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EVALUATION OF SULFUR CIRCULATION LEACHATE MANAGEMENT SYSTEM - DEMO-PILOT BIODEGRADATION EXPERIMENTS -

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Abstract: The objective of this study is to evaluate the performance of a leachate management system using sulfur circulation type for the early stabilization of waste landfill. The following research points with pilot plant were focused on; 1) the characteristics of denitrification, 2) sulfide oxidation for sulfate recovery, and 3) nitrification by aerating discharged leachate. We found when sulfate (SO_4^{2-}) was added in leachate, sulfate reduction bacteria decompose organic matter by using SO_4^{2-} as an electron acceptor and simultaneously sulfur oxidation-denitrification bacteria use sulfides (H_2S, HS^-, S^{2-}) as electron donors, therefore, two species of microorganisms can exist not competitively but through commensalism relation on substrate utilization. During aeration, the concentration of NO_3^--N increased from near zero up to 470 mg/L. Eventual denitrification efficiency in the simulated waste landfill was observed to be approximately 16%. Sulfate reduction bacteria produced S^{2-} and sulfur oxidation bacteria oxidized S^{2-} to SO_4^{2-} through aeration. Thus, it is possible that when the system is applied to actual landfill, the dosage of sulfate can be reduced by the recovery of available sulfate. This system was thought to be effective and applicable for the leachate treatment in waste landfill as well as for the early stabilization of landfill site.

Key Words: landfill stabilization, leachate recirculation, sulfate reduction, sulfur oxidation, sulfur-based denitrification

INTRODUCTION

The number of waste landfill which are already closed or in operation is 1,302 in Korea at present, and most of closed landfills are believed to be poorly constructed landfills. Such poorly constructed landfills have negative impacts on human hygiene and environment due to release of landfill gas and leachate, therefore, reduction of negative impact and efficient re-utilization by improvement of such landfills is the most important thing in waste management in Korea.

One of the serious problems in the improvement of landfills is landfill waste treatment including leachate. Landfill waste is characterized by different stabilization periods and leachate is generated until landfill is finally stabilized. Because the quantity and quality of leachate are different from waste mass and characteristics, landfill elapsed time, cover soil, landfill management type, landfill design ele-

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ment and climatic condition, until now little attention has been paid to the proper understanding of leachate quality and quantity in Korea.[1] It also requires developing a suitable processing technology considering above situations. In addition, because costs of equipment for the leachate treatment facility account for more than 30% of whole cost, the selection of economical and efficient methods is important.

The methane gas produced at the landfill site is generally used as a source of energy. The methane composition of biogas and rate of gas production is the highest in methane fermentation phase of anaerobic degradation of solid waste in landfill. In final maturation phase, both methane composition and rate of gas production are maintained at a reduced level for an extended period of time. The collection and purification of methane gas produced is economically possible only for a limited number of years which is usually short as compared to the age of landfill; in other words, it is limited to methane fermentation phase of the anaerobic degradation of waste. In final maturation phase, the collection and purification are uneconomical to be used as a source of energy.[2]

Methane gas production in the final maturation phase lasts for an extended period of time due to the slow conversion of microbially resistant lignocellulosic material into methane under the anaerobic conditions prevailing in a landfill, therefore, generation of methane gas is inevitable. However, if the methane gas is not collected and escapes into the atmosphere, it leads to many problems, global warming being the most prominent one.[3]

Another problem is nitrogen removal in landfill leachate. The problem of leachate treatment is attributed to the excess of organic matter and the existence of materials that disturb coagulation of leachate.

Given the above situation, recently, as a novel technology for the landfill treatment and management, research considering the whole landfill as one bioreactor has been conducted.[4,5] Shortly, the core concept of this technology is leachate recirculation containing sulfur. Compared with the conventional method, this technology can simultaneously accomplish the purpose of early landfill stabilization and removal of organic matter and nitrogen.

