

Evaluation of industrial organic waste as an alternative external carbon source for denitrification in the biological nutrient removal process

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Abstract—The mixed liquor of organic wastes (MLOW) produced from a 1,4-butanediol production process was tested as an external carbon source for denitrification in the biological nutrient removal (BNR) process. The fraction of non-biodegradable chemical oxygen demand (NBDCOD) in the MLOW was estimated to be approximately 0.2% by measuring the oxygen uptake rate (OUR). The specific denitrification rate (SDNR) of MLOW and methanol from a nitrate utilization rate (NUR) test was confirmed to be approximately 13.02 and 12.68 mgN/gVSS/hr, respectively. The results indicated that the denitrification capability of microorganisms applying the MLOW was similar to that of using methanol as an external carbon source for the BNR process. The feasibility of MLOW for a stainless steel wastewater treatment plant (WWTP) was investigated. The low concentration of effluent nitrogen indicated a denitrification capability for MLOW similar to that for methanol. These results support the potential of MLOW as a substitute for methanol in the BNR process.

Key words: Organic Waste, 1,4-Butanediol, Denitrification, External Carbon Source, Wastewater Treatment Plant

INTRODUCTION

For efficient removal of nitrogen in the biological nutrient removal (BNR) process, the heterotrophic denitrification to convert the nitrate ($\text{NO}_3\text{-N}$) into the nitrogen gas (N_2) must occur successfully with the nitrification to transform the ammonia into the nitrate [1]. The denitrification reaction occurs via the action of heterotrophs. In this reaction, the nitrate is transformed into nitrite and subsequently into nitrogen gas by using nitrate as an electronic acceptor and using a carbon source as an energy source for the growth of heterotrophs. In the case of insufficient organic carbon in the influent wastewater in the BNR process, an additional carbon source should be provided for efficient denitrification. Among the several carbon sources such as methanol, ethanol, acetic acid and glucose that are commercially available as an external carbon sources, methanol is most commonly used because it is relatively cheap and is easily assimilated by heterotrophs [2-5]. However, although the nitrogen is removed very efficiently using methanol as an external carbon source, it suffers from the disadvantages of unstable supply and fluctuating price. Further, when wastewater with a high nitrate concentration is treated by using methanol, methanol can inhibit microorganism growth due to the accumulation of nitrites during denitrification [6].

These limitations of methanol have driven researchers over the last two decades to develop other external carbon sources such as industrial by-products and wastes [7]. Henze et al. [8] reported that the limitations of commercial organic compounds such as methanol could be overcome if the industrial wastewater, for example, brewery wastewater, was used as an external carbon source instead of

methanol. Cappai et al. [9] reported that food industry effluents could be a good carbon source due to their high C/N ratio and high content of readily biodegradable organic fraction. They estimated the feasibility of industrial effluents discharged from ice cream and beet sugar factories as an external carbon source by determining their denitrification potential. Their experiments revealed that the addition of these industrial effluents doubled the efficiency of N removal in a pilot-scale sequencing batch reactor (SBR). The specific denitrification rate (SDNR) of these industrial effluents was 3.28 mg $\text{NO}_3\text{-N/gVSS/hr}$ and 2.72 mg $\text{NO}_3\text{-N/gVSS/hr}$, respectively. Rodríguez et al. [10] investigated the change of denitrification capacity of microorganisms in a full-scale plant when the agro-food wastewater was injected as an external carbon source. They found that this industrial wastewater could be used for the removal of a significant amount of nitrate due to high concentrations of fermentation products in the agro-food waste, and that the SDNR for the potato processing wastewater was 4.128 mg $\text{NO}_3\text{-N/gVSS/hr}$. Swinarski et al. [11] estimated the effects of dosing three different types of industrial wastewater (effluents from a distillery, a brewery and a fish-pickling factory) on the denitrification capability of process biomass originating from the Wschód wastewater treatment plant (WWTP) in Gdańsk, in northern Poland, through a nitrate utilization rate (NUR) test using a batch reactor. They observed that when using three kinds of industrial wastewater as an external carbon source, the SDNR ranged from 2.4 to 6.0 mg $\text{NO}_3\text{-N/gVSS/hr}$. Those industrial wastewaters were found to function as an alternative to methanol to enhance the denitrification capability at Wschód WWTP. Fernández et al. [12] used an SBR to test three kinds of industrial wastewater as an external carbon source: the wastewater from a sweets factory, a soft drink factory, and a dairy plant. The results indicated that the maximum SDNR for the three organic carbon sources ranged from 42 and 48 mg $\text{NO}_3\text{-N/gVSS/hr}$.

