

## Simultaneous autotrophic & heterotrophic denitrification by the injection of reformed spent sulfidic caustic (SSC) in a pilot-scale sewage treatment plant

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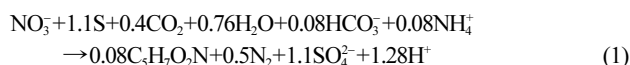
**Abstract**—Spent sulfidic caustic (SSC), produced from petroleum plants, contains high levels of H<sub>2</sub>S and alkalinity. It can be used to denitrify nitrate-nitrogen via a biological nitrogen removal process, as both the electron donor and buffering agent for sulfur-based autotrophic denitrification. However, SSC also contains some recalcitrant organic compounds such as BTEX, so it has to be refined. To remove BTEX, air stripping was conducted in a laboratory scale, and as a result, over 93% of the BTEX were removed within 30 min. For the reformation of the refined SSC, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, methanol and organic material, produced from a biodiesel production plant, were supplemented, and referred to as new sulfidic caustic I (NSCI), II (NSCII), III (NSCIII), respectively. Thereafter, these products were applied to a modified Ludzack-Ettinger (MLE) process to evaluate their effects on the effluent COD and TN concentrations. As a result, there was no increase in the COD level on the injection of NSC due to the removal of BTEX via air stripping. In addition, compared to no NSC injection, 44.0% more TN was removed with an injection of NSC III, which were the most effective conditions. Thus, the application of NSC to the biological nitrogen removal process was successfully performed. These results may contribute to the development of resource recovery technology.

**Key words:** Autotrophic Denitrification, Spent Sulfidic Caustic, New Sulfidic Caustic, Biological Nitrogen Removal, Modified Ludzack-Ettinger Process

### INTRODUCTION

Spent sulfidic caustic (SSC) is produced from the olefin processes of petrochemical plants, such as naphtha cracking and ethylene production. Under the Waste Management Act in Korea, SSC is classified as hazardous waste, which requires high attention. Most SSC is incinerated with auxiliary fuel, resulting in air pollution problems and relatively high operating costs. Therefore, the reuse of SSC becomes increasingly important from both economic and environmental points of view.

Autotrophic denitrification, which has recently received increasing attention due to its lower chemical cost and reduced sludge production compared to heterotrophic denitrification [1], uses reduced sulfur compounds (H<sub>2</sub>S, S, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>) and consumes alkalinity depending on the reduced sulfur species that are oxidized. Eq. (1) is a stoichiometric equation showing an example of sulfur-based autotrophic denitrification.



With regard to total nitrogen (TN) removal, ammonia nitrification and autotrophic denitrification consume more alkalinity than heterotrophic denitrification. In an effort to supply adequate alkalinity, sulfur and limestone autotrophic denitrification (SLAD) systems have been studied [2-4]. Liu and Koenig [5] studied the optimum sulfur : limestone volume ratio in a continuous packed bed reactor

and concluded that the alkalinity supplied by limestone depended on the biological-chemical interactions during autotrophic denitrification and limestone dissolution. Nevertheless, autotrophic denitrification using the SLAD system encounters some difficulties in its application as a wastewater treatment system, due to the differences in the dissolution of elemental sulfur and limestone.

However, SSC contains a high concentration of dissolved hydrogen sulfide, as well as high alkalinity as a result of the formation of caustic soda. For this reason, both the sulfur content and alkalinity of SSC are readily available for autotrophic denitrification. Park et al. [6] observed the variation in the microbial community on the injection of SSC and confirmed the increased distribution ratio of *Thiobacillus denitrificans* using fluorescence *in situ* hybridization (FISH). SSC also contains some volatile organic compounds (VOCs) such as benzene and toluene [7,8]; therefore, VOCs in the SSC should be removed for stable injection into a wastewater treatment process.

