

ASSESSMENT OF SUBSTRATE REMOVAL CHARACTERISTICS ACCORDING TO ACCLIMATION PERIODS BY OUR AND NUR TESTS

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Abstract : In this study, substrate removal characteristics were analyzed to reduce the cost of external carbon dosage at Sudokwon Landfill Site Management Corporation in Korea by utilizing oxygen uptake rate (OUR) and nitrate uptake rate (NUR) tests. To estimate and evaluate the substrate removal characteristics obtained by the batch tests, the lab-scale MLE process was operated. By-products of J Co. (sugar manufactory) and S Co. (fine chemical industry) were selected as the concerned carbon sources through a comparison of carbon and nitrogen contents. MeOH was tested as a control experiment. Until the steady state, the fraction of RBDCOD_{OUR} concentration to COD concentration of J Co., S Co. by-products and MeOH increased and reached levels of 98%, 82%, and 100%, respectively. During the 20th operating day, the fraction of RBDCOD_{NUR} concentration to COD concentration was 95%, 81%, and 83%, respectively. These fractions of RBDCOD_{NUR} concentration to RBDCOD_{OUR} concentration increased according to acclimation periods and reached levels of 99%, 97%, and 81%, respectively, on the 20th day. The results obtained from the lab-scale MLE process operation using the concerned carbon sources as external carbon were similar to that observed by OUR and NUR tests.

Key Words : External Carbon, OUR Test, NUR Test, Landfill Leachate, Alternative External Carbon Source

INTRODUCTION

Landfill leachate has resulted in severe environmental problems. These days, safe management of landfill leachate is one of the most important public concerns (Kim *et al.*, 2001). The characteristic of wastewater varies, depending on the type of deposited waste, the age of the landfill and the contents of carbonaceous materials and water. However, the carbon contents of leachate have dramatically decreased with age while the ammonia contents have been relatively maintained (Im *et*

al., 2003). Therefore, an external carbon source was required to denitrify nitrate in a biological nutrient removal process treating old landfill leachate. This resulted in a high dosage cost of external carbon materials for maintaining a biologically stable treatment of old landfill leachate. Methanol has been commonly used as an external carbon source because of its great capability for denitrification and relatively low cost (Lee *et al.*, 2000).

Conventionally, the COD concentration of concerned carbon materials was used to judge the adaptability of alternative external carbon sources and to calculate the dosage. However, that value would not represent the real organic contents used to denitrify and the COD concentration was

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generally large. Therefore, the calculated external carbon dosage was underestimated. Moreover, the effluent COD concentration increase caused by non-biodegradable carbon which contained the alternative carbon source was not estimated in this manner. Municipal solid waste and by-products or wastewater from industry which contained high contents of carbonaceous materials seemed to have a high applicability as an alternative external carbon source. However, they were usually treated at a wastewater treatment plant or in a landfill at additional cost.

In this study, the suitability of the by-product of a sugar manufactory and fine chemistry as an alternative carbon source were tested to reduce the cost of external carbon dosage at Sudokwon Landfill Site Management Corporation, Korea. Substrate removal characteristics, such as the variation of readily biodegradable substrate contents according to acclimation time, type of substrate, and electron acceptor were analyzed by OUR and NUR tests. To estimate and evaluate the substrate removal characteristics obtained by the batch tests the lab-scale MLE process was operated.

MATERIALS AND METHODS

Concerned Carbon Source

To select the concerned by-product as the alternative carbon source, about 60 industrially manufactured by-products around the city of Inchun, Korea were investigated for their carbon and nitrogen contents. Table 1 shows the characteristics of concerned carbon sources, such as carbon and nitrogen contents and the ratio of carbon to nitrogen contents. By the comparison of carbon and nitrogen contents, the by-products of J Co. (sugar manufactory) and S Co. (fine chemical industry) were selected for their concerned carbon sources. It was suitable to use alternative carbon sources, as these materials have a high organic content and relatively low nitrogen content. This resulted in a high ratio of carbon to nitrogen. MeOH was tested as a control experiment. $SCOD_C$, NH_4^+-N , $NO_3^- -N$, TSS, VSS and the alkalinity of mixed liquor were measured.