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N/gVSS/hr. The effluents from SBR were nitrate-free with low chemical oxygen demand (COD) concentrations after 4 to 6 hours of reaction. Recently, Lee et al. [13] estimated the effect on autotrophic and heterotrophic denitrification capability when the spent sulfidic caustic (SSC) discharged from petrochemical plant was used as an external carbon source in a pilot-scale 4-stage bardenpho process. They found the SSC did not have a toxic effect on nitrification, and the autotrophic and heterotrophic denitrification was enhanced by using the SSC as an external carbon source.

We evaluated the mixed liquor of organic wastes (MLOW) arising from a 1,4-butanediol manufacturing process as an external carbon source to treat the wastewater from a stainless steel (SS) manufacturing plant. This evaluation was performed through the following procedures: 1) investigating the characteristics of the organic waste and identifying the presence of toxicants by the analysis of organic components, 2) estimating the fraction of non-biodegradable COD (NBDCOD) by an oxygen uptake rate (OUR) test, 3) assessing the denitrification capability of microorganisms in case of dosing the MLOW by NUR test, and 4) studying the possibility of field application using the MLOW as an alternative external carbon source by a pilot plant test and field test at the WWTP of an SS manufacturing plant.

MATERIALS AND METHODS

1. Organic Waste from 1,4-Butanediol Manufacturing Process

Three types of organic wastes, namely BCO (Butanol Column Overhead), MCO (Methanol Column Overhead), and VD (Vacuum Distillator) according to their discharged locations, are generated from a petrochemical company in Korea during the manufacture of 1,4-butanediol. 1,4-Butanediol is produced by adding hydrogen to the 1,4-butyndiol that is a product of acetylene and formaldehyde. Currently, these organic wastes are outsourced for incineration. Before mixing the three organic wastes proportional to the generation rate of each, the waste from MCO should be detoxified because of the formaldehyde (HCOH) contained, which inhibits the microbial growth in the BNR process. MCO waste containing 10% formaldehyde was detoxified by adding sodium hydroxide (NaOH) to the waste according to the Canizzaro reaction [14], in which the formaldehyde is converted to formic acid and methanol, thus detoxifying the formaldehyde-containing waste. The molar ratio of NaOH to HCOH was 4.0 at 60 °C. Therefore, the mixed waste liquor of BCO, VD and the detoxified MCO was evaluated as an external carbon source. To assess the MLOW as an external carbon source, its characteristics such as COD, pH, and water content were investigated. Organic compounds in the MLOW were also analyzed to confirm the presence or absence of any toxicants.

2. Acclimation of Sludge to the MLOW

To be feasible as an external carbon source, the MLOW should not increase the COD of the effluent, and its denitrification capability should be similar to that of. To evaluate the MLOW as an external carbon source, we performed OUR and NUR tests to determine the NBDCOD fraction of MLOW and the denitrification capability of the microorganisms, respectively. Prior to the startup of OUR and NUR tests, the microorganisms were acclimated to the MLOW and methanol for two weeks using two batch reactors, each with an effective volume of 5 L and a stirring mixer and a blower. Two-liter

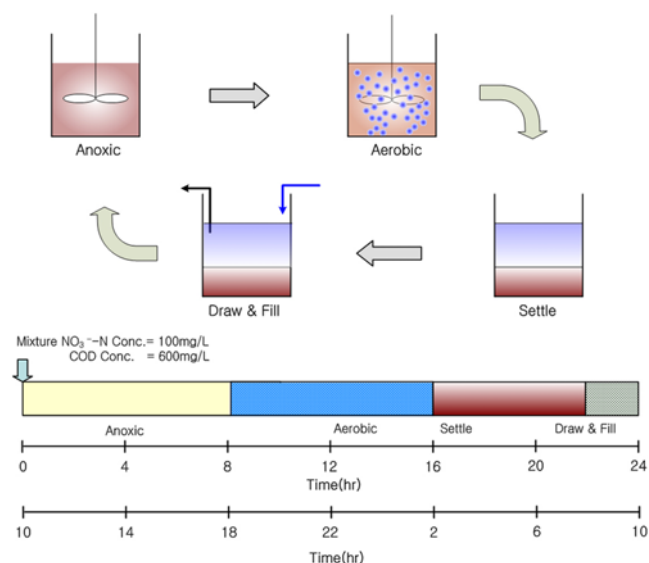


Fig. 1. Operation mode for the acclimation of microorganisms in the batch reactor.