VOCs are easily vaporized from liquid phase to gas phase. Of the available wastewater treatment processes, the activated sludge process is one of the most significant emission sources. During aeration, oxygen is transferred into the wastewater, while the pre-dissolved VOCs will be emitted to the atmosphere from the wastewater. Roberts and Dandliker [9] indicated that the mass transfer rate of VOCs was proportional to that of oxygen in an agitated vessel.

In this study, the SSC was refined by air stripping and reformed by the addition of organic materials. The reformed SSC was injected into an anoxic vessel in a pilot-scale modified Ludzack-Ettinger (MLE) process. The autotrophic and heterotrophic denitrification ratios were then monitored. This strategy was successfully performed, and these results may contribute to the development of re-

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source recovery technology.

## MATERIALS AND METHODS

### 1. Air Stripping of SSC

As shown in Table 1, SSC contains some volatile organic compounds (VOCs) such as BTEX. To remove VOCs from SSC, air stripping was used. The air stripping process consisted of a continuously stirred tank reactor (CSTR) unit of 2 L, a delivery pump, a blower and an air diffuser. To evaluate the VOCs removal efficiency from the SSC with respect to aeration time, 30 L/min of air was provided to the solution of SSC, with samples taken every 10 min for 60 min. Thereafter, the benzene, toluene, ethylbenzene, xy-

lene, phenols, methylmercaptan and ethylmercaptan levels were monitored.

### 2. Reactor Operation

#### 2-1. MLE Process

The pilot-scale MLE process used for the autotrophic denitrification of the SSC consisted of anoxic (1), anoxic (2), aerobic (1), aerobic (2) and aerobic (3) tanks, with a clarifier. This process was operated with 8 hr of HRT in each condition and the effective volumes of the anoxic (1), anoxic (2), aerobic (1), aerobic (2) and aerobic (3) tanks were all 0.59 m<sup>3</sup>. During this process, the mixed liquor was recycled from aerobic (3) tank to anoxic (1) tank at 2Q and the sludge recycle ratio was fixed in 1Q. The SSC was injected from an SSC storage tank. The reactor was inoculated with activated sludge obtained from a municipal sewage treatment plant and acclimatized with raw wastewater. The characteristics of the raw wastewater are presented in Table 2.

#### 2-2. Operating Conditions

The SSC injected into the MLE process was refined by aeration. Since SSC has an insufficient sulfur compared to NaOH, it is supplemented with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (Daejung Co., Korea), methanol (J.T. Baker, USA) and organic material, respectively, to keep a balance between electron donor and alkalinity. The organic material is a byproduct of the biodiesel production plant and its characteristics are presented in Table 3. The refined and reformed SSC are referred to as new sulfidic caustic (NSC). NSCI, NSCII and NSCIII had been supplemented with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, methanol and organic material, respectively. The characteristics of the NSCs are presented in Table 4.

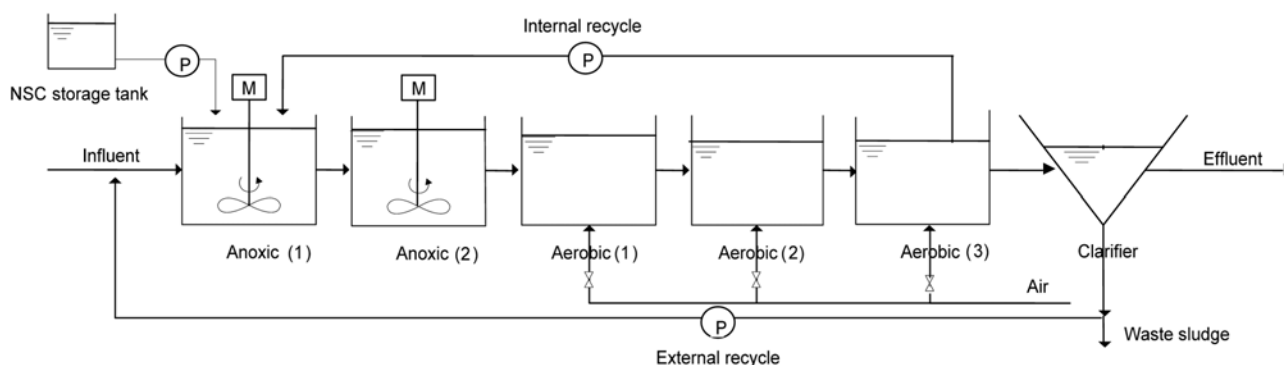
The reactor was operated under different operating conditions as

