

Analysis of nitrite accumulation with different recycle water properties in municipal wastewater treatment plant

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ABSTRACT

This research analyzed the effect of nitrification on the characteristics of recycle water, which is the effluent of sludge treatment process from a municipal wastewater treatment plant (MWTP). The laboratory-scale reactors were operated in various operation conditions for about 200 d. Operation results of laboratory-scale reactors showed that stable nitrification was induced using recycle water, and over 80% of nitrite conversion efficiency was obtained. The nitrite conversion rate was 0.37 kg NO₂-N/m³ d for the anaerobic digester supernatant, 0.32 kg NO₂-N/m³ d for the sludge decanter effluent, and then 0.17 kg NO₂-N/m³ d for the sludge thickener supernatant in order. These results showed that nitrite conversion rate was effected by ammonium nitrogen concentration and chemical oxygen demand fraction. The limit of solid retention time (SRT) was analyzed based on track study. Also, improvement of nitrite conversion rate was detected adjusting SRT from reactor operation result. The result of this research can be used as an important data for treatment of recycle water in MWTP, using nitrification.

Keywords: Nitrogen; Nitrification; Recycle water; Sludge thickener supernatant; Anaerobic digester supernatant; Sludge decanter effluent

1. Introduction

The concepts of “Sustainable Development” and the “Environmentally Sound and Sustainable Development (ESSD)” were announced from “Club of Rome” in the year 1972 and “World Commission on Environment and Development (WCED)” in the year 1987. These concepts were developed for the minimization of environmental pollution and for the effective use of energy resource. Accordingly, many research groups have studied about the wastewater treatment process with the advantage of economy, environment, and energy. The focus of

government attention is also increased regarding the same [1]. For instance, in 2013, the “Korea Institute of Science and Technology Information” (KISTI) announced the 10 future core technologies for social-issue solution through “2013 Emerging Tech Seminar”, and the wastewater treatment (ANAMMOX, anaerobic ammonium oxidation) was included. This technology uses anaerobic oxidizing bacteria with ammonium nitrogen and nitrite as a substrate under anaerobic condition. This process requires the maintenance of anaerobic condition and stable supply of nitrite. Therefore, it means that not only the research and technical development for anaerobic ammonium oxidation should

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be preceded but also the research for nitrification. As mentioned before, as the interest for nitrogen removal method development that has the advantage of economy, environment, and energy has increased, the interest on nitrification has increased as well [2,3]. Nitrification is the process of conversion of ammonium nitrogen into nitrite by ammonium oxidizing bacteria. Nitrification is that ammonium nitrogen is converted into nitrate [4,5]. If the nitrification is applied to biological nutrient removal (BNR), both oxygen and carbon source that are necessary for nitrification and denitrification can be reduced. Especially, the electric energy by supplying oxygen in wastewater treatment takes about 40% of municipal wastewater treatment plant's (MWTP) total electricity consumption [6]. If oxygen can be saved by nitrification, it will be advantageous for reducing the energy and operational cost of MWTP. However, nitrification was affected by many environmental and operational conditions that pose the difficulty to induce nitrification stably [7–9]. There are two methods to inhibit the conversion of nitrite: the first is to accumulate nitrite using the difference in activation energy (68 kJ/mol, 44 kJ/mol) of ammonium nitrogen oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), and the second way is using the difference in growth rate. Many researchers are using the second way for nitrification, using the difference in growth rate of AOB and NOB to accumulate the nitrite [8,9]. AOB and NOB's maximum growth rate in high temperature (35°C) is about 1 and 0.5 d⁻¹ [10]. That is, operating in high temperature for short retention time, NOB is discharged in effluent. On the other hand, AOB stays in bioreactor, naturally leading to its high-density growth. Due to this reason, AOB takes the dominant position in bioreactor. The ammonium nitrogen entering the bioreactor is converted into nitrite by AOB under aerobic condition. Converted nitrite by AOB cannot be converted into nitrate by controlled NOB and is accumulated in the form of nitrite [11,12]. The resulting sludge in water treatment process of MWTP contains high concentration of polluted materials, and hence untreated release or reclamation can bring about serious water pollution. Non-removal recycle water from sludge treatment process is reported as one of the main problems of MWTP [7].

The main characteristics of recycle water are represented as low flow and high concentration of polluted materials. However, most of the domestic MWTP do not possess the extra recycle water treatment process. Instead, recycle water is returned to water treatment process combining with incoming sewage leading to the increased pollutant loads of water treatment process. Especially,

nitrogen causes more pollution when compared with other pollutants. In advanced research result, nitrogen load of water treatment process in MWTP is increased up to 47% because of recycle water [13]. This research was operated in a laboratory-scale nitrite reactor using sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent, which belongs to recycle water. Based on the result, nitrite conversion efficiency change was analyzed according to recycle water's characteristics.