Table 1. Initial operating conditions in the batch reactor for microbial acclimation

Filtered COD (mg/L)	NO ₃ -N (mg/L)	C/N ratio	MLVSS (mg/L)
600	100	6.0	4,000

excess sludge with a concentration of 8,000 mg MLVSS/L taken from the WWTP of the SS manufacturing plant was seeded into two batch reactors so that mixed liquor volatile suspended solids (MLVSS) concentration in each reactor could be maintained at 4,000 mg/L. Each batch reactor was operated according to the operation mode as shown in Fig. 1 under the following cycle: anoxic condition, 8 hr; aeration, 8 hr; settling, 7 hr; and drawing and filling, 1 hr. The initial ratio of COD to nitrate (NO₃-N) in each batch reactor was maintained at 6.0 by adding a carbon source and KNO₃ solution. The initial operating conditions for the acclimation of microorganisms are summarized in Table 1.

3. Estimation of Non-biodegradable Fractions of Organic Waste through OUR Test

To estimate the NBDCOD fraction of the MLOW, the biodegradability of the MLOW was evaluated by measuring the OUR of microorganisms with the injection of MLOW as the substrate according to the procedure of Ekama et al. [15]. The Biovision R-2001 respirometer, manufactured by Environsoft Co., Ltd., used for the measurement of OUR consisted of a pre-aeration basin, a respiration chamber, a dissolved oxygen (DO) meter and a peristaltic pump. The influent flow rate to the respiration chamber was set at a rate of 0.53 L/min and the volume of the respiration chamber was 0.75 L. Before measuring the OUR, the 2-liter sludge acclimated to the MLOW was aerated in the pre-aeration basin for more than 1 hour until the organics in the sludge were completely removed and the sludge became an endogenous condition. This endogenous sludge was then fed into the respiration chamber until an initial ratio of substrate to microorganism (S_0/X_0) of 0.25 g SCOD/g MLVSS was attained. After the DO concentration of the sludge flowing into the

respiration chamber was measured for 60 seconds, the stream flow was changed by a solenoid valve and the DO concentration of the sludge at the output of the respiration chamber was measured again for 60 seconds. OUR was calculated as the difference between influent and effluent DO values at the respiration chamber using the following Eqs. (1) and (2). Although the respirometer measured DO concentrations at 2-second intervals, the average DO value over the 10-second period just before the flow direction was changed by the solenoid valve used for the OUR calculation.

$$\Delta \text{OUR} = \frac{Q}{V} \cdot (\text{DO}_{in} - \text{DO}_{out}) \cdot T_d \quad (1) \quad [16]$$

Where,

ΔOUR = Oxygen uptake rate due to the consumption of readily biodegradable COD (RBDCOD) per 1 L of batch reactor during unit measurement interval of DO, $\text{mg O}_2/\text{L}$

Q = Influent flow rate to the respiration chamber, L/min

V = Volume of respiration chamber, L

DO_{in} = Inlet DO at respiration chamber, $\text{mg O}_2/\text{L}$

DO_{out} = Outlet DO at respiration chamber, $\text{mg O}_2/\text{L}$

T_d = Time interval of DO measurement, min

The RBDCOD concentration of the MLOW was calculated by using the following Eq. (2).

$$C_{RBD} = \frac{1}{(1 - Y_H)} \cdot \sum \text{OUR} \cdot \frac{(V_{ml} + V_{ww})}{V_{ww}} \quad (2)$$

Where,

C_{RBD} = Concentration of RBDCOD for mixed liquor of organic wastes, mg COD/L

V_{ml} = Sludge volume to be injected for OUR test, L

V_{ww} = Volume of mixed liquor to be injected for OUR test, L

Y_H = Heterotrophic yield, $\text{mg COD/mg COD} = \frac{\text{Biomass produced}}{\text{Substrate consumed}}$

$$= \frac{\text{COD}_{\text{degraded}} - \sum \text{OUR}}{\text{COD}_{\text{degraded}}}$$

$\text{COD}_{\text{degraded}}$ = Consumed COD concentration, mg COD/L

$\sum \text{OUR}$ = Sum of $\sum \text{OUR}$ during the period for RBDCOD to be degraded, $\text{mg O}_2/\text{L}$