The objective of this study is to evaluate the performance of a leachate management system using sulfur circulation for the early stabilization of waste landfill. The areas of focus (with a pilot plant) were: (1) the characteristics of denitrification, (2) sulfide oxidation for sulfate recovery, and (3) nitrification by aerating discharged leachate.

MATERIALS AND METHODS

Experimental Methods

Pilot plant system was demonstrated at Sudokwon Landfill Sites. Sudokwon Landfill Sites are located over Incheon and Kimpo (in the west of Korea).

System Description

Recirculating leachate over waste in landfills has been shown to increase the quantity and quality of methane gas for recovery as well as possibly to reduce the concentration of contaminants in leachate and enhance the settling of the waste. In this study, the degradation of lignocellulosic material was studied under sulfidogenic condition. In conventional landfill site, the organic matter is degraded to methane and carbon dioxide as the final end products by methane producing bacteria. In the proposed gas control and lignocellulose degradation strategy,[6] sulfate is added as an electron acceptor and the degradation of organic matter is carried out under sulfidogenic conditions by sulfate reducing bacteria. The overall degradation reaction with sulfate as terminal electron acceptor would be as follows:

$$2(CH_2O) + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (1)$$

Theoretically, the major end products of sulfate reduction are carbon dioxide and sulfide.

The leachate along with the produced sulfide, which will remain in the leachate if a high pH is maintained, is collected and treated to convert sulfide to sulfate and then recirculated back at the top of a landfill site. In addition to the control of methane gas production, sulfate reduction can also enhance the stabilization of waste, which has been suggested by recent research considering the wide range of organic substrates used by sulfate reducing bacteria along with the thermodynamic and kinetic aspects of sulfate reduction.[2,6)]

Nitrate contamination of ground and surface waters caused by leachate has become an increasingly serious problem. As an alternative to remove nitrate, the biological autotrophic denitrification process has been receiving more attention recently, due to its two major advantages compared to biological heterotrophic processes, namely: 1) no need for an external organic carbon source (methanol or ethanol) which lowers the cost and risk of the process and 2) less sludge production, which minimizes the handling of sludge. Studies on autotrophic denitrification processes have been divided into two major categories: hydrogen-based and sulfur-based autotrophic denitrification. Because it is difficult to handle hydrogen gas and generating hydrogen is expensive, recently, much more attention has been on sulfur-based autotrophic denitrification.[7,8)] The overall degradation reaction with sulfate as terminal electron acceptor would be as follows:

$$a(S^{2-}, S, S_2O_3^{2-}) + bNO_3^- \rightarrow cSO_4^{2-} + (b/2)N_2 \quad (2)$$

Schematic diagram of pilot plant is presented in Figure 1. The system mainly consists of waste landfill facility and leachate treatment facility. The details of system and operating conditions are shown in Table 1.

Waste landfill facility : Simulated waste landfill plant for the stabilization of waste is a concrete structure of 7,000 W×7,000 L×6,000 H (aboveground 4 m, underground 2 m). Waste height is about 4 m, and total waste volume is approximately 196 m^3. Wastes from Block C of the 1st landfill site which was located in Sudokwon Landfill Sites used in the plant, and the major component was municipal solid waste excluding food wastes. Leachate collection tank (S4) has a total working volume of 1.44 m^3 (1,200 W×1,200 L×4,000 H (1,000 He)), and average retention time of leachate is 6~7 hours. Blackout curtain in the scarp and the floor is installed to prevent leachate leakage and underground water pollution. And after gravel and additional post alveolus were spread in the bottom, waste was dumped and geotextile was covered. Spray pipe for leachate recirculation was provided with waste landfill facility between top soil and landfilled waste zone. Then, soil was covered and rainwater exclusion equipment was established to prevent leachate dilution due to excessive rainwater inflow. Gas exhaust pipe and sampling bag were prepared to collect the gas generated in the system.