2. Materials and methods

2.1. Characteristics of influent

The sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent from the sludge treatment process sampled an MWTP in Seoul, South Korea. Collected samples were moved to a laboratory and combined in large-sized mother reactors for complete mixed condition. The mixed samples were refrigerated at 4°C ± 1°C to prevent the change of characteristics. Table 1 showed the characteristics of influent in this research. Sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent contain high-density of polluted materials. Also, large difference of pollutants concentration was observed in recycle water. Anaerobic digester supernatant and sludge decanter effluent contained higher ammonium nitrogen than sludge thickener supernatant. The analysis methods of water quality in this research were conducted by standard method [14].

2.2. Laboratory-scale reactors

The laboratory-scale reactors used for nitrification were made by acrylic cylinder and the operational volume of each reactor was 8 L. The water bath to maintain the temperature (35°C ± 0.5°C) was installed outside of reactors to minimize the effect of temperature. The source of inoculum was aeration reactors of MWTP in Seoul, South Korea. The reactors were operated in aerobic condition for nitrification, and oxygenator and air-stone were installed for supplying oxygen. The oxygenator was operated during overall operation days. Hence, the DO was maintained over 2 mg/L during overall operation days. Reactors were operated at the same hydraulic retention time (HRT) and solid retention time (SRT). Mechanical mixer was installed at the top of reactors to maintain the complete mixed condition. Fig. 1 shows the schematic diagram of laboratory-scale reactor.

Table 1
Characteristics of recycle water in this research

Parameter	Sludge thickener supernatant		Anaerobic digester supernatant		Sludge decanter effluent	
	Range (mg/L)	Median (mg/L)	Range (mg/L)	Median (mg/L)	Range	Median
Chemical oxygen demand	8,200~12,000	10,200	14,000~19,000	16,000	1,410~1,932	1,680
Biological oxygen demand	3,600~5,600	4,300	1,040~1,130	1,100	1,046~1,128	1,106
Total nitrogen	250~360	280	890~1,220	1,120	906~1,210	1,140
NH ₄ ⁺ -N	205~215	210	935~955	945	946~950	948

3. Results and discussion

3.1. Results of reactors operation

The operating strategy for nitrification was to shorten SRT step by step in this research. The operational results of sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent are shown in Fig. 2, Tables 2–4 show summaries of operation results. In Fig. 2a, sludge thickener supernatant operated SRT was 4~0.5 d and during A1, stable ammonium nitrogen was removed and the removed ammonium nitrogen was accumulated in effluent. A2 shows different result from period A1, to observe nitrite in effluent. During A3, removal of stable ammonium nitrogen and high concentration of nitrite in effluent were detected because AOB dominated in reactor, due to NOB wash-out through change of SRT in the reactor [10]. During A4, concentration of ammonium nitrogen in effluent was rapidly increased because SRT was too short for ammonium nitrogen oxidation [7,8]. Fig. 2b shows the operation results of anaerobic digester supernatant. Reactor of anaerobic digester supernatant was operated SRT 8~1 d. The reason for longer operated SRT than sludge thickener supernatant in Fig. 2a was to provide enough time for ammonium oxidizing nitrification due to the high concentration of ammonium nitrogen. During B1, ammonium nitrogen was removed stably, the removed ammonium nitrogen was converted into nitrite in effluent. Removal of stable ammonium nitrogen and detection of nitrite in effluent were taken in B2 similar to A2. During B3, almost removed ammonium nitrogen was converted. B4 shows that operating conditions for ammonium oxidation were not formed. Fig. 2c shows the reactor operation results of sludge decanter effluent and the operated SRT ranged 8~1 d. Sludge decanter effluent was started with long SRT considering high concentration of ammonium nitrogen and organic compound. C1 shows the removal of stable ammonium nitrogen and conversion to nitrate; C2 shows the removal of stable ammonium nitrogen and detection

of nitrite. Stable ammonium nitrogen was removed and high concentration of nitrite was accumulated during C3, and the high concentration of ammonium nitrogen was observed during C4. Also, similar results were shown in same operated conditions, it seems that operated results were verified.

3.2. Effects of ammonium nitrogen load

Fig. 3 shows the ammonium nitrogen removal efficiency and rate according to ammonium nitrogen load in the period that showed the maximum nitrite conversion efficiency of sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent. Ammonium nitrogen load is estimated based on the ammonium nitrogen concentration in influent and it is 0.21~0.22 kg $\text{NH}_4^+\text{-N}$ for sludge thickener supernatant, 0.88~0.94 kg $\text{NH}_4^+\text{-N}$ for anaerobic digester supernatant and 0.94~0.95 kg $\text{NH}_4^+\text{-N}$ for sludge decanter effluent. Nitrite conversion efficiency was more than 80% because the ammonium nitrogen load was analyzed using data of A3, B3, and C3. However, there was a rate difference between ammonium nitrogen removal rate and nitrite conversion rate [nitrite mass in effluent/(volume of reactor \times retention time)] according to ammonium load. When the ammonium nitrogen load is high in influent, ammonium nitrogen removal rate and nitrite conversion rate were higher compared with low ammonium nitrogen load. Therefore, anaerobic digester supernatant and sludge decanter effluent can be expected to have high nitrite conversion rate than sludge thickener supernatant.