**Table 1. Characteristics of the SSC used in this study**

Item	Value
pH	13.1-13.5 (13.3) <sup>a</sup>
TOC (mg/L)	1,104-1,638 (1,314)
S <sup>2-</sup> (mg/L)	15,200-17,600 (16,400)
Alkalinity (mgCaCO <sub>3</sub> /L)	50,000-64,000 (57,300)
Phenols (mg/L)	1.8-33.8 (17.8)
Benzene (mg/L)	7.8-63.1 (28.6)
Toluene (mg/L)	0.2-7.8 (2.9)
Ethylbenzene (mg/L)	N.D. <sup>b</sup>
Xylene (mg/L)	N.D.

<sup>a</sup>( ) is mean value

<sup>b</sup>N.D.; not detected



**Fig. 1. Schematic diagram of the pilot-scale MLE process used in this study.**

**Table 2. Characteristics of the raw wastewater used in this study**

Item	pH	SS (mg/L)	TCOD <sub>Cr</sub> (mg/L)	SCOD <sub>Cr</sub> (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	TN (mg/L)	TP (mg/L)	Alk. (mg CaCO <sub>3</sub> /L)
Value	6.3-7.6 (7.1) <sup>a</sup>	90.0-240.0 (165.0)	86.1-254.0 (151.8)	31.1-96.7 (62.5)	8.2-31.3 (20.3)	10.5-31.7 (21.2)	1.2-4.0 (2.9)	90.0-260.0 (168.6)

<sup>a</sup>( ) is mean value during the operating days

**Table 3. Characteristics of organic material used in this study**

Item	pH	COD <sub>Cr</sub> (mg/L)	BOD <sub>5</sub> (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	TN (mg/L)	TP (mg/L)	Alk. (mg CaCO <sub>3</sub> /L)
Value	7.7	87,500	9,320	4.2	10.0	12.0	2,300

**Table 4. Characteristics of NSCs**

Items	NSCI	NSCII	NSCIII
Additive <sup>b</sup> , Additive/SSC	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O, 0.18 (w/v)	Methanol, 0.01 (v/v)	Organic material, 0.15 (v/v)
pH	13.1-13.5 (13.3) <sup>a</sup>	13.1-13.5 (13.3)	12.9-13.2 (13.0)
Alkalinity (mg CaCO <sub>3</sub> /L)	50,000-64,000 (57,300)	49,500-63,360 (56,727)	42,500-54,400 (48,705)
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	30-340 (195)	29-337 (193)	26-290 (166)
S (mg/L)	15,200-17,600 (16,400)	15,048-17,424 (16,236)	12,920-14,960 (13,940)
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> -S (mg/L)	46,000	-	-
COD <sub>Cr</sub> <sup>c</sup> (mg/L)	-	12,000	13,125
SO <sub>4</sub> <sup>2-</sup> (mg/L)	2,446-8,381 (4,725)	2,421-8,297 (4,678)	2,079-7,124 (4,016)

<sup>a</sup>( ) is mean value<sup>b</sup>Assay of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O and methanol is 99.0 and 99.8%, respectively<sup>c</sup>Calculated COD by additives**Table 5. Operating conditions**