4. Evaluation of Denitrification Capability through NUR Test

The denitrification capability was evaluated with two batch reactors in which microbes were acclimated to the MLOW and methanol separately. The denitrification capability for each case using the SDNR was calculated with the concentration data of COD and NO_3^- -N for the anoxic condition. The samples were taken from each batch reactor at time intervals of 0, 10, 20, 30, 60, 90, 120, 180, 240 and 360 min. In this experiment, the initial ratio of COD to NO_3^- -N was 6.0, which was consistent with that for the experiment of microbial acclimation. During the anoxic condition, the DO concentration was maintained below 0.1 mg/L , the speed of the stirring mixer at 50 RPM, the temperature between 20 and 22, and the pH between 6.5 and 7.7.

5. Pilot Plant and Full-scale Operation to Treat Stainless Steel Wastewater

The final research purpose was to use the MLOW as an external carbon source capable of substituting for methanol in the WWTP of the SS manufacturing plant. To investigate the feasibility of using the MLOW as an external carbon source, a pilot plant test was initially performed, followed by a field application test performed by injecting the MLOW in a full-scale plant. The WWTP of the SS manufacturing plant consisted of an anoxic reactor for denitrification, an aeration reactor for nitrogen gas removal and a settler for solid/liquid separation. In this WWTP, the insufficient carbon source for the denitrification was supplemented by injecting methanol into the

Table 2. Design criteria of pilot plant

Reactor	Width (cm)	Length (cm)	Height (cm)	Volume (L)
Anoxic	25.0	73.3	40.0	73.3
Aeration	25.0	12.75	40.0	12.8
Clarifier	Diameter 40.0 cm × Height 10.0 cm			41.9

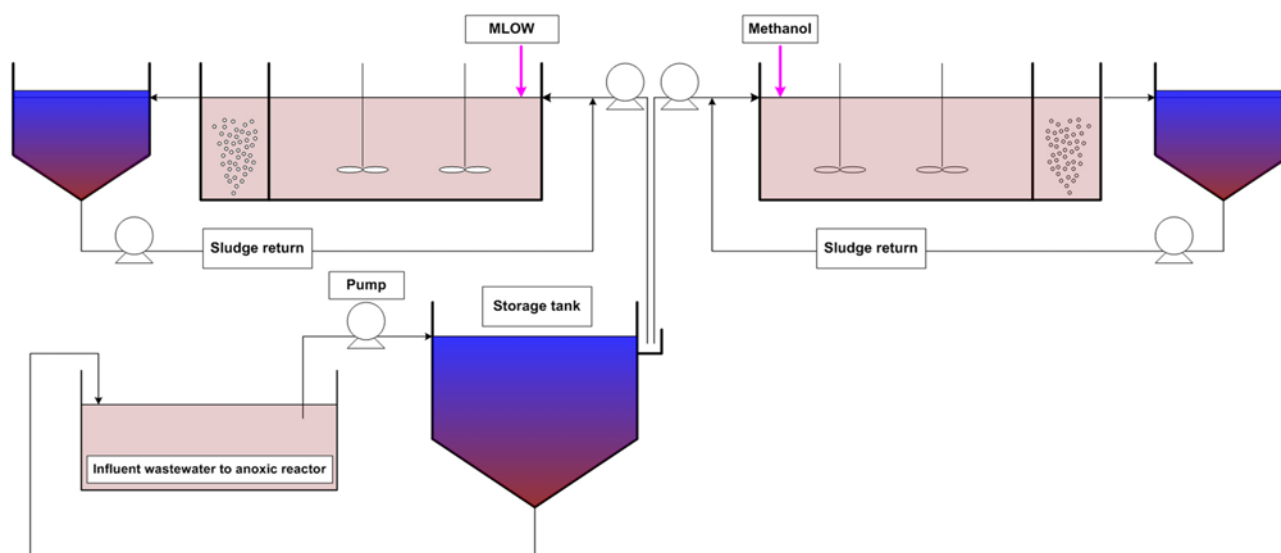


Fig. 2. Schematic diagram of the pilot plant.

Table 3. Operating conditions of the pilot plant

Influent flow rate (mL/min)	Injection rate of external carbon source (mL/min)		Hydraulic retention time (hr)			Sludge return ratio (%)
	Methanol	MLOW	Anoxic	Aeration	Clarifier	
207	0.023	0.047	5.9	1.0	3.3	50

anoxic reactor at a ratio of methanol injection rate to influent flow rate to the anoxic reactor of 0.000113.