All analyses were performed according to the procedures in the Standard Methods (AWWA, 1998).

Table 1. Characteristics of concerned carbon sources

Contents	By-product as carbon source		
	Sugar manufacture	Fine chemical	MeOH($\times 10$)
COD(mg/L)	260,000mg/L	50,000mg/L	118,000mg/L
T-N(mg/L)	350mg/L	-	-
C/N ratio	715	-	-

Assessments of Readily Biodegradable COD (RBDCOD)

Readily Biodegradable Chemical Oxygen Demand (RBDCOD) concentration, representing the contents of readily biodegradable substrate using oxygen as the electron acceptor, was measured by an oxygen uptake rate (OUR) test. Figure 1. shows the respirometry set-up (Autoload & Biotox, Envion-Soft) used to measure OUR. It consisted of a DO meter, the respiration chamber and the pre-aeration vessel. The effective volume and flowrate of the respiration chamber were 0.75 L and 0.75 L/min, respectively. In the pre-aeration vessel, 2L of prepared sludge was aerated until it produced an endogenous condition. Endogenous sludge was continuously poured into the respiration chamber and the DO value of mixed liquor in the respiration chamber was measured. Sludge flow changed when the solenoid valve was turned on/off. Therefore, the respiration chamber was isolated and the DO value was measured after one minute. The difference of these DO values was automatically stored and calculated by the installed computer. Figure 2. shows the schematic diagram of a solenoid valve system in the respirometer used in this study.

The standard OUR test for RBDCOD concentration estimating involves the addition of a wastewater sample to endogenous sludge as well as continuous, and monitoring of the respiration rate until it returns to the endogenous level (Ekama *et al.*, 1986). Because the manipulation of the initial substrate to micro-organisms (S_0/X_0) was very important to gain the reliable respiration

curve in the OUR test, the ratio of the initial S_0/X_0 was manipulated from 0.15 to 0.20 according to the literature review (Yu liu, 1996) and the preliminary test. To exclude the oxygen uptake for nitrification and particle organic compounds, the inhibitor of nitrification ATU (Allylthio urea) 9 mg/L was added and concerned carbon sources were filtered with a GFC-10 filter. A summary table for experimental conditions of the OUR test is given in Table 2.

Table 2. Operating condition for OUR test

Contents	OUR test
Sludge	J WWTP (wastewater treatment plant)
COD (mg/L)	450
MLVSS (mg/L)	2,500 ~ 3,000
Volume (L)	2
S_0/X_0 ratio	0.15 ~ 0.20
Operating periods(day)	20

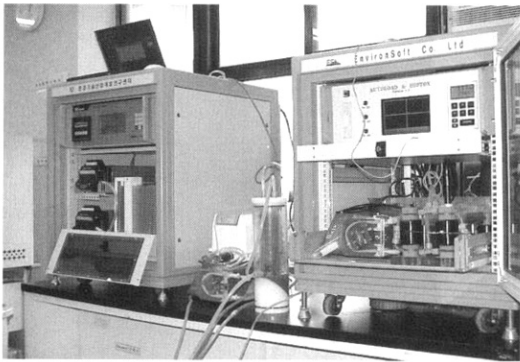


Figure 1. Respirometer(Autoload & Biotox)

were conducted according to the acclimation time of each concerned carbon source. These experiments were conducted with the sludge from J Wastewater Treatment Plant, Busan. The effective volume of each reactor equipped with a stirrer and blower was 5L.

To estimate the substrate removal characteristics according to acclimation periods, the batch reactor using each concerned carbon source for denitrification had been operated for 20 days. Every 4 days, an OUR experiment was conducted with 2 L of sludge from a batch reactor and the NUR experiment was conducted with the other sludge. The initial nitrate and COD concentrations were manipulated at 50 mg/L and 500 mg/L using KNO_3 and each carbon source, respectively, in order to exclude the limitations of the substrates. Therefore, the initial COD/Nitrate ratio was reached to 10 higher than the 4 ~ 5 generally required for complete denitrification. Table 3 shows the summary of the operating conditions for the NUR test. The initial MLVSS (mixed liquor volatile suspended solid) concentration was 2.5 ~ 3 g/L and the temperature was manipulated as $25 \pm 2^\circ C$ during experimental periods.