Condition	A	B	C	D	E
SSC dosage (mL SSC/L influent)	-	0.43	0.86	2.3	2.2
Injected sulfur concentration (mg S/L influent)	-	23.1-27.4 (25.9)	43.1-51.1 (48.5)	15.9-38.6 (31.1)	15.3-37.2 (30.0)
Influent NH <sub>4</sub> <sup>+</sup> -N concentration (mg NH <sub>4</sub> <sup>+</sup> -N/L)	15.4-31.3 (22.3) <sup>a</sup>	15.8-22.3 (20.9)	8.3-27.7 (19.0)	16.4-25.9 (22.2)	19.8-28.1 (24.9)
Injected COD concentration (mg COD/L)	-	-	-	27.4	28.8
Influent S/N ratio	-	1.1-1.3 (1.2)	2.3-2.7 (2.5)	0.7-1.7 (1.4)	0.6-1.5 (1.2)
HRT (hr)	8	8	8	8	8

<sup>a</sup>( ) is mean value during the operating days

presented in Table 5. To estimate the amount of heterotrophic denitrification alone, no NSC was initially injected under condition A. Based on Eq. (1), 2.5 mg sulfur would be required for the autotrophic denitrification of 1 mg of nitrate-nitrogen. Under condition B, half of the NSC amount required was injected for acclimating activated sludge to NSC, and then the NSC was injected at the S/N ratios required to denitrify the nitrate in the reactor. NSCI, NSCII and NSCIII were injected under C, D and E conditions, respectively.

### 3. Analytical Methods

All samples under each set of conditions were tested within seven days of sampling. For each sample, the NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup> concentrations were determined by ion chromatography (DX-300, DIONEX, USA). The soluble chemical oxygen demand (COD<sub>Cr</sub>) and NH<sub>4</sub><sup>+</sup>-N concentrations were measured with an auto analyzer (AA3, Bran+Luebbe, Germany) after filtration of the sample through a 1.2 μm of glass microfiber filter. The BTEX concentrations were measured by using gas chromatography-mass spectrometry (GC-MS HP 5973N, USA). The pH and dissolved oxygen concentrations were measured with an Orion Research pH meter (Model 230A, USA) and a YSI DO meter (Model 58, USA), respectively. The sulfur content was measured by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES Thermo Jarrell Ash, USA). The alkalinity and suspended solids were measured by using standard methods [10]. The stored samples were kept in refrigerated at 4 °C until analyzed.

## RESULTS AND DISCUSSION

### 1. Removal Efficiencies of BTEX by Air Stripping

As the SSC is produced from petrochemical plants, it contains

recalcitrant organic compounds such as BTEX. BTEX is a member of the class of compounds known as volatile organic compounds (VOCs). VOC chemicals are easily vaporized from liquid phase to gas phase. During aeration, oxygen is transferred into wastewater, while the pre-dissolved VOCs will be emitted to the atmosphere from the wastewater. The stripping rates of VOCs during aeration can be estimated using the two-film theory, which has been widely used to estimate the oxygen transfer rate in aeration systems. The stripping efficiency increases with increasing Henry's law constant [11]. Roberts and Dandliker [9] showed that the mass transfer rate of VOCs was proportional to that of oxygen in an agitated vessel.

Table 6 shows the concentrations of BTEX in the SSC with respect to the aeration time. The mean BTEX concentrations in the SSC were 57.75, 33.60, 15.07 and 159.15 mg/L, respectively. The BTEX concentrations were sharply decreased within 10 min of aeration, and the removal efficiency gradually increased during 30 min of aeration. After 30 min, the BTEX removal efficiencies were 98.5,

**Table 6. Concentrations of BTEX in the SSC with aeration time**

Items	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	Xylene (mg/L)
Reaction time				
0 min	57.75	33.60	15.07	159.15
10 min	14.44	7.13	2.04	25.5
20 min	1.62	1.79	1.31	16.3
30 min	0.86	1.15	0.91	9.9
60 min	0.56	0.82	0.26	1.1