As shown in Fig. 2, two pilot plants with the same design criteria were used for this purpose. The pilot plants consisted of the anoxic reactor, aeration reactor and settler. As an external carbon source, the MLOW was supplied to one pilot plant and methanol to the other to compare denitrification capability. The design criteria of the pilot plant are given in Table 2. The dimension of each reactor was determined by considering the actual reactor size of the SS manufacturing plant's WWTP. The influent flow rate to the pilot plant was 0.298 m³/day, equating to a hydraulic retention time of 10.3 hours, which was identical to that of the actual plant. The injection rate of the external carbon source to the pilot plant was determined based on the actual ratio of methanol injection rate to the anoxic influent rate in the anoxic reactor. Table 3 shows the detailed operating conditions of the pilot plant.

After the pilot plant test, the field application test in the full-scale plant was performed for more than three months by using the MLOW as an external carbon source instead of methanol. By considering the assimilation of microorganisms and the change of effluent quality in the full-scale plant, the MLOW was injected stage-by-stage

by mixing with methanol, as shown in Table 4. After seven weeks, at which time the microorganisms were completely assimilated into the MLOW, only the MLOW was injected into the full-scale plant with no mixing with methanol. The samples were taken from two anoxic zones of full scale plant, line 1 and line 2, and then the concentration COD and NO_x-N (i.e., sum of nitrite and nitrate) of each sample was analyzed.

RESULTS AND DISCUSSION

1. Characteristics of the Mixed Liquor of Organic Wastes (MLOW)

We analyzed the chemical properties of the MLOW, including the organic concentration and the results are shown in Table 5. The COD, representing the organic portion of the MLOW, was measured as 550,000±30,000 mg/L, equivalent to about 45% of the methanol COD. The concentrations of suspended solid and of nutrients such as total nitrogen (TN) and total phosphorus (TP) were very low. The analytical data demonstrated that the use of MLOW as an external carbon source would not cause any increase of organics and nutrients in the effluent of a WWTP if the MLOW does not contain non-biodegradable organics.

The water content and organics in the MLOW were analyzed and the results are shown in Table 6. In the MLOW, the water content was 65.9% and that of butanol-related chemicals in organics such as 1-butyl alcohol, 1,4-butanediol, methanol, and n-propyl alcohol was 34.1%. This result confirmed the absence in the MLOW of any toxicants such as formaldehyde and of non-biodegradable organ-

Table 4. Mixing ratio of injected methanol and the MLOW at the full-scale plant

Experimental case	Mixing rate of methanol and MLOW (COD eq. %)		Operation days (days)
	Methanol	MLOW	
Set 1	90	10	7
Set 2	80	20	8
Set 3	70	30	9
Set 4	60	40	14
Set 5	50	50	12
Set 6	0	100	40

Table 5. Average concentrations of the MLOW used for an external carbon source

COD (mg/L)	SS (mg/L)	TN (mg/L)	TP (mg/L)	pH
550,000	<1.0	<0.5	<0.02	<8.0

Table 6. Average compositions of the MLOW for external carbon source

(Unit: wt%)

Water	1-Butyl alcohol	1,4-Butanediol	Methyl alcohol	n-Propyl alcohol	Acetic acid
65.9	17.3	8.5	4.8	0.6	2.9

Table 7. Result of OUR test for evaluating RBDCOD in the MLOW

Respiration rate (mg O ² /g VSS/hr)			Sum of oxygen uptake rate (mg O ² /L)	Yield (g COD/g COD)	COD composition			
Initial end.	Final end.	Max.			RBDCOD		NBDCOD	
					mg/L	%	mg/L	%
5.13	23.61	58.57	284.61	0.43	528,861	99.79	1,139	0.21

End.: endogenous

ics such as aromatic compounds.

2. Non-biodegradable Fraction of the Mixture of Organic Wastes

To estimate the content of NBDCOD in the MLOW, the OUR test was conducted using the sludge acclimated to the MLOW through the operation of the batch reactor in this study. Table 7 shows the organic compositions of the MLOW and the respiration rate measured by the OUR test. Fig. 3 shows the time variation of specific respiration rate (i.e., the respiration rate per unit time and unit MLVSS). The OUR test result revealed a maximum specific respiration rate of 58.57 mg O₂/g VSS/hr and a yield of 0.43, which were similar to the values reported in the literature [17]. The content of RBD-COD in the MLOW was approximately 99.8%, which supported the conclusion that the use of MLOW as an external carbon source did not increase the COD in the effluent of the BNR process due to the very low NBDCOD content of 0.2%.