3.3. Comparison of ammonium nitrogen removal rate and nitrification

In Fig. 4, the ammonium nitrogen removal rate and nitrite conversion rate is compared during the maximum

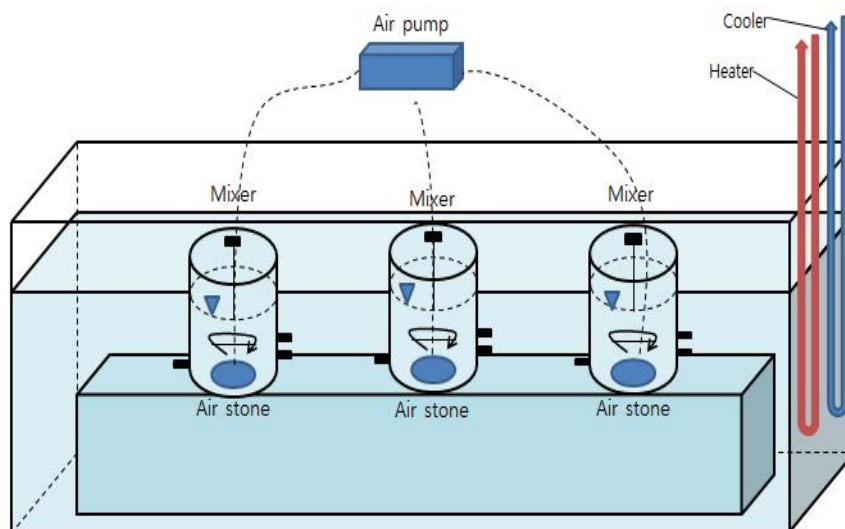


Fig. 1. Schematic diagram of laboratory-scale reactor.

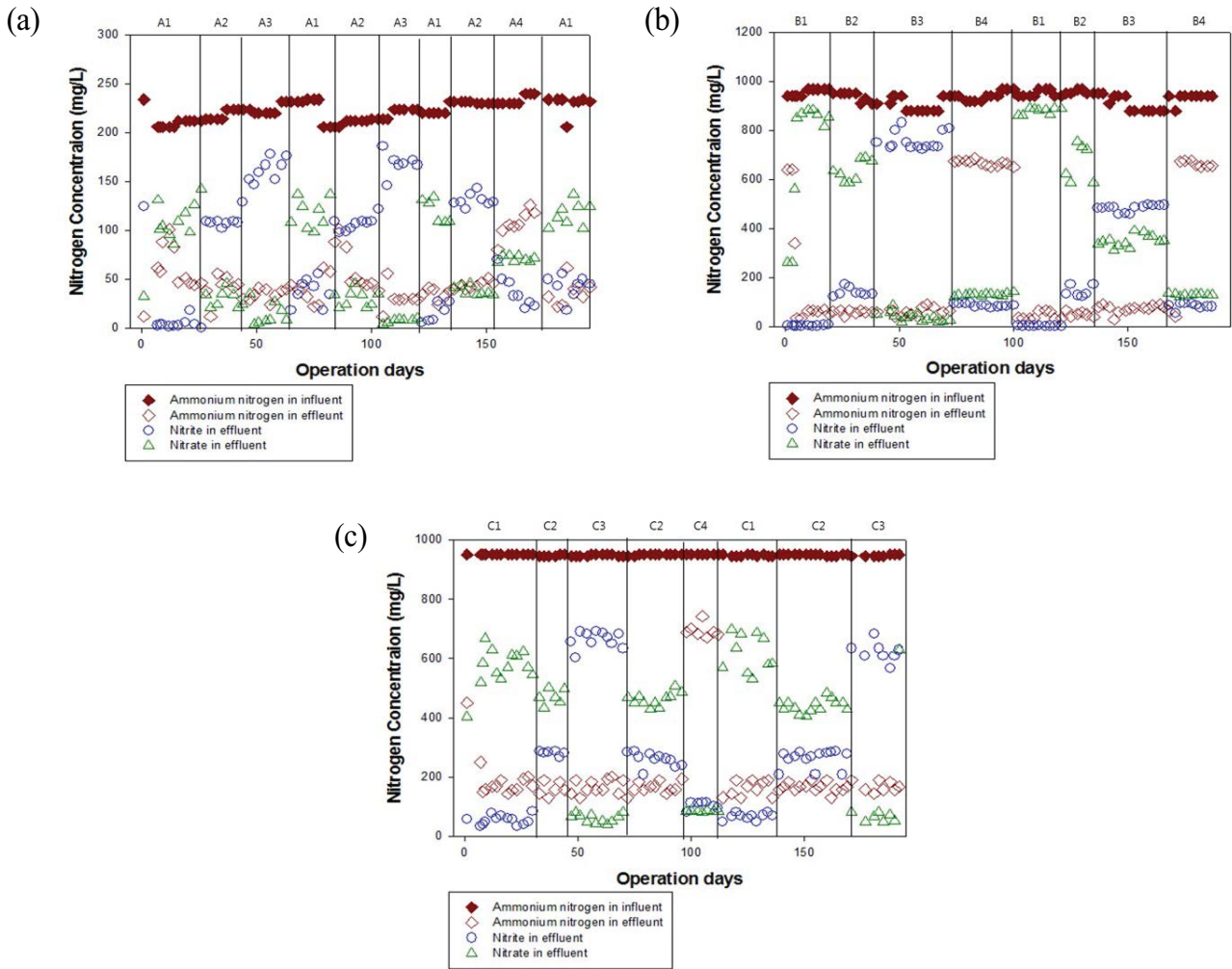


Fig. 2. Operation results of recycle water in laboratory-scale reactor. (a) Sludge thickener supernatant, (b) anaerobic digester supernatant and (c) sludge decanter effluent.