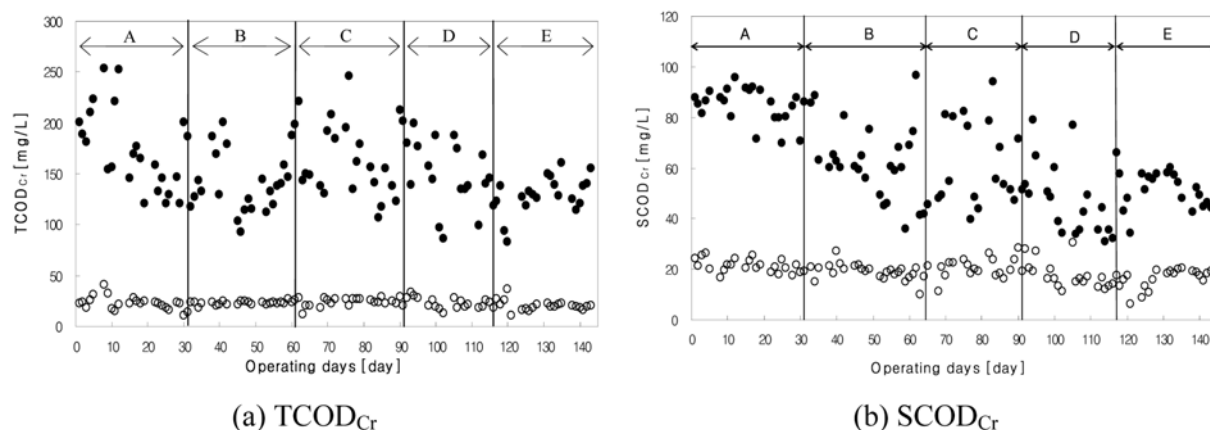


Fig. 2. COD concentrations in the influent (●) and effluent (○) in each condition.

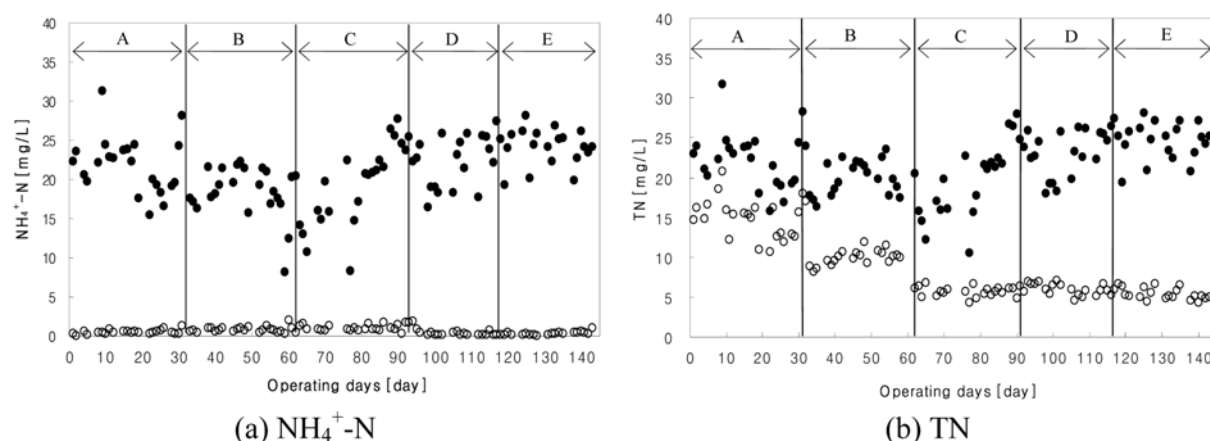


Fig. 3.  $\text{NH}_4^+\text{-N}$  and TN concentrations in the influent (●) and effluent (○) in each condition.

96.6, 94.0 and 93.8%, respectively. High removal efficiencies were achieved with a 30 min of aeration time. Thus, air stripping was an adequate and cost-effective approach for the removal of BTEX from SSC.