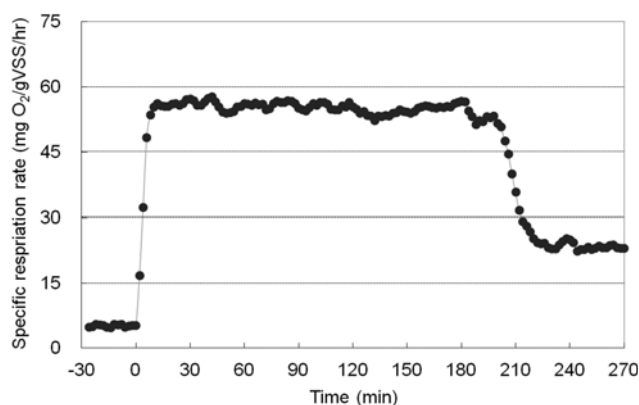


Fig. 3. Time variation of specific respiration rate of the MLOW for estimation of the NBDCOD fraction through the OUR test.

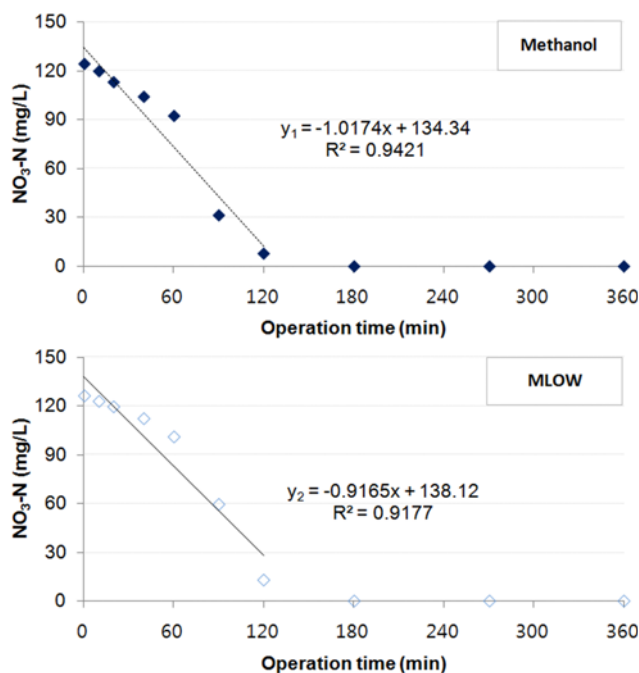


Fig. 4. Experiments for measuring the denitrification rate with methanol and the MLOW.

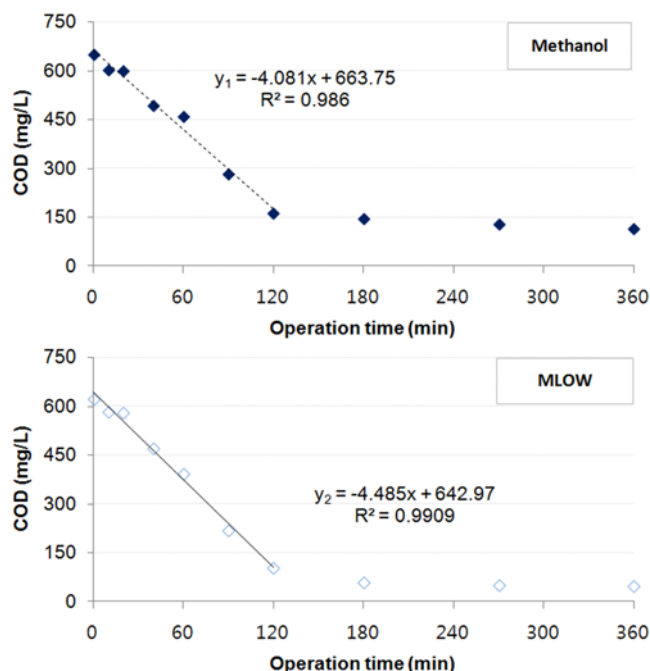


Fig. 5. Experiments for measuring COD removal rate during denitrification with methanol and the MLOW.