Table 2
Summary of operation result in sludge thickener supernatant

Period	HRT = SRT (d)	Removed ammonium nitrogen (mg L)		Nitrite in effluent (mg L)		Ammonium nitrogen removal efficiency (%)		Nitrite conversion efficiency (%)	
		Range	Median	Range	Median	Range	Median	Range	Median
A1	4	105~212	187	0.1~56	18	51~91	80	0~27	7
A2	2	105~202	168	98~143	109	51~94	78	53~80	66
A3	1	158~206	194	122~186	167	74~94	85	69~92	89
A4	0.5	114~150	124	20~70	33	48~65	54	16~47	26

HRT: hydraulic retention time; SRT: solid retention time.

nitrite conversion efficiency period in sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent. In case of ammonium nitrogen removal rate in Fig. 4a, sludge thickener supernatant 0.20 kg NH₄⁺-N/m³ d, anaerobic digester supernatant 0.42 kg NH₄⁺-N/m³ d and sludge decanter effluent 0.39 kg NH₄⁺-N/m³ d were shown on the basis of median value. In Fig. 4b, nitrite

conversion rate is 0.17 kg NO₂⁻-N/m³-d, 0.37 kg NO₂⁻-N/m³ d and 0.32 kg NO₂⁻-N/m³ d on the basis of median. The maximum ammonium nitrogen removal rate and nitrite conversion rate was shown in anaerobic digester supernatant. Especially, it shows higher rates for about 50% compared with sludge thickener supernatant, and about 10% compared with sludge decanter effluent. It is judged

Table 3
Summary of operation result in anaerobic digester supernatant

Period	HRT = SRT (d)	Removed ammonium nitrogen (mg L)		Nitrite in effluent (mg L)		Ammonium nitrogen removal efficiency (%)		Nitrite conversion efficiency (%)	
		Range	Median	Range	Median	Range	Median	Range	Median
B1	8	899~916	905	2~8	4	35~92	87	0~1	0.4
B2	4	830~911	886	124~488	151	93~97	96	12~59	16
B3	2	790~900	830	54~832	732	90~97	94	61~92	84
B4	1	234~316	282	76~96	87	25~33	30	26~39	31

Table 4
Summary of operation result in sludge decanter effluent

Period	HRT = SRT (d)	Removed ammonium nitrogen (mg L)		Nitrite in effluent (mg L)		Ammonium nitrogen removal efficiency (%)		Nitrite conversion efficiency (%)	
		Range	Median	Range	Median	Range	Median	Range	Median
C1	8	500~819	780	34~85	61	53~86	82	4~12	8
C2	4	756~816	788	208~287	269	79~86	83	26~37	35
C3	2	750~816	782	568~692	650	79~86	83	74~89	83
C4	1	208~279	261	82~114	112	22~29	27	31~55	41

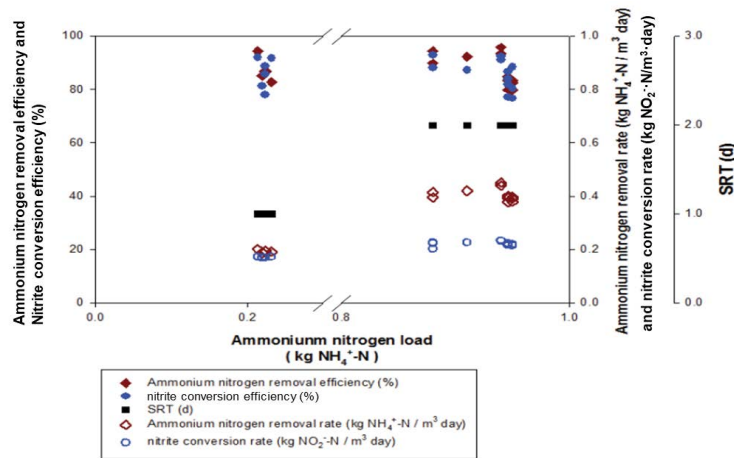


Fig. 3. Comparison of ammonium nitrogen removal rate and efficiency, and nitrite conversion rate and efficiency according to ammonium nitrogen load.

to be effective for applying nitrification to anaerobic digester supernatant. In case of sludge thickener supernatant, SRT was shorter than anaerobic digester supernatant; however, low ammonium nitrogen removal rate and low nitrite conversion rate were effected by low ammonium nitrogen concentration. Also, in case of sludge decanter effluent, low rate is judged from low nitrite conversion efficiency even with the same SRT of anaerobic digester supernatant and similar ammonium nitrogen concentration.