Leachate treatment facility : The leachate

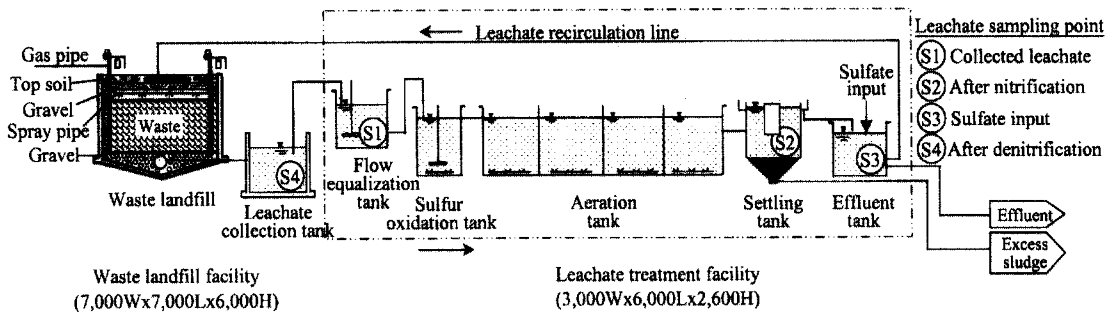

Figure 1. Schematic diagram of pilot plant.

Table 1. Operating conditions of the pilot plant

Waste landfill facilities	
Landfill	
Main mechanism	sulfate reduction sulfur-based denitrification
Landfill size (mm)	7,000 W×7,000 L×6,000 H
Average waste depth (m)	4
Total waste volume (m^3)	196 (MSW 101, construction waste 95)
Seeding	raw leachate (the 1st landfill site in Sudokwon Landfill Sites)
Leachate circulation rate (L/day)	75
COD/SO_4^{2-}	0.5~0.8
Dominant species	Sulfate reduction bacteria, Sulfur-based denitrification bacteria
Leachate collection tank	
Size (mm)	1,200 W×1,200 L×4,000 H (1,000 He*)
Leachate retention time (day)	10~20
Leachate treatment facilities	
Flow equalization tank	
Size (mm)	800 W×800 L×800 H (600 He*)
Leachate retention time (hr)	2~5
Sulfur oxidation tank	
Main mechanism	sulfide oxidation
Reactor size (mm)	350 W×350 L×900 H (600 He*)
Leachate flowrate (L/day)	75
Dissolved oxygen (mg/L)	1.0~1.5
HRT (day)	1
Dominant species	Sulfur oxidation bacteria
Aeration tank	
Main mechanism	nitrification
Reactor size (mm)	600 W×900 L×900 H (600 He*) ×4SET
Leachate flowrate (L/day)	75
Dissolved oxygen (mg/L)	2.5~3.0
HRT (day)	6~8 (7.5)
SRT (day)	80~100
MLSS (mg/L)	5,000~6,000
F/M ratio	0.1~0.3
Dominant species	Nitrification bacteria
Settling tank	
Reactor size (mm)	Ø300×500 H (400 He*)
Leachate flowrate (L/day)	75
Settling time (hr)	4
Sludge return rate (Q)	0.25

*He : effective height

treatment facility consists of a reserve tank for flow equalization of leachate (S1: to evaluate denitrification efficiency), a tank of sulfur oxidation, a leachate aeration tank for nitrification, a settling tank (S2: to evaluate efficiency of sulfate reduction and nitrification) and an effluent tank (S3: to evaluate sulfate input) for recirculation of mixed solution with leachate and sulfate. Dissolved oxygen (DO) concentration in sulfuric oxidation tank (350 W×350 L

×900 H) was kept 1.0~1.5 mg/L and retention time was controlled to 1 day. DO concentration in leachate aeration tank (600 W ×900 L×900 H, 4 SET) for nitrification was kept 2.5~3.0 mg/L and retention time was set to 6~8 days, MLSS and F/M ration were maintained to 5,000~6,000 mg/L and 0.1~0.3, respectively. Settling time of settling tank (Ø300×500 H) and sludge return ratio (Q) were kept 4 hours and 0.25, respectively. Effluent tank to return a mixed solution with leachate and sulfate was provided in the system.

