reported that the ammonia-nitrogen removal rate decreased when the DO concentration was 0-0.1 mg/L. Carrera *et al.* [2] used two different industrial carbon sources, one containing mainly ethanol and the other one methanol, for completing the denitrification process in a two-stage ASP. Their results showed that the maximum denitrification rate reached with ethanol was about 6 times higher than that with methanol. This proved that easily biodegradable carbon was required for a complete denitrification process. However, the ethanol or other external carbon source would be expensive and inconvenient. Their raw wastewater was suggested to be an appropriate source for improving the denitrification rate.

Simultaneous nitrification-denitrification (SND) without alternating anoxic/oxic conditions was selected for improving the capacity of the treatment plants. This was based on the idea of achieving high nitrogen removal through a high denitrification rate, and saving aeration energy through lower amounts of oxygen required in the single aeration tank. This requires no major structural changes in the treatment plants. SND notably requires optimum influent concentrations and operating DO concentrations.

The Oxidation-Reduction Potential (ORP) value was widely introduced as an efficient parameter for optimizing DO control. However, relatively little ORP data is available for the simultaneous, non-alternating, nitrification-denitrification process. Collivignarelli and Bertanza [3] proposed to control the aeration by controlling the ORP value as a constant for the SND in a single-stage activated sludge system. However, their research was applied to community wastewater with low organic carbon and nitrogen concentrations.

Zhao *et al.* [4] reported the success of using ORP to control nitrogen removal, the in 3-stage Bardenpho and 2-stage intermittent aeration processes. Their results showed that the ORP can be effectively used for DO control in a narrow range. Ndegwa *et al.* [5] confirmed that the ORP was a good parameter for the aeration control system, and was better than the DO concentration when the system needed to be controlled at low DO concentrations.

The main objective of this study was, therefore, to investigate the optimum carbon and nitrogen ratio for upgrading single-stage SND treated high nitrogen concentration wastewater from the frozen seafood industry. By applying the various ratios of influent fed to UASB and ASP, different nitrogen removal efficiencies were observed, under low DO concentrations which were controlled by the application of ORP.

2. Methodology

2.1 A representative frozen seafood factory

A representative frozen seafood factory (shrimp processing) produces wastewater containing a high concentration of nitrogen (about 200 mg/L). Their existing treatment plant consisted of an UASB working with the two-stage ASP (with the nitrogen removal units, and nitrification and denitrification tanks).

However, in the past, complete denitrification could not take place. This was because less organic carbon was fed to the denitrification tank, after treatment by the UASB (influent COD was reduced from 2,000 mg/L to 400 mg/L). The operator solved this problem by by-passing raw wastewater partially to the denitrification tank, which was about 44% by volume. Fig. 1 shows the schematic diagram of this representative plant. Table 1 shows the chemical characteristics of its wastewater [6].

Nevertheless, Boonyarattaphan *et al*. [7] reported that the effluents from this treatment plant showed that amounts of nitrate-nitrogen, from the two-stage ASP, were discharged to the post treatment unit, a constructed wetland. Thus the ASP with nitrogen removal units could not function well. The effluent from the ASP contained nitrate-nitrogen of 52.2 ± 8.9 mg/L [8] (number of samples = 10, and the samples were collected once a week).

Table 1 Wastewater characteristics from the representative treatment plant.

Parameter (mg/L)	Sample	Average ± Standard deviation
BOD_5	Inf.	862.0±184.6
	Eff.	2.0±0.7
COD	Inf.	1618.2±629.0
	Eff.	34.9±23.0
SS	Inf.	323.0±182.0
	Eff.	20.5±17.2
TKN	Inf.	185.3±48.3
	Eff.	11.2±14.8
NO_3-N	Inf.	3.1±4.3
	Eff.	17.9±12.4