3.4. Organic matter and chemical oxygen demand fraction

The nitrite conversion rate of recycle water was each 0.17 kg NO₂-N/m³ d for sludge thickener supernatant,

0.37 kg NO₂-N/m³ d for anaerobic digester supernatant and 0.32 kg NO₂-N/m³ d for sludge decanter effluent. The major reason for difference of nitrite conversion rate was the difference in concentration of ammonium nitrogen. However, considering influence by organic matter of nitrification, the chemical oxygen demand (COD) fraction was analyzed based on microbial oxygen utilization rates. Fig. 5 shows the results of the COD fraction in the sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent. COD fraction showed clear difference in each wastewater. In case of sludge thickener supernatant, S₅ (soluble substrate) took most parts of 45%, in case of anaerobic digester supernatant, 75% of S₁ (soluble inert) and in case of sludge decanter effluent, 46% of

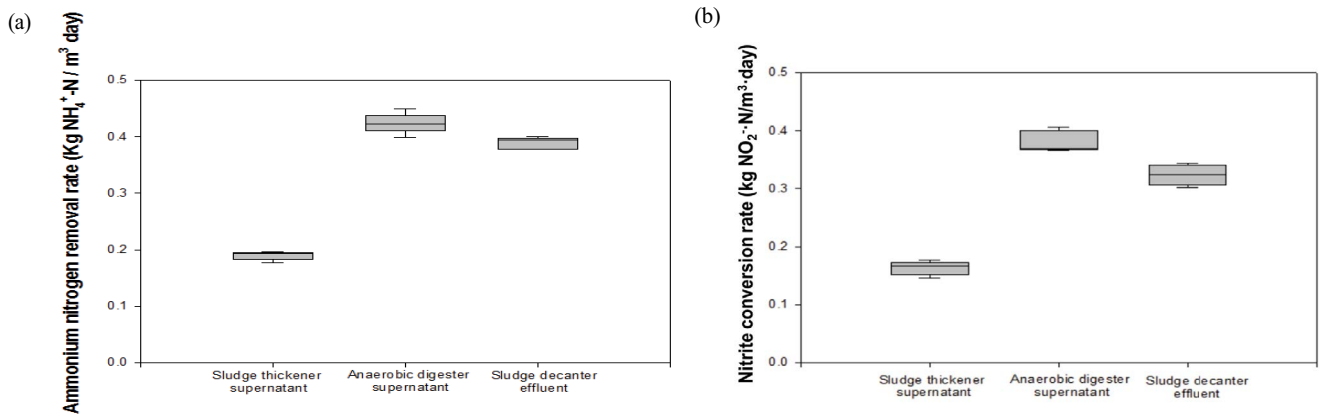


Fig. 4. Comparison of ammonium nitrogen removal rate and nitrite conversion rate during higher nitrite conversion efficiency periods.