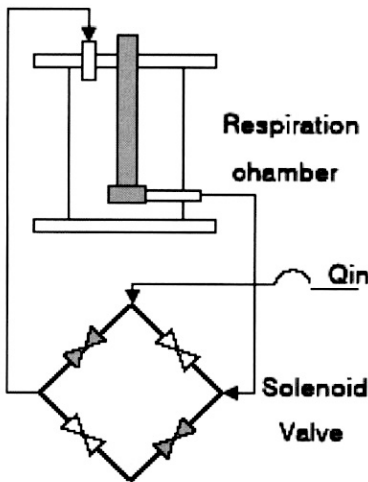


Figure 2. Solenoid valve system

Assesment of Carbon Contents for Denitrification

The batch nitrogen uptake rate (NUR) experiments to assess the carbon contents for denitrification

As shown from Figure 3., the overall NUR batch experimental procedure consisted of four phases. At the beginning of the anoxic condition, the concerned carbon source and nitrate was added and this phase was maintained for 6 hours. To remove the residual carbon in the mixture, aeration was performed for 8 hours. After this phase, the mixture was settled and the supernatant was drained to exclude non-biodegradable substrate effects on the next anoxic phase. Then, the distilled water was added to the settled sludge until the total

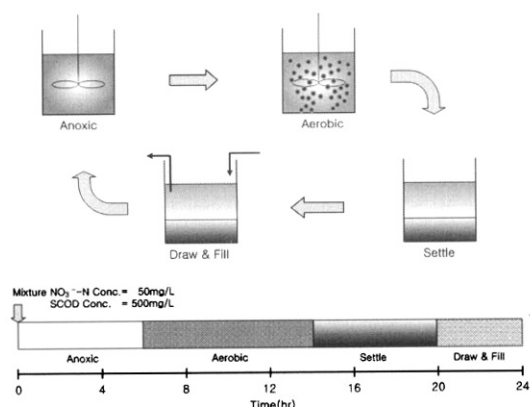


Figure 3. Operating procedure for NUR test

Table 3. Operating condition for NUR test

Contents	NUR test
Sludge	J WWTP (wastewater treatment plant)
COD (mg/L)	500
NOX	50
MLVSS (mg/L)	2,500 ~ 3,000
C/N ratio	10
Volume (L)	3
Operating periods(day)	20

mixture volume was 5 L. The sampling time was appropriately controlled to assess the denitrification rate and COD removal rate. To calculate the reaction rate, the COD and nitrate concentration of

Table 4. Characteristics of leachate on Sudkwon landfill

Contents	Unit : mg/L						
	pH	BOD	COD _{Cr}	SS	T-N	NH ₄ ⁺ -N	T-P
Influent concentration	7.7	241	1,600	95	1,550	1,450	14.9
Water quality standard of discharge	5.8~8	70	800	70	300	100	8

Table 5. Operating conditions of the lab-scale MLE process

Contents	Anoxic	Aerobic	Total
Flow rate (L/day)		7.5	
HRT (day)	2.3	5.7	8.0
Volume (L)	17.25	42.75	60
Sludge Recycle (%)		200	
Internal Recycle (%)		400	
External Carbon	J. Co. and S. Co. by-product, MeOH		

the filtered sample was analyzed by AA3 (Auto Analyzer3, Branerbe).

Application of Concerned Carbon Sources in the Lab-Scale MLE Process

Figure 4. shows the schematic of a lab-scale MLE (Modified Ludzack-Ettinger) process similar to the Sudkwon Landfill Site Management Corporation plant used in this study. The total working volume of the lab-scale reactor was 60 L. The concerned carbon sources were added as the external carbon source to offer electron donors for denitrification. The influent characteristics and the operating conditions are shown in Tables 4 and 5. As shown in Table 4, the biodegradable organic contents in landfill leachate were kept very low in order to remove the high contents of nitrogen. The influent flowrate was 7.5 L/d and HRT (Hydraulic Retention Time) was 8 days. The sludge recycle and the internal recirculation ratios were 200% and 400%, respectively.