3. Denitrification Capacity of the MLOW

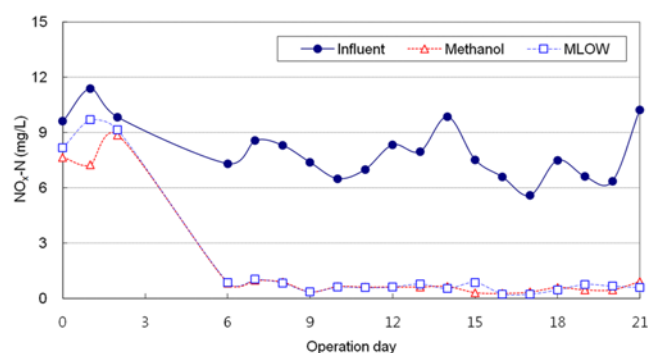
The denitrification capability for MLOW was evaluated using NUR measurement. Figs. 4 and 5 show the temporal variations in the concentrations of NO₃⁻-N and SCOD for the cases of methanol and MLOW. The results of Fig. 4 confirmed that most of the NO₃⁻-N was removed within 120 min at an initial COD/N ratio of 6.0 gCOD/ gNO₃⁻-N. The SDNR for methanol and the MLOW was 12.68 mg N/g VSS/hr and 13.02 mg N/g VSS/hr, respectively. Based on Figs. 4 and 5, the amount of COD required to remove 1 g of NO₃⁻-N for methanol and the MLOW was 4.01 g, and 4.89 g consumed COD/g removed NO₃⁻-N, respectively. This indicated that the denitrification capability of the MLOW was similar to that of methanol. However, compared to methanol, a greater amount of the MLOW was needed as an external carbon source for removing the same amount of NO₃⁻-N due to its lower COD content than that of methanol. As shown in Table 8, these values were similar to the previous study results achieved by using methanol as an external carbon source and were higher than the studies conducted by using industrial organic effluent and waste, and thermal hydrated sludge as an external carbon sources. Based on the previous study results and the present NUR test result, we concluded that MLOW could be used to replace methanol as an alternative external carbon source.

4. Application Test on a Pilot-scale and at a Full-scale Wastewater Treatment Plant (WWTP) of the Stainless Steel (SS) Manufacturing Plant

The possibility of field application for MLOW as an external carbon source was evaluated by operating two pilot plants at the WWTP of a stainless steel manufacturing plant and by the test of a full-scale plant that was designed two lines parallel system consisting of 1st, 2nd anoxic reactors, aeration reactor and settler. In the test of the full-scale plant, the MLOW was simultaneously injected at 1st anoxic reactors of lines 1 and 2. Fig. 6 shows the temporal variation of the

Table 8. COD/N ratio and SDNR of each carbon sources

Carbon Source	COD/N	SDNR (mgN/gVSS/h)	Reference
Methanol	4.6	4.28	Bilanovic et al. [18]
	3.57	29	Lee & Welander [19]
	3.7	6.72	Carrera et al. [20]
	4.01	12.68	The present study
MLOW	4.89	13.02	The present study
Sugar solution	10.2	3	Prentice [21]
Thermal hydrolyzed sludge	6.9	11.9-15.9	Barlindhaug & Odegaard [22]
Distillery fusel oil	2.22	13.8	Monteith et al. [23]
Methanol still bottoms	3.66	7.1	Monteith et al. [23]

**Fig. 6. Temporal variation of NO_x-N concentration during denitrification using methanol or the MLOW as an external carbon source in a pilot plant for treating wastewater from a SS plant.**

influent and effluent NO_x-N (i.e., sum of nitrate and nitrite) concentrations during the operation of the pilot plant while using either the MLOW or methanol as an external carbon source. After five days of pilot plant operation, the effluent NO_x-N concentration was

lower than 1 mg/L for both cases. During the full-scale application testing using the MLOW as an external carbon source, the variation of the NO_x-N and COD concentrations at the anoxic zone of the full-scale plant was observed. The NO_x-N concentration was maintained below 0.1 mg/L over the entire test period, except for the four days after first injection. The COD concentration was stably maintained below the target water quality of the full-scale plant after the initial seven-week period taken for complete acclimation to the MLOW, as shown in Fig. 7. These results revealed that the MLOW could be used as an external carbon source to replace methanol at the WWTP of the SS plant because there was almost no difference between the results using the MLOW and methanol for denitrification during the pilot plant operation. Furthermore, no problem was encountered after changing the external carbon source from methanol to the MLOW in the full-scale plant testing.