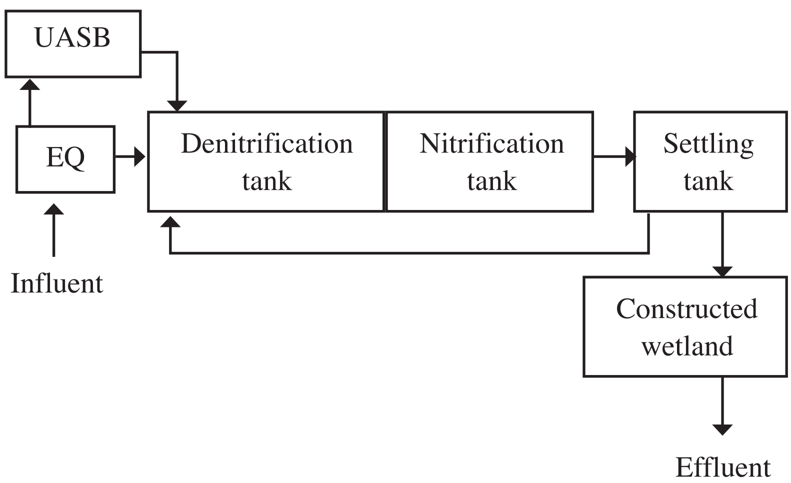

Fig. 1. Schematic diagram of the representative plant [9].

2.2 Reactor system

Therefore, in this study, using the wastewater from this factory, pilot-scale SND experiments were investigated. A pilot-scale single-stage ASP, with about a 75 liter aeration capacity, was used for the experiments. The temperature, ORP, and pH were recorded every 10 minutes by online-analyzers (WTW, pH/Oxi 340i). An air pump used in the experiments was automatically controlled at ORP of 0 $\pm$ 50 mV [9, 10]. To maintain the ORP of 0 $\pm$ 50 mV, the control system for the volume of air supplied can vary from 1 to 75 L/min. However, the system required at least 5 L/min to ensure good mixing conditions. The aeration control system was programmed. The actual situation and processes were continuously monitored and recorded at about 10 minute intervals, with the help of computer programming and online-analyzers.

2.3 Experimental design

The SND experiments were conducted with various C:N ratios, by varying the ratio of raw wastewater and effluent from the UASB. The adding of sugar (commercial grade) was required to increase the organic carbon in the influent fed to the aeration tank. The SND processes were controlled at a Hydraulic Retention Time (HRT) of 48 hours (similar to the actual HRT at the treatment plant, HRTs of the nitrification and denitrification tank were 24 hours each). Table 2 shows all operating conditions for the experiments. The volume of surplus sludge was controlled to maintain a solids content of 3.0-4.0 g/L. The sludge retention time (SRT) was not a concern in this study because, in the actual situation, it is very rare to find a local treatment plant in which surplus sludge is discharged continuously. Most of the operators are only concerned about the SV_{30} values in the aeration tank.

In the first phase, raw wastewater from the equalization tank was fed directly to the pilot-scale aeration tank. The second phase was conducted using the same conditions as in the representative plant (control). The ratio of wastewater from the equalization tank and the effluent from the UASB was 44 to 56 percent by volume. In the third and fourth phases, sugar was intentionally added to the wastewater from the equalization tank to increase the COD concentrations.

Table 2 Operating Conditions for the experiments.

Parameter	Phase			
	1	2	3	4
HRT (hr)	48	48	48	48
MLSS (g/L)	3.4±0.3	3.4±0.3	4.0±0.2	4.0±0.2
MLVSS (g/L)	2.7+0.2	2.7+0.1	3.3+0.2	3.1+0.3
DO_{range} (mg/L)	0.3-0.8	0.3-0.8	0.3-0.8	0.3-0.8
COD_{inf} (mg/L)	1280	934	2160	2686
TKN_{inf} (mg/L)	192	207	202	218
COD:TKN	7:1	4.5:1	10:1	12:1

2.4 Sampling and analytical methods

Samples of activated sludge and effluent were taken every day. Ten days of sampling after the steady-stage condition was required. The influent was analyzed once a week (wastewater from the factory). COD, BOD_5, DO, total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), nitrite nitrogen ($N\bar{O}_2$-N), nitrate nitrogen ($N\bar{O}_3$-N), and suspended solids (SS) were analyzed according to the Standard Methods for the Examination of Water and Wastewater [11]. Particle sizes of activated sludge were measured by laser particle size analyzer (COULTER LS 230).

3. Results and discussion

3.1 Overall removal efficiencies

First of all, the results confirmed that the single aeration tank permitted both carbon and nitrogen removal. The SND can treat high concentrations of COD (up to 2,686 mg/L). Table 3 shows the removal efficiencies in each phase. The COD removal efficiency reached 94-97 percent, and 99 percent for BOD_5 removal. Total nitrogen (TN) removal varied from 20 to 90 percent, while COD:TKN changed from 4.5:1 to 12:1. The removal of suspended solids varied from 86 to 98 percent. This SND process might be a solution for upgrading the existing wastewater treatment plant (as used in this representative plant). The carbon removal rates were as high as those from single-stage ASP, which required a high DO concentration (over 2 mg/L). With this SND, not only the same COD removal capacity, but an increased TN removal rate was achieved.