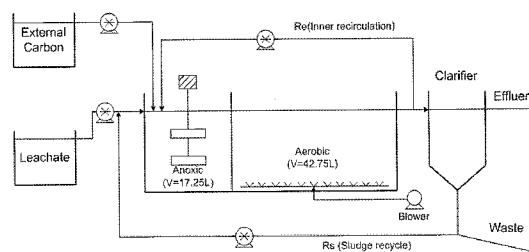


Figure 4. Schematic diagram of the lab-scale MLE process

RESULTS & DISCUSSION

Assessment of Readily Biodegradable COD (RBDCOD)

Figure 5. shows the variation of the RBD-COD_{OUR} concentration fraction to the total COD concentration according to acclimation periods and carbon sources. At the beginning of the test, these fractions of J. Co. by-product, S. Co. by-product, and MeOH were 59%, 66%, and 56%, respectively. It should be noted that the readily biodegradable fraction was nearly 60%. However high the COD concentration of the substrate was, the RBDCOD concentration was low when the micro-organisms were not acclimated to that substrate. These results were in accordance with previous studies (Hallin *et al.* 1998), which insisted that the micro-organisms were required to acclimate in order to degrade non-adapting substrates.

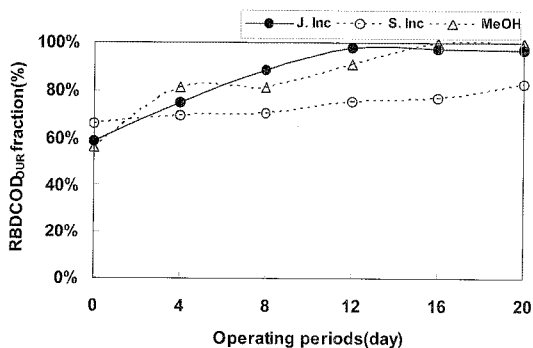


Figure 5. Variation of the fraction of RBDCOD_{OUR} to COD concentration with acclimation periods

The fraction of RBDCOD_{OUR} to COD concentration increased as acclimation periods increased but the tendencies of the increase were different according to the substrates. This increasing tendency lasted 12 days in the case of dosing with the J. Co by-product as an alternative external carbon source but lasted 16 days in the case of dosing with the S. Co by-product and MeOH. Until the steady state, the fraction of RBDCOD_{OUR} to COD concentration of J Co., S Co. by-products and MeOH increased and reached levels of 98%,

82%, and 100%, respectively. The difference between the RBDCOD_{OUR} and COD concentration was revealed as being caused by non-biodegradable substrate contents in the concerned external carbon sources. If the by-product of J. Co. and S. Co. are added as the alternative external carbon source, effluent COD concentration would increase as much as the contents of non-biodegradable substrates.

Assessment of Carbon Contents for Denitrification

RBDCOD_{OUR} concentration calculated by an OUR test was not equal the contents could be used for the denitrification because it was the removed COD concentration using oxygen as an electron acceptor. Those contents could be exactly measured by a NUR test because nitrate was used as an electron acceptor. Figure 6. shows the variation of the fraction of the RBDCOD_{NUR} to the total COD concentration according to acclimation periods and applied carbon sources. As shown in Figure 6., the fraction of RBDCOD_{NUR} to COD concentration was more sensitive to acclimation periods than the fraction of RBDCOD_{OUR} to COD concentration. This difference of increasing tendency was caused by the types of electron accepters and the variations in the micro-biological community. During the experimental periods, the mixture experienced anoxic conditions everyday. It could be explained by the domination of denitrifying micro-organisms with acclimation periods. At the beginning of the test, these fractions of