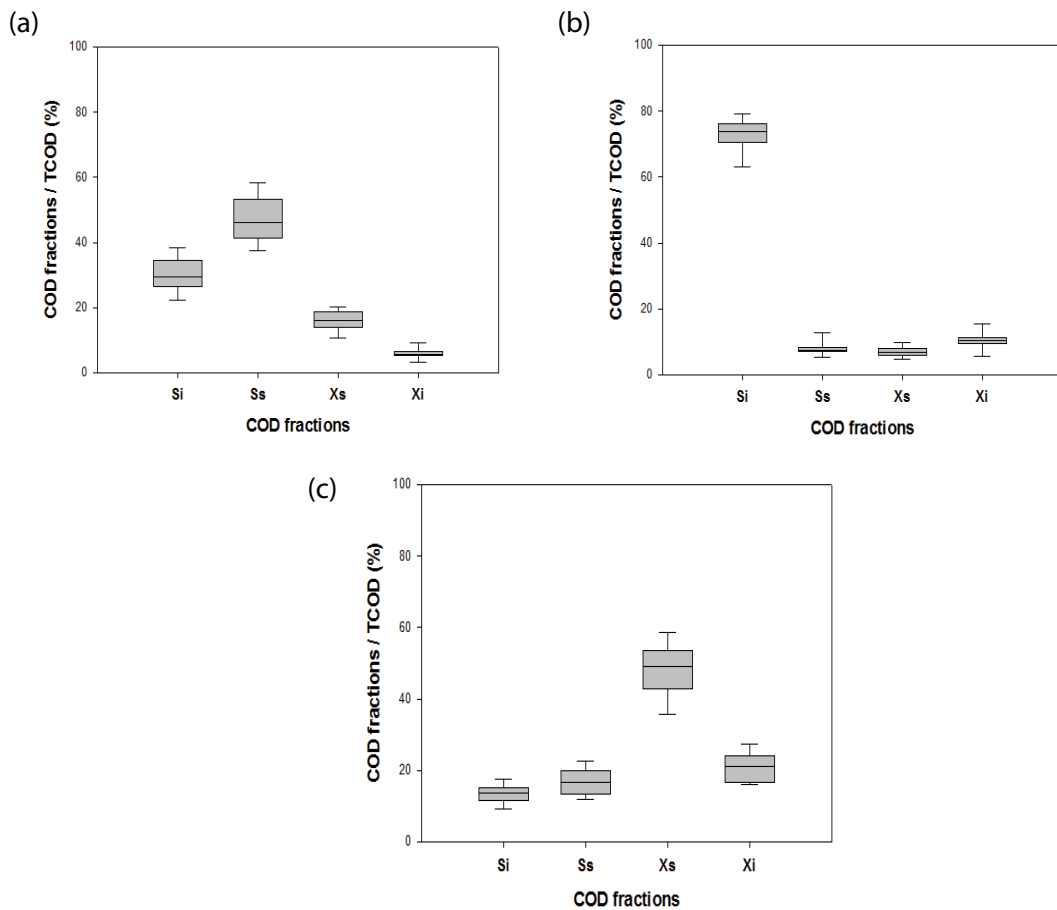


Fig. 5. COD fraction of sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent.

X_s (soluble inert) took most parts. Also, in case of biodegradable organic matter (substrate organic matter, summation of S_s and X_s), sludge thickener supernatant was about 60%, anaerobic digester supernatant was about 15%, and sludge decanter effluent was about 65%. In the anaerobic digester supernatant, the ratio of biodegradable organic matter showed less than other ratio of recycle water. This could be analyzed to have less amount of organic matter

that can be decomposed by heterotrophic bacteria, which is competitive to AOB for oxygen. Generally, heterotrophic bacteria are dominant to AOB for oxygen, and preferentially consume the initial reaction component, S_s [13]. Therefore, low S_s ratio in influent, ammonium nitrogen oxidation was started faster than similar condition influent. Ratio of S_s is effect to reaction time for ammonium nitrogen removal and nitrite production. Also, it seems to occur