Leachate generated from waste landfill is first collected in leachate collection tank and flowed flow equalization tank and leachate aerating equipment. Leachate aerating equipment was separately operated on sulfide oxidation tank for sulfate recovery and aeration tank for nitrification because if excess aeration is generated in sulfur oxidation reaction, there is a possibility that sulfide (S^{2-}) is changed to other forms of sulfides (S, $S_2O_3^{2-}$ etc) not sulfate (SO_4^{2-}). Therefore, the sulfate recovery ratio can be maximized. Based on the sulfate and sulfide concentration of leachate after oxidation and considering enough quantity for the reaction in waste landfill, sodium sulfate was intermittently injected to leachate. This leachate is circulated to the lower part of soil layer in waste landfill by a leachate circulation device. Leachate flows through sulfide oxidation, sulfide creation, sulfur-based denitrification reaction area and then it gradually passes leachate collection tank and aeration equipment. After deciding whether sodium sulfate is injected or not, it is transferred again by leachate circulation device. The all processes are controlled by automatically.

Analytical Method and Item

To measure leachate quality of each reactor, analysis was basically conducted by Standard Methods[9] and DR/4000 Spectrophotometer Handbook.[10] Samples were collected at four points [collected leachate (S1), after nitrification (S2), sulfate input (S3, only for sulfate), and after denitrification (S4)]. And other items such as COD, T-N, NH_3-N, NO_3^--N, SO_4^{2-} and S^{2-} were also analyzed. Table 2 shows analytical methods for items above.

Table 2. Analytical methods

Parameter	Methods
COD	5220C (Closed Reflux, Titrimetric Method)*
T-N	10071 (TNT Persulfate Digestion Method)**
NH_3-N	10031 (Salicylate Method)**
NO_3^--N	10020 (Chromotropic Acid Method)**
SO_4^{2-}	8051 (SulfaVer 4 Method)**
S^{2-}	8131 (Methylene Blue Method)**

*Standard Methods[9]
**DR/4000 Spectrophotometer Handbook[10]

RESULTS AND DISCUSSION

Chemical oxygen demand (COD) concentration was analyzed as an index for organic matters. The results are illustrated in Figure 2. Average COD of influent to leachate treatment process was 2,018 mg/L. It reduced to 1,038 mg/L after nitrification. 50% of decrease ratio was shown in aeration tank. However, after denitrification in waste landfill, COD value of effluent leachate increased 2,012 mg/L. This is attributed to organic matter eluted by the decomposition of waste. And it is also partly caused by the fact that sulfur oxidation denitrification bacteria use sulfur ions such as S^{2-}, S, $S_2O_3^{2-}$ as substrates instead of organic matter for denitrification.

If sulfate is added in the leachate at an actual landfill, sulfate reduction bacteria will decompose organic matter by using SO_4^{2-} as electron acceptor. Sulfur oxidation denitrification bacteria use the sulfides (H_2S, HS^-, S^{2-}) created as electron donors, so that two microorganism species exist not competitively but through commensalism relation on substrate utilization, and then the system is expected to be driven smoothly.

Figure 3 shows the T-N variations of leachate. Average T-N value of influent to leachate treatment process was 940 mg/L, and after nitrification through aeration tank is

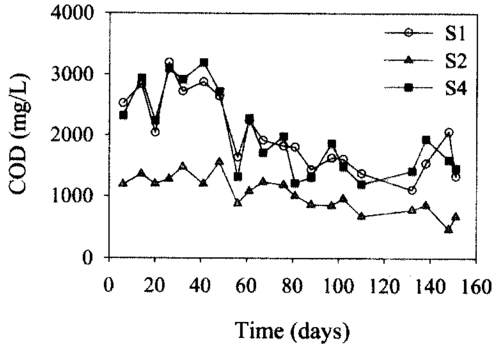

Figure 2. COD changes with respect to time in each reactor.