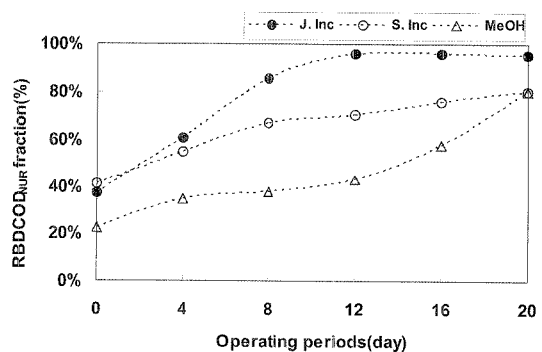


Figure 6. Variation of the fraction of RBDCOD_{NUR} to COD concentration with acclimation period

J. Co. by-product, S. Co. by-product, and MeOH were 37%, 41%, and 23%, respectively. The fraction of $\text{RBDCOD}_{\text{NUR}}$ to COD concentration increased with acclimation periods but the rates of increase were different with substrates. This pattern lasted for 12 days in the case of feeding the by-product of J. Co and S. Co as an external carbon source but lasted to end of the test in the case of MeOH. On the 20th operating day, the fraction of $\text{RBDCOD}_{\text{NUR}}$ to COD reached 95%, 81% and 83%, respectively. These values were smaller than those of $\text{RBDCOD}_{\text{OUR}}$.

Assessment of the Ratio of $\text{RBCCOD}_{\text{NUR}}$ to $\text{RBDCOD}_{\text{OUR}}$

As we have seen in previous results, the carbon contents could change depending on the types of substrates and electron accepters. Moreover, the ratio of the $\text{RBDCOD}_{\text{NUR}}$ to the $\text{RBDCOD}_{\text{OUR}}$ concentration changed with the type of substrate and the acclimation periods. The variation of the ratio of RBDCOD 's calculated by the OUR and NUR test is revealed in Figure 7. It was shown from Figure 7. that the ratio of RBDCOD 's reached 95% after the 12th operating day. It should be noted that those substrate contents calculated by the OUR test could almost be used to denitrify and the residual substrate contents would be so small as not to cause competition between heterotrophs with nitrifiers in aerobic reactors followed anoxic reactors. Therefore, it appears that the by-product of J. Co and S. Co. had applicability as an alternative external carbon source. However, in the case of feeding the MeOH, the ratio of the $\text{RBDCOD}_{\text{NUR}}$ to the $\text{RBDCOD}_{\text{OUR}}$ concentration continuously increased to the end of the test. In this case, obtaining a final ratio required more time to acclimate with MeOH.

As shown from Figure 7., the ratio of RBD - COD and the acclimation characteristics according to the carbon source was different. At the beginning of the test these fractions of J. Co. by-product, S. Co. by-product, and MeOH were 64%, 62%, and 40%, respectively. On the 20th operating day, these fractions were 99%, 97%, and 81%, respectively.

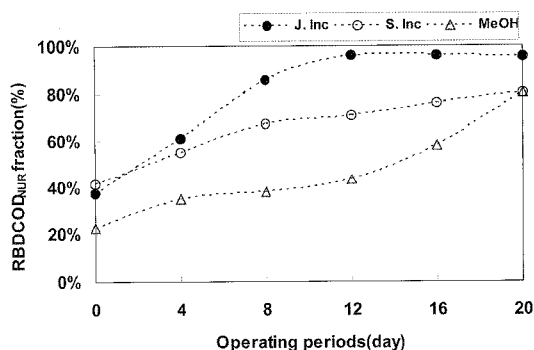


Figure 7. Variation of the ratio of $\text{RBDCOD}_{\text{NUR}}$ to $\text{RBDCOD}_{\text{OUR}}$ concentration with acclimation periods