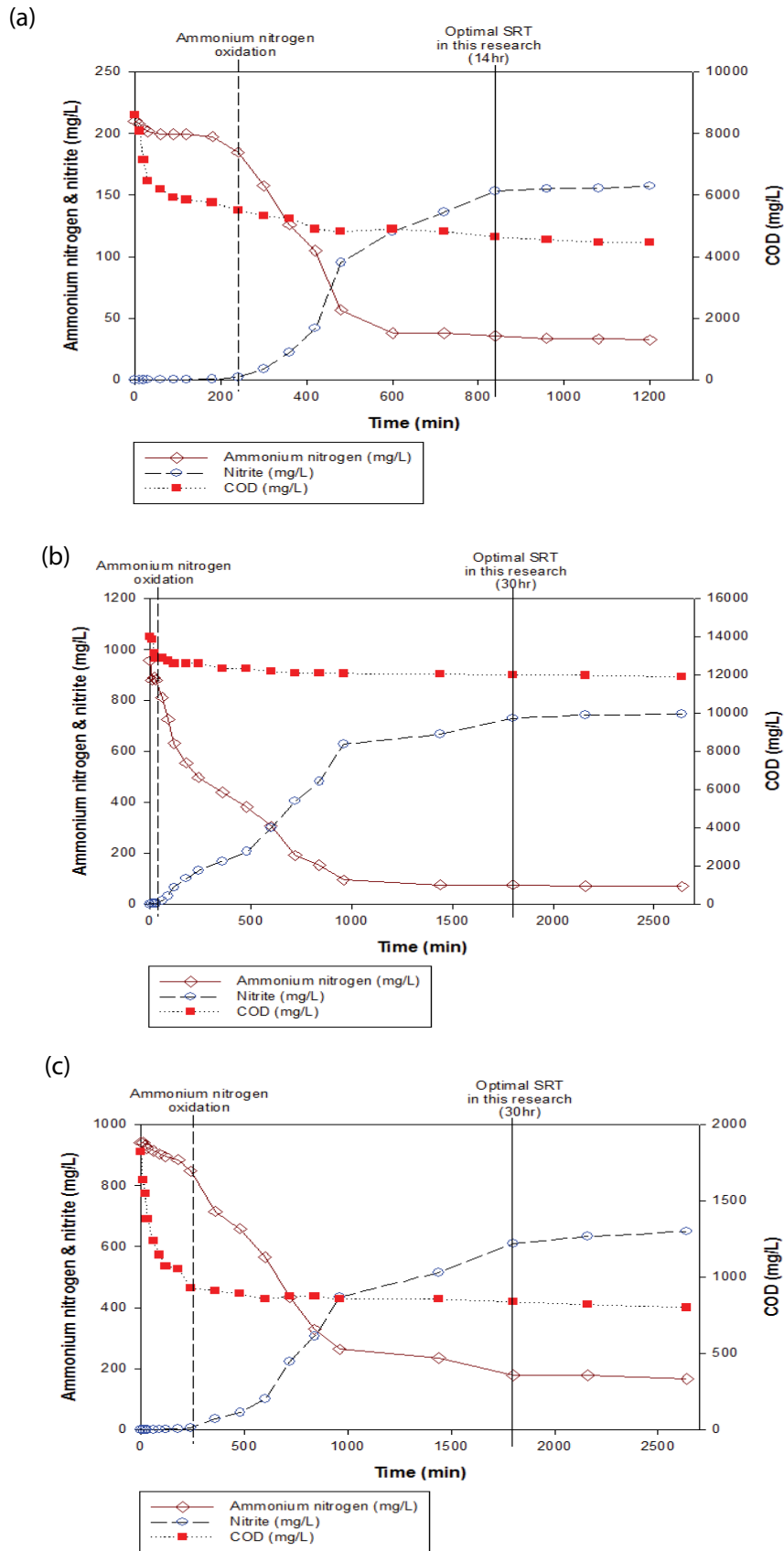


Fig. 6. Change of ammonium nitrogen, nitrite and COD according to retention time.

the difference of rate due to the organic oxidation before ammonium nitrogen oxidation caused by a mass of S_5 in sludge thickener supernatant and sludge decanter effluent.

3.5. Estimate of optimal SRT and rate change based on track study

In Fig. 6, according to the reaction time of sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent sludge thickener supernatant, a track study was taken to analyze the concentration of ammonium nitrogen and organic compound change. It was operated in the period of high nitrite conversion efficiency. The ammonium nitrogen oxidation by autotrophic bacteria occurred after the organic matters oxidation by heterotrophic bacteria. However, Fig. 6 shows that ammonium oxidation in anaerobic digester supernatant starting time was relatively faster compared with sludge thickener supernatant and sludge decanter effluent. This result was shown for the reason of lower ratio of S_5 . Ammonium oxidation in anaerobic digester supernatant started faster than sludge thickener supernatant and sludge decanter effluent. Change concentration rate of ammonium nitrogen and nitrite nitrogen decreased after the retention time, this point could be decided as the optimal SRT. Through the track study, the estimated optimal SRT was shown as 14 h (0.59 d) of sludge thickener supernatant, and 30 h (1.25 d) of anaerobic digester supernatant and sludge decanter effluent. This optimal SRT based on track study can be obtained high nitrite conversion efficiency even operating with shorter optimal SRT based on track study.

Fig. 7 compared the ammonium nitrogen removal rate and nitrite conversion rate using the SRT based on track study and SRT based operated result of reactor. SRT based on the track study result was shorter than the SRT based on the operated result of reactor, therefore the increased ammonium nitrogen removal rate and nitrite conversion rate could be confirmed. First of all, in case of ammonium nitrogen removal rate, 0.13 kg NH_4^+-N/m^3 d, 0.25 kg NH_4^+-N/m^3 d and 0.26 kg NH_4^+-N/m^3 d were increased in sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent, and the nitrite conversion rate was 0.12 kg $NO_2^- -N/m^3$ d, 0.22 kg $NO_2^- -N/m^3$ d

and 0.20 kg $NO_2^- -N/m^3$ d. Especially in case of anaerobic digester supernatant, when operating in SRT based on track study, more than 0.7 kg NH_4^+-N/m^3 d of ammonium nitrogen removal rate and more than 0.6 kg $NO_2^- -N/m^3$ d of nitrite conversion rate can be expected. Besides the reactor operation results, estimating the optimal SRT for nitrification using track study can be offered for proper SRT estimating methods in various waste waters.

4. Conclusions

- The stable nitrification was led for a long term in sludge thickener supernatant, anaerobic digester supernatant and sludge decanter effluent. According to the influent, nitrite conversion efficiency showed difference however it showed more than 80% in SRT 1 d or SRT 2 d.
- According to ammonium nitrogen load, ammonium nitrogen removal and nitrite conversion showed a difference in rate, which anaerobic digester supernatant (0.42 kg NH_4^+-N/m^3 d, 0.37 kg $NO_2^- -N/m^3$ d) and sludge decanter effluent (0.39 kg NH_4^+-N/m^3 d, 0.32 kg $NO_2^- -N/m^3$ d) are faster than sludge thickener supernatant (0.2 kg NH_4^+-N/m^3 d, 0.17 kg $NO_2^- -N/m^3$ d).
- In the case of anaerobic digester supernatant contained less S_5 compared with sludge thickener supernatant and sludge decanter effluent. Start time of ammonium oxidation in the anaerobic digester supernatant was shorter than others. Also, applying the estimated SRT based on track study, 0.7 kg NH_4^+-N/m^3 d of ammonium nitrogen removal rate and 0.6 kg $NO_2^- -N/m^3$ d nitrite conversion rate can be expected.
- Due to the difference between ammonium nitrogen concentration and COD fraction in recycle water, the nitrification was influenced. When applying treatment of recycle water to nitrification, it is judged to be advantageous in order of anaerobic digester supernatant – sludge decanter effluent – sludge thickener supernatant.