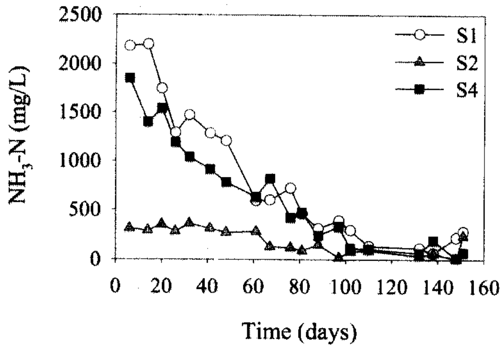

Figure 4. NH_3-N changes with respect to time in each reactor.

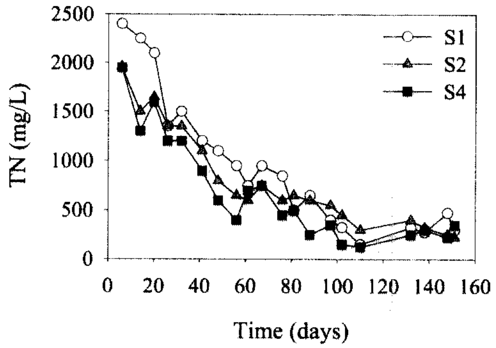

Figure 3. T-N changes with respect to time in each reactor.

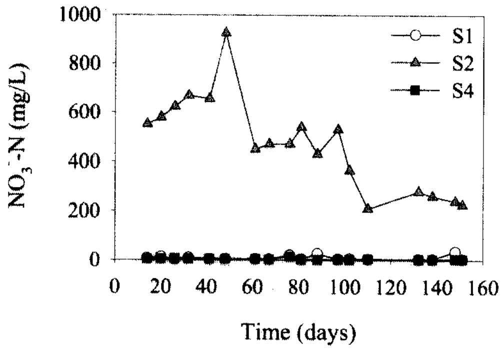

Figure 5. NO_3^--N changes with respect to time in each reactor.

803 mg/L. And effluent COD value was 678 mg/L by circulating waste landfill and after denitrification. Denitrification efficiency was 16%.

Figure 4 shows NH_3-N concentration change with respect to time in each reactor. NH_3-N removal efficiency was 78% after nitrification. This may be attributed to the fact that S^{2-} is utilized in nitrification process, which is operated with commensal conditions between sulfate reduction bacteria and sulfur oxidation denitrification bacteria. While the nitrification ratio appeared low on the whole, it is because of the influence of toxic materials such as free ammonia and heavy metals in leachate.

NO_3^--N change in each reactor is shown in Figure 5. After reaction in waste landfill, NO_3^--N removal ratio was 99% and the system appeared greatly superior in denitrification. In case of system that circulates only leachate without adding sulfate, denitrification bacteria and organic matter oxidation bacteria compete with each other for using organic matter as an electron donor. However, the system with the circulation of leachate containing sulfate, sulfate reduction bacteria and sulfur oxidation denitrification bacteria exist in commensal relation on the utilization of organic matter, therefore the decrease of denitrification efficiency by the deficiency of organic matter may be lessened.[11] If this result applies to actual landfill for stabilization, excellent treatment effect is expected for nitrification removal or denitrification to give activating sulfur oxidation denitrification bacteria in landfill layer. On the other hand, the concentration of NO_3^--N was increased with the decrease of NH_3-N after nitrification process.

Figure 6 shows the SO_4^{2-} change of leachate. Average SO_4^{2-} concentration of leachate in

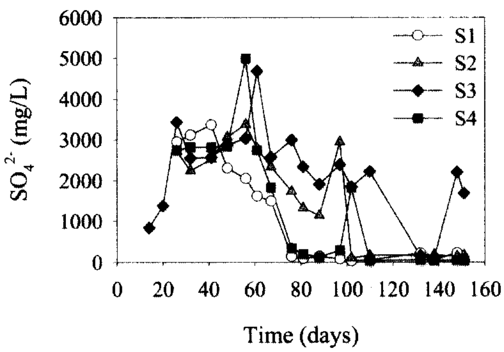

Figure 6. SO_4^{2-} changes with respect to time in each reactor.