Application of Concerned Carbon Source in the Lab-Scale MLE Process

Figure 8. revealed that the COD concentration of the anoxic reactor and effluent in the lab-scale MLE process were added to the concerned carbon sources to create an electron donor for denitrification. The operating periods with each tested substrate were about 100 days. The data used to calculate the average effluent quality and the standard deviation were selected when process performance appeared to reach the pseudo-steady state. As shown in Figure 8., in the case of MeOH, the COD concentrations of the anoxic reactor and effluent were almost similar. It was proven that effluent COD is the most prevalent non-biodegradable organic material found among the landfill leachate. But, in the case of J. Co. and S. Co. by-products, the average removed COD concentrations in the aerobic reactor were about 50 mg/L and 130 mg/L, respectively. It was calculated that the increased COD concentration caused by adding the concerned carbon sources for complete denitrification was about 7,000 mg/L. Assuming that the removed COD concentration at the anoxic reactor would be $\text{RBDCOD}_{\text{NUR}}$ concentration and the sum of the removed COD concentration at the anoxic and the aerobic reactor would be $\text{RBDCOD}_{\text{OUR}}$ concentration, those results obtained during the lab-scale MLE process operation, when added to the concerned carbon sources as an external carbon source, are similar to the results of the OUR and NUR tests.

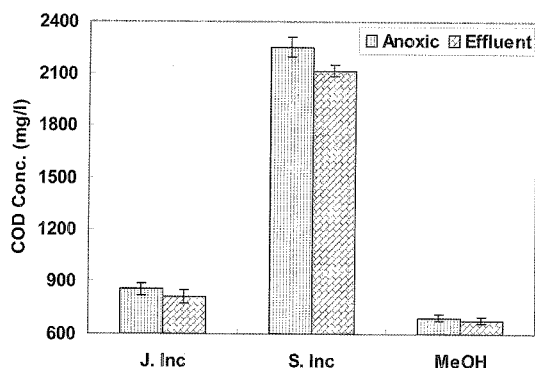


Figure 8. COD profile in the lab-scale MLE process added concerned carbon sources

Besides, the average effluent COD concentrations in the lab-scale MLE process added to the by-product of J. Co, S. Co., and MeOH were 800 mg/L, 2,100 mg/L, and 680 mg/L, respectively. Those results were in agreement with the fraction of non-biodegradable contents in the byproducts of J. Co. (2%) and S. Co. (18%) when using an OUR test. It is clear that the OUR and NUR tests can provide important information, such as the removal characteristics of concerned carbon sources that affected the effluent COD and determined its applicability of external carbon sources.

CONCLUSION

From the results of the OUR and NUR test to analyze the substrate removal characteristics and the application test using the lab-scale MLE process added to the by-products of sugar manufactory and fine chemistry to reduce the cost of external carbon dosage at Sudokwon Landfill Site Management Corporation, the following conclusions were drawn.

- 1) The fraction of $\text{RBDCOD}_{\text{OUR}}$ and $\text{RBDCOD}_{\text{NUR}}$ to COD concentration increased with acclimation periods but the rate of increase was different depending on the types of tested substrate.
- 2) The fractions of $\text{RBDCOD}_{\text{OUR}}$ to COD concentration that could be removed in the aerobic condition increased for 12 days in the case of feeding the by-product of sugar manufactory but increased for 16 days in the case

of the by-product of fine chemistry and MeOH. It was calculated that 2% of the sugar manufactory and 18% of the fine chemistry by-product COD concentrations were non-biodegradable.

- 3) The fractions of the $\text{RBDCOD}_{\text{NUR}}$ to COD that could be removed in anoxic conditions were reached the steady state at 12 days in the case of feeding the by-product of sugar manufactory and fine chemistry, but continuously increased in the case of MeOH. On the 20th operating day, the fraction of $\text{RBDCOD}_{\text{NUR}}$ to COD reached 95%, 81%, and 83%, respectively.
- 4) The fraction of the $\text{RBDCOD}_{\text{NUR}}$ to $\text{RBDCOD}_{\text{OUR}}$ increased with acclimation periods and reached 99%, 97%, and 81% on the 20th day, respectively. In the case of feeding the MeOH, more acclimation time was needed because the fraction was continuously increased to the end of the test.
- 5) Based on the results of the application of concerned carbon sources in the lab-scale MLE process, it is clear that the OUR and NUR test provided important information, such as removal characteristics of concerned carbon sources that affected the effluent COD and determined the applicability of external carbon sources.

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