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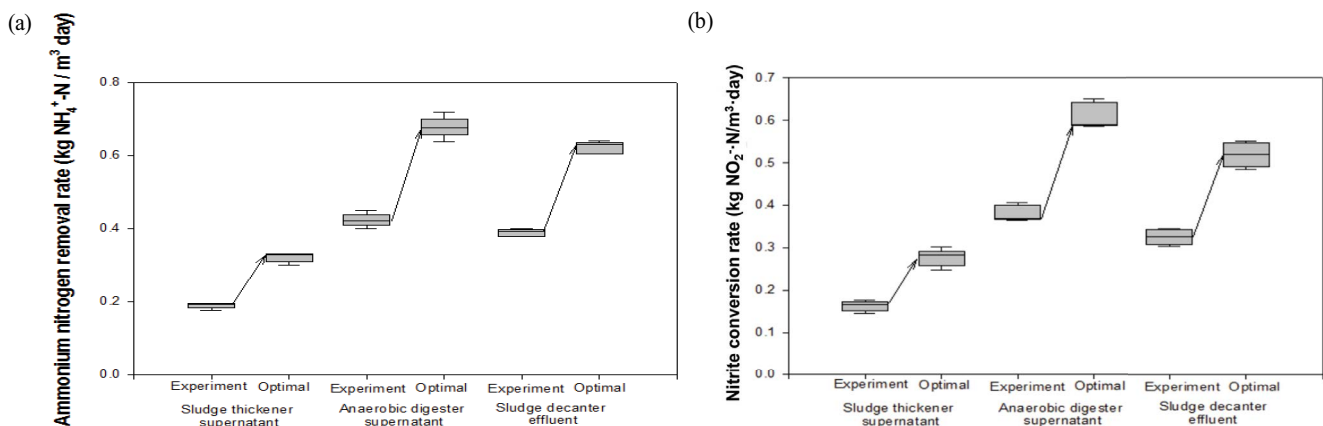


Fig. 7. Comparison of ammonium nitrogen removal rate and nitrite conversion rate according to SRT (reactor operation experiment vs. track study).

References

- [1] H. Lee, S. Lee, Z. Yun, Evaluation of temperature effects on biofilm nitrification system with various organic and solid concentrations for high strength reject water treatment, *J. Korean Soc. Water Environ.*, 27 (2011) 769775.
- [2] A. Gali, J. Dosta, S. Lopez-palau, J. Mata-Alvarez, SBR technology for high ammonium loading rates, *Water Sci. Technol.*, 58 (2008) 467472.
- [3] W. Zeng, L. Li, Y. Yang, S. Wang, Y. Peng, Nitrification and denitrification of domestic wastewater using a continuous anaerobic–anoxic–aerobic (A₂O) process at ambient temperatures, *Bioresour. Technol.*, 101 (2010) 80748082.
- [4] P. Regmi, M. Miller, B. Holgate, R. Bunce, H. Park, K. Chandra, B. Wett, S. Murthy, C. Bott, Control of aeration, aerobic SRT and COD input for mainstream nitrification/denitrification, *Water Res.*, 57 (2014) 162171.
- [5] E. Isanta, C. Reino, J. Carrera, J. Perez, Stable Partial nitrification for low-strength wastewater at low temperature in an aerobic granular reactor, *Water Res.*, 80 (2015) 149158.
- [6] D. Kang, *Advanced Wastewater Treatment by Microalgae-Bacteria Consortium*, Ph.D. Thesis, Myungji University, 2016.
- [7] K. Gil, J. Im, Long term operation of laboratory nitrification reactor using anaerobic digester supernatant of municipal wastewater treatment plant and piggery wastewater, *J. Korean Soc. Hazard. Mitig.*, 12 (2012) 279286.
- [8] H. Sun, X. Lu, Y. Peng, S. Wang, J. Ma, Long-term nitrification performance of ammonium-rich landfill leachate, *Chin. J. Chem. Eng.*, 23 (2015) 18881893.
- [9] M. van Loosdrecht, M. Jetten, Microbiological conversions in nitrogen removal, *Water Sci. Technol.*, 38 (1998) 17.
- [10] K. Gil, Nitrification of anaerobic digester supernatant from sludge processing in MWTP, *J. Korean Soc. Water Environ.*, 22 (2006) 540545.
- [11] Y. Schneider, M. Beier, K. Rosenwinkel, Nitrous oxide formation during nitrification and nitrification of high-strength wastewater, *Water Sci. Technol.*, 67 (2013) 24942502.
- [12] J. Mulder, M. van Loosdrecht, C. Hellings, R. van Kempen, Full scale application of the SHARON process for treatment of rejection water of digested sludge dewatering, *Water Sci. Technol.*, 43 (2001) 127134.
- [13] K. Gil, J. Im, Changes of COD fraction according to nitrification using piggery wastewater, *J. Korean Soc. Hazard Mitig.*, 11 (2011) 237243.
- [14] AHPA (American Public Health Association), *Standard Methods for the Examination of Water and Wastewater*, 20th ed., Washington, D.C., 1998.