With the ORP control system, the DO concentrations in this study were, on average, 0.36 ± 0.08, 0.42 ± 0.08, 0.58 ± 0.10, and 0.55 ± 0.10 mg/L, in the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} phases of the experiments, respectively. With very small changes in DO concentrations, the controlled ORP of 0 ± 50 mV, can be an effective parameter for aeration control, when operating at low DO conditions [12, 13].

3.2 Floc sizes and the SND process

The results of nitrogen removal showed that both the nitrification and denitrification processes took place in the same aeration tank. This might be explained through the concept of there being a different layer in the activated sludge floc. Pochana and Keller [14] reported that a biofilm floc of 200 μm size and above will have an anoxic microniche in the internal part of thick flocs. Nitrification might occur on the surface layer, meanwhile, denitrification occurs in the inner layer. Table 4. shows the average particle size in each phase, measured by a Laser Particle Size Analyzer (COULTER LS 230).

Table 3 Average removal efficiencies from experiments.

Parameters	COD	BOD_5	TN	SS
Phase 1 at C:N = 7:1				
Inf. (mg/L)	1280	900	192	200
Eff. (mg/L)	83.6	5.1	55.1	4.5
Removal efficiency (%)	93.5	99.4	71.3	97.8
Phase 2 at C:N = 4.5:1				
Inf. (mg/L)	934	635	207	188
Eff. (mg/L)	51.8	3.2	165.9	26.4
Removal efficiency (%)	94.5	99.5	19.9	86.0
Phase 3 at C:N = 10:1				
Inf. (mg/L)	2160	1470	202	216
Eff. (mg/L)	74.0	4.7	20.1	5.6
Removal efficiency (%)	96.6	99.7	90.0	97.4
Phase 4 at C:N = 12:1				
Inf. (mg/L)	2686	1815	218	221
Eff. (mg/L)	123.1	12.6	3.3	13.8
Removal efficiency (%)	95.4	99.3	98.5	93.7

where TN = TKN + NO_2^--N + NO_3^--N
Number of samples in each phase were 10 (samples collected every day).

Table 4 Average particle size in each phase.

Phase	**Particle sizes (Mean ± S.D, μm)**
1	113.6 ± 126.2
2	152.4 ± 242.7
3	107.7 ± 141.4
4	86.0 ± 81.2

Measured by Laser Particle Size Analyzer (COULTER LS 230).

Zhang and Zhou [1] reported that floc sizes of 90 - 180 μm can provide anaerobic denitrification under anoxic conditions in the floc. Meanwhile, Chu *et al*. [15] confirmed that floc, which was thicker than 30 μm, under low operating DO concentration of 0.5 mg/L, was the anoxic layer. The results fitted in with the observations of particle size distribution in this study. The particle sizes in every phase of these experiments were over 100 μm, except in the 4th phase. Although, the biggest sizes of the particles occurred in the 2nd phase, the highest SND can not take place. This result proved that the floc size might not be the only important factor in the SND process.

3.3 Nitrogen removal efficiency

Concerning the highest overall TN removal in the 4th phase, the COD:TKN was 12:1. Significantly, the TN removal efficiencies increased from 19.91, 71.32, 90.03, and up to 98.05 percent, when increasing COD:TKN from 4.5:1 up to 12:1. The influent TKN was about 200 mg/L, in every phase. Table 5. shows the nitrogen contents in each phase.

In the second phase, the COD:TKN was 4.5:1, as the control phase (same COD:TKN as in the representative factory). TKN and TN removal efficiencies were lower than those in the other phases. The ammonia concentration in the effluent was 14.1 ± 5.4 mg/L, while effluent TKN was average at 33.7 ± 7.5 mg/L. This value suggested that under low DO conditions and low C:N ratio, the nitrification process can not be completed. Zhao *et al*. [4] confirmed that the percent of nitrification increased with increasing acetate and methanol dosages (increasing COD concentrations). In the second phase, not only was there high TKN and NH_3-N in the effluent, but also $N\bar{O}_3$-N in the effluent was over 100 mg/L (118.0±5.0 mg/L). These results showed that denitrification can not occur, even under low DO concentration. The effect of an insufficient carbon source was the main factor in this incomplete denitrification in the SND.