The use of MLOW as an external carbon source offers a cost benefit compared to the use of methanol because the MLOW is by-product discharged from the 1,4-butanediol production process. Consequently, the company producing the MLOW has a plan to provide it as a carbon source for the full-scale SS manufacturing plant at a price 65% cheaper than that of methanol. Therefore, if the MLOW is

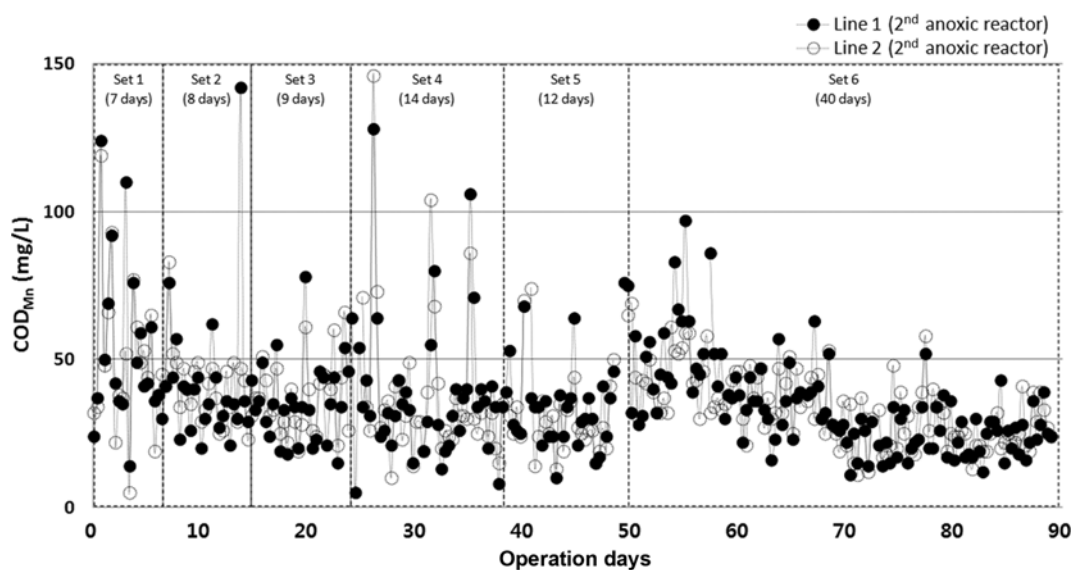
**Fig. 7. Temporal variation of COD concentration in the two anoxic zones during denitrification using a mixture of methanol and the MLOW in the full-scale plant.**

Table 9. Economical benefit using MLOW instead of methanol as an external carbon source at stainless steel wastewater treatment plant

Parameter	Methanol	MLOW
Injection ratio between methanol and MLOW ^a	1	2.22
Unit price (\$/ton)	441.7 ^b	154.6
Requirements (ton/year)	3,000	6,660
Total price (million\$/year)	1.325	1.029
Annual cost savings (%)	-	22.3

^aInjection ratio to maintain a same COD concentration. COD for the MLOW is about 45% of methanol

^bAnnual average methanol price reported by Methanex in 2012

applied as a carbon source for denitrification instead of methanol in the full-scale plant, a chemical cost savings of 22.3% will be achieved, as shown in Table 9, even though 2.2 times more MLOW must be injected, compared to methanol, due to MLOW's lower COD concentration. Further, a financial benefit of more than 1 million dollars is expected to be gained by the company producing and selling the MLOW as an external carbon source due to the sale income and to the removed requirement to treat the MLOW as a wastewater. By following this eco-industrial ecology approach, it is therefore considered that the establishment of a network between the company producing the MLOW and the WWTP consuming the MLOW will become a successful business model offering both economic and environmental benefits for both companies.

CONCLUSIONS

The MLOW produced from the 1,4-butanediol process was tested as an external carbon source for the denitrification in a BNR process. More than 25% of the MLOW was found to consist of butane-series constituents without toxicants, based on the analysis of the MLOW's characteristics. The fraction of NBDCOD in the MLOW was less than 0.2%, as indicated by the OUR test. The NUR test revealed an SDNR for the MLOW of 13.02 mgN/gVSS/hr, which was similar to that of methanol (12.68 mgN/gVSS/hr). The results of the pilot plant operation and the field application tests revealed low NO_x-N and COD concentrations in the effluent. These results supported the conclusion that the MLOW produced from the 1,4-butanediol process could be effectively used as an external carbon source capable of replacing methanol. Such replacement is expected to offer a chemical cost savings of more than 22% for the SS WWTP and of more than 1 million dollars for the company producing the MLOW.

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