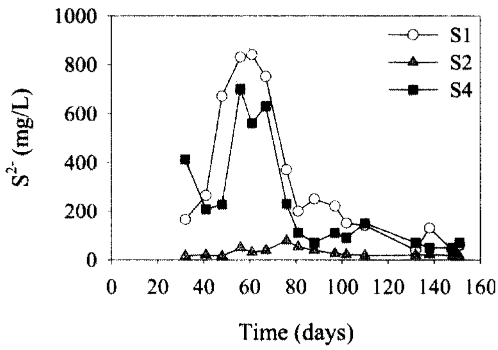

Figure 7. S^{2-} changes with respect to time in each reactor.

denitrification process was 2,204 mg/L and after denitrification, sulfate concentration was 1,400 mg/L. This result can be explained as follows: at first, SO_4^{2-} is consumed as an electron acceptor for the decomposition of organic materials by sulfate reduction bacteria. But, as an electron donor, sulfur oxidation denitrification bacteria used soluble sulfides (H_2S, HS^-, S^{2-}) that are by-products of sulfate reduction bacteria in denitrification process, then generated SO_4^{2-}. For this reason, there was little difference in SO_4^{2-} concentration before and after denitrification process. In addition, from the fact that SO_4^{2-} concentration increased after aeration process, we can understand the recovery of sulfate attained by only simple aeration.

Figure 7 shows S^{2-} changes in each reactor. Average S^{2-} concentration was 30 mg/L before denitrification and increased up to 234 mg/L after denitrification. This shows that sulfide such as S^{2-} is consumed as an electron donor by sulfur oxidation denitrification bacteria, and sulfate is simultaneously reduced to S^{2-} by sulfate reduction bacteria in great quantities. Also, S^{2-} is greatly reduced from average 320 to 30 mg/L after the aeration process, we can infer that S^{2-} is easily removed by simple aeration.

CONCLUSIONS

Leachate that is generated in waste landfill was stored in leachate collection tank and leachate was aerated. After adding sodium sulfate, leachate was cycled to the waste below soil layer. With this circulation, this system can maximize the efficiency of leachate treatment and promote the decomposition of landfill waste.

Based on the above results, the main conclusions can be summarized as follows;

1. The COD value of leachate was increased in waste landfill. This is attributed to organic matter eluted by the decomposition of waste. And it is also partly caused by the fact that sulfur oxidation denitrification bacteria use sulfur ions such as S^{2-}, S, $S_2O_3^{2-}$ as substrates instead of organic matter for denitrification.
2. When sulfate (SO_4^{2-}) is added in leachate, sulfate reduction bacteria decompose organic matter by using SO_4^{2-} as an electron acceptor and simultaneously sulfur oxidation-denitrification bacteria use sulfides (H_2S, HS^-, S^{2-}) as an electron donor. Therefore, we can understand that two species of microorganisms can exist not competitively but through commensalism relation on substrate utilization.
3. During aeration, the concentration of NO_3^--N increased from near zero up to 470 mg/L. Eventual denitrification efficiency in the simulated waste landfill was observed to be approximately 16%. These results indicate

that the system was very effective for nitrogen removal efficiency and nitrification.

4. Sulfate reduction bacteria produced S^{2-} and sulfur oxidation bacteria oxidized S^{2-} to SO_4^{2-} through aeration. Thus, it is possible that when the system is applied to actual landfill, the dosage of sulfate can be reduced by the recovery of available sulfate.

Consequently, this system was thought to be effective and applicable for the leachate treatment in waste landfill as well as for the early stabilization of landfill site.

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