When compared with the representative factory (schematic diagram of the wastewater treatment plant is shown in Fig. 1), Fig. 2 shows that the TN removal capacities at the representative factory was slightly higher than that in the 1st phase, and much higher than that in the 2nd phase (same C:N ratio). This phenomenon confirms that to upgrade the single-stage ASP for nitrogen removal, the C:N ratio was the main factor to reach this high capacity. The SND process can provide high TN removal efficiency as in the two-stage ASP working with the UASB, when the C:N ratio is high enough.

Table 5 Details of nitrogen concentrations in each phase.

Parameters (mg/L)	Phase			
	1	2	3	4
Influent				
TKN	192	207	202	218
NH_3-N	76.8	118.0	117.6	143.5
NH_B-N: TKN	0.4	0.6	0.6	0.7
Effluent				
TKN	22.0±3.9	33.7±7.5	7.9±1.2	1.8±0.2
NH_3-N	4.2±1.0	14.1±5.4	2.9±0.8	1.0±0.1
NO_2^--N	0.16±0.04	0.22±0.07	0.50±0.13	0.66±0.11
NO_3^--N	26.5±2.5	118.0±5.0	8.7±1.4	0.77±0.39
TN	55.1±4.5	165.9±9.6	20.1±2.5	3.26±0.54
TKN removal (%)	88.5	83.7	96.0	99.2
TN removal (%)	71.3	19.9	90.0	98.5

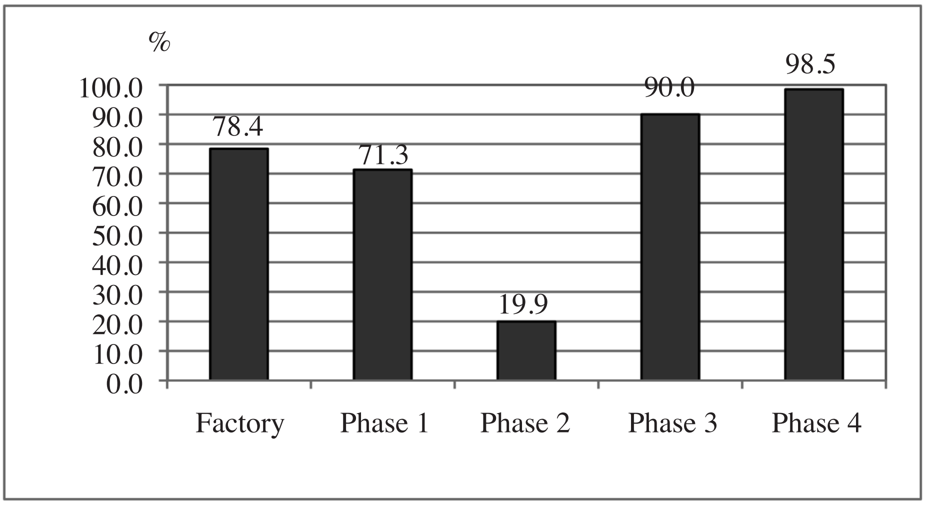

Fig. 2. Comparison of total nitrogen removal efficiencies.

3.4 Optimum COD:TKN for the SND

External carbon sources, such as acetate, methanol, ethanol or glucose, were commonly used in laboratory scale experiments [16]. However, those substances are expensive and might not be an economical solution. Therefore, in the 3rd and 4th phases, the wastewater from the equalization tank was mixed with sugar (commercial grade) for increasing the COD concentration. The influent BOD_5 in the 3rd and 4th phase were 1,470 and 1,815 mg/L, respectively. The BOD_5:COD ratio was 0.7, nearly equal to BOD_5:COD in the 1st phase (100 percent raw wastewater from the equalization tank). This ratio showed the condition of biodegradable carbon availability.