## 2. Removal Efficiencies of COD, $\text{NH}_4^+\text{-N}$ and TN

Park et al. [6] reported that the injection of SSC increased the COD concentration in the effluent. The COD in the effluent was increased by approximately 1.4 mg/L by the injection of 1 mL SSC/L influent. Fig. 2 shows the COD concentration. The mean COD removal ratios under conditions A, B, C, D and E were 86.2, 83.6, 84.8, 83.4 and 83.1%, respectively. The mean COD concentrations in the effluents were 22.7, 22.9, 23.9, 23.6 and 20.1 mg/L, respectively. The COD concentrations under conditions B, C, D and E did not increase compared to condition A. These results show that the injection of SSC induced an increase of COD in the effluent, but the injection of NSC did not increase COD in the effluent. This was attributed to the fact that the SSC had been refined by air stripping removing the recalcitrant organic compounds. This result shows that the removal of BTEX from SSC using air stripping is very appropriate for the stabilization of COD concentration in the effluent.

Villaverde et al. [12] reported that the optimal pH ranges for *Nitrosomonas* spp. and *Nitrobacter* spp. were 7.9–8.2 and 7.2–7.6, respectively. The denitrification efficiency is also quite sensitive to pH, with the optimal pH of the majority of denitrifying bacteria being

around 7 to 8 [1,13]. Park et al. [6] reported that an excess of SSC induced failure of the nitrification process because the injection of SSC, which has a high pH of 13.3, increased the pH of the aerobic tank to above 9.0.

On the basis of the operating results observed in the previous experiments, SSC was reformed by the addition of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , methanol and organic materials. As is shown Fig. 3(a), the nitrification efficiencies under conditions A, B, C, D and E were 97.7, 95.9, 94.9, 97.7 and 98.8%, respectively. Thus, by the addition of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , methanol and organic material, no nitrification failure was detected due to the high pH induced by the NSC injection. Therefore, the SSC reformation strategy was desirable.

Fig. 3(b) shows the TN concentrations in the influent and effluent of the pilot-scale MLE process. The TN removal efficiencies under conditions A, B, C, D and E were 34.0, 51.6, 70.0, 72.2 and 78.0%, respectively. Compared to the observations under condition A, with no SSC injection, additional TN removals of 36.0, 38.2 and 44.0% occurred under conditions C, D and E, respectively.

## 3. Heterotrophic/Autotrophic Denitrification

Under condition A, with only heterotrophic denitrification and no SSC injection, the COD was reduced by 7.2 mg as 1 mg of nitrate-nitrogen was denitrified. The available organic material in SSC for heterotrophic denitrification was about 2,100 mg COD/L, because the mean concentration of organic material in the SSC was 1,300

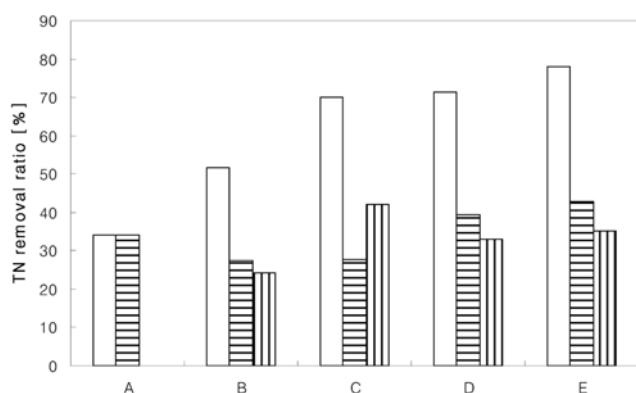


Fig. 4. The efficiencies of total (□), heterotrophic (▨) and autotrophic (▩) denitrification in each condition.

mg TOC/L or 3,500 mg COD/L, and the concentration of non-biodegradable organic material was estimated to be 1,400 mg COD/L. The autotrophic denitrification efficiencies under B, C and D conditions were calculated as follows:

$$aD = tD - hD \quad (2)$$

where,  $aD$  is the efficiency of autotrophic denitrification,  $tD$  the efficiency of total denitrification, and  $hD$  the efficiency of heterotrophic denitrification, which was considered to have been caused by the addition of available organic material by SSC.