The results in Table 5 show that a COD: TKN of 12:1 proved to be the best ratio (from 4.5, 7, and 10) for TN removal in the SND process. However, this 12:1 ratio was not the best for carbon removal efficiency (COD and BOD_5 removal were lower than those in the 3rd phase). Furthermore, Wang *et al*. [17] conducted their experiment using SND with a membrane bioreactor. They reported that the C:N ration has no extreme effect on COD removal, but affects ammonia-nitrogen and total nitrogen removal. Ying *et al*. [18] reported on the optimum C:N ratio for the SND in a sequencing batch bioreactor of 6 to 8. A similar trend was reported by Chiu and Chung [19]. They adjusted the COD/NH_3-N ratio up to 11.1, and found that the SND in the sequencing batch bioreactor achieved complete removal of NH_3-N and COD. However, it has to be noted that the sequencing batch reactor provides a cyclical operation of an alternating anoxic/oxic system in a single aeration tank. But the single aeration tank in this study allowed the SND without the temporal or spatial alternation of oxic/anoxic conditions.

3.5 Aeration in the SND

With the ORP control system, as mentioned above, the DO concentrations in this study were, on average, 0.36 ± 0.08, 0.42 ± 0.08, 0.58 ± 0.10, and 0.55 ± 0.10 mg/L, from the 1st to the 4th phase of experiments. By observation, the operating DO concentrations varied between 0.3-0.8 mg/L. The SND has the benefit of reducing the consumption of aeration energy. The volume of air supplied to the aeration tank was observed in order to define the amount of aeration energy consumed. The volume of air supplied to the aeration tank, with controlled ORP at 0 ± 50 mV, were 5, 3, 6, and 8 L/minute, in the experiment periods 1 to 4, respectively. Fig. 3 shows the amount of air supplied, per mg of COD and TN removed, from the 1st to the 4th phase.

Each period of experiments was fed with different influent loading. Therefore, air supply rates were calculated in terms of liter of air supplied per milligram of substrate removed. The amount of air supplied per mg of COD removed was less than that for TN removed (by calculation). It can be seen that the air supplied in each phase was not dramatically different. It is noticeable that the least aeration energy was consumed, from a higher concentration of COD, and not from the lowest concentration as expected. However, the 3rd phase showed a satisfactory ratio of air supplied to the substrate removed. Since aeration energy is the main part of energy consumption from the whole system of the ASP treatment plants, it can be assumed that the less volume of air supplied to the aeration tank means less energy consumption.

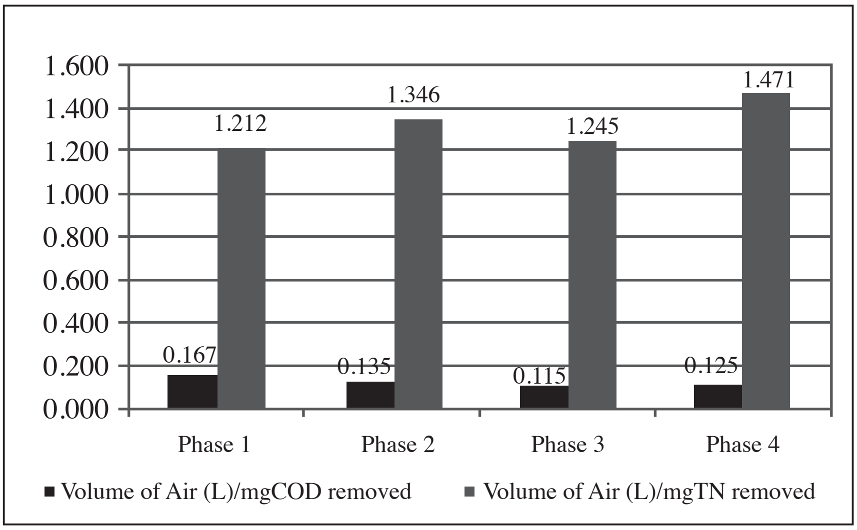

Fig. 3. The amount of air supplied in the aeration tank in each phase.

4. Conclusions

The results of this study indicate that the simultaneous nitrification-denitrification process, under low operating DO condition, might be suitable for upgrading a single-stage ASP for nitrogen removal in the seafood industry. The following conclusions were drawn:

1. Less oxygen concentration than the recommended value (about 1-2 mg/L) can provide 99 percent of BOD_5 removal in the SND.
2. The optimum C:N ratio was the main factor for controlling the rate of total nitrogen removal. The optimum COD:TKN in this study was 10:1. This can provide for both satisfactory simultaneous carbon and nitrogen removal.
3. The floc size might not be the main factor in the SND process. However, the particle sizes in this study were bigger than 80 μm.

5. Acknowledgments

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