Fig. 4 shows the total, heterotrophic and autotrophic denitrification efficiencies. It was proposed that the TN was removed via denitrification pathways, as the majority of COD removal occurred in the anoxic reactor. As mentioned previously, the TN removal efficiencies under conditions A, B, C, D and E were 34.0, 51.6, 70.0, 72.2 and 78.0%, respectively. The autotrophic denitrification efficiencies under conditions B, C, D and E were 24.3, 42.2, 32.9 and 35.1%, respectively. The condition C showed the highest level of autotrophic denitrification using NSC when  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  was supplemented for the autotrophic denitrification. However, under conditions C, D and E, similar denitrification efficiencies were achieved, with mean effluent TN concentrations of 5.61, 5.71 and 5.39 mg/L, respectively. This result shows that the additions of methanol and organic material produced from a biodiesel production plant increased the heterotrophic denitrification ratio and induced simultaneous heterotrophic and autotrophic denitrification. Thus, reformation of SSC through organic material is an appropriate and cost-effective method for increasing in the removal of TN.

#### 4. Sludge Production

New cells (sludge), carbon dioxide and water are the end products of biological wastewater treatment. The treatment of excess sludge and its disposal are currently challenging issues for wastewater treatment plants due to economic, environmental and regulation factors. Therefore, there is a considerable impetus on exploring and developing strategies and technologies for reducing excess sludge production during biological wastewater treatment processes [14].

Compared to conventional heterotrophic denitrification, autotrophic denitrification produces less biomass, minimizing the handling of sludge. The common values of maximum growth rates of autotrophic denitrifying microorganisms are  $0.11\text{--}0.20\text{ h}^{-1}$  [15,16], which are similar to those ( $0.062\text{--}0.108\text{ h}^{-1}$ ) of heterotrophic denitrifying micro-

organisms [17]. The biomass yields were  $0.40\text{--}0.57\text{ g VSS/g NO}_3^- \text{--N}$  for the autotrophic denitrifying microorganisms [15,16], as compared to  $0.8\text{--}1.2\text{ g VSS/g NO}_3^- \text{--N}$  for the denitrifying heterotrophic microorganisms [17].

Under condition E, the autotrophic denitrification ratio on the injection of NSC was 35.1%. In this case, the theoretical amount of sludge produced from the removal of  $\text{NO}_3^- \text{--N}$  via autotrophic denitrification ranged from 35.1 to  $50.0\text{ g VSS/day}$ . However, if 35.1% of  $\text{NO}_3^- \text{--N}$  is removed by the injection of methanol for heterotrophic denitrification, the theoretical amount of sludge produced from the removal of  $\text{NO}_3^- \text{--N}$  via heterotrophic denitrification will range from 70.2 to  $105.3\text{ g VSS/day}$ . Thus, the recovery of SSC as an alternative external carbon source for autotrophic denitrification may contribute to reducing the amount of sludge produced.

## CONCLUSIONS

The reuse of SSC for autotrophic denitrification in a biological nitrogen removal process is important for industrial ecology. The application of SSC to a wastewater treatment process, without any refinery and reformation of the SSC, would be inadequate because SSC contains some BTEX and has an insufficient S/NaOH ratio. Through the refinement and reformation, SSC was applied to the MLE process, with the effect on the effluent COD and TN concentrations evaluated.

VOCs such as BTEX are easily vaporized from liquid phase to gas phase. These organic compounds were removed from SSC by air stripping. Through the air stripping of SSC, over 93% BTEX removal efficiency was achieved within 30 min of aeration. For reformation of the refined SSC,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , methanol and organic material, produced from a biodiesel production plant, were supplemented, and referred to as NSCI, NSCII and NSCIII, respectively.

As NSC was injected into the anoxic (1) tank, no increase on the effluent COD was observed, due to the removal of the BTEX via air stripping. Compared to no NSC injection, 44.0% more TN was removed with an injection of NSCIII, which were the most effective conditions. The autotrophic denitrification efficiency was calculated to be 35.1%, which shows that our process is a more cost effective method for supplementing the organic wastewater produced from industry.

Consequently, the application of NSC to a biological nitrogen removal process was successfully performed. These results may contribute to the development of resource recovery technology.

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