Original Article

Biological Treatment of 1,4-Dioxane in Wastewater from Landfill by Indigenous Microbes Attached to Flowing Carriers

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ABSTRACT

Laboratory and field experiments revealed that indigenous microbes attached to flowing carriers can remove 1,4-dioxane, a recalcitrant substance, from wastewater in landfill facilities. The 1,4-dioxane reduction efficiency of microbes collected from two landfills were different. Landfill Y exhibited higher biodegradation activity than landfill Z. The wastewater of landfill Y contained low biodegradable organic matter as the biochemical oxygen demand (BOD)/chemical oxygen demand (COD) ratio was low, and contained a significantly high proportion of organic carbon in 1,4-dioxane to dissolved organic carbon (> 4.0%). These environmental conditions might have contributed to the high 1,4-dioxane degradation activity of the microbes in landfill Y. Furthermore, the results of the batch experiments suggested that reducing biodegradable organic matter by aeration during pretreatment can accelerate biodegradation. The results also showed that the removal rate constant by stripping and biodegradation for both the batches increased with increasing water temperature. At landfill Y, even at a low temperature of 3°C in the aeration tank that received flowing carriers, over 20% of 1,4-dioxane was removed from wastewater, and a removal rate of 57% was observed at 17°C.

Keywords: 1,4-dioxane, landfill wastewater, biological treatment, temperature dependency

INTRODUCTION

The contaminant 1,4-dioxane is of emerging concern, and has been found throughout various water environments, such as groundwater, surface water, and landfill leachate. The International Agency for Research on Cancer determined that 1,4-dioxane could be carcinogenic to humans and classified it at the 2B level [1]. It is also hepatotoxic and causes an intra-nasal atrophy or dysplasia; however, it is also widely used as a solvent and reactant in a variety of chemical and pharmaceutical industries. Therefore, there are substantial amounts of waste products containing 1,4-dioxane in landfills, which could pollute the surrounding environment with 1,4-dioxane efflux. To reduce the risk of contamination in aquatic environments, the Ministry of the Environment of Japan set the effluent standards for leachate and seepage water from landfill to 0.5 and 0.05 mg/L, respectively, in 2013. In a large survey conducted in Japan, 1,4-dioxane was widespread and at concentration exceeding the standard values of seepage

water in several percent of landfill [2]. However, it is difficult and expensive to determine and eliminate pollution sources; therefore, this is not realistic in many cases.

It is difficult to remove 1,4-dioxane from wastewater through conventional physicochemical processes, such as coagulation and activated carbon adsorption, and biological treatments, such as an activated sludge process, due to its high solubility and poor biodegradability [3–6]. Thus, an advanced oxidation process (AOP) that combines ozone oxidation, ultraviolet light, Fenton-type reaction, and hydrogen peroxide technologies is the only effective method of decomposing 1,4-dioxane at present [7–11]. However, the AOP requires high volumes of chemical and large amounts of energy, with high operating costs. Therefore, a method for 1,4-dioxane removal from wastewater that is less expensive and consumes less energy, and can be applied in small-scale facilities such as landfills in suburbs is desirable.

Over the past decade, several studies on 1,4-dioxane biodegradation have been conducted, which suggest a

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Fig. 1 Flowing carriers before (a) and after immersion in the wastewater treatment plant of landfill Y (b) and landfill Z (c).

greater potential for bioremediation in the laboratory as these facilitate a high biodegradation rate [12–19]. However, these studies only examined the biodegradation rate of 1,4-dioxane by laboratory experiments or small pilot plants. Therefore, 1,4-dioxane reduction in field experiments has not yet been achieved, and there are no peer-reviewed publications on 1,4-dioxane removal by accelerating the activity of indigenous microorganisms in the field, to the best of our knowledge.

In this study, the possibility of continuous and low-cost removal of 1,4-dioxane in wastewater from landfill was explored in both a laboratory and the field. The purpose of this study was to estimate 1,4-dioxane biodegradation rates by the microbial population collected from two landfill sites; determine the effects of the addition of phosphate, the presence of other organic matter, and water temperature on the removal rates; and monitor the long-term removal ratio of 1,4-dioxane in wastewater from the treatment plant of a landfill site by adding flowing carriers to accelerate the activity of the indigenous microorganisms.

MATERIALS AND METHODS

Microbial population used in the 1,4-dioxane removal experiment

Polyethylene white tubes with a diameter and length of 15 mm, specific surface area of $1,000 \text{ m}^2/\text{m}^3$, and specific gravity of 0.98 were used as flowing carriers, and were immersed in the aeration tank of the wastewater treatment plant of landfill Y, which treats wastewater initially containing approximately 1.0 mg/L of 1,4-dioxane. The carriers were then collected after 45 days (**Fig. 1**). Similar to landfill Y, flowing carriers were immersed in the tank of the wastewater treatment plant at landfill Z for 45 days, which treats wastewater

initially containing approximately 0.25 mg/L of 1,4-dioxane. Both landfill Y and Z are inert waste landfill sites located in mountainous region, and have filled up waste plastics, metal chips, glass chips, ceramic chips, rubbles, and scrap rubbers. The microorganism-adhered flowing carriers collected from each landfill were used for the following laboratory scale experiments to estimate 1,4-dioxane removal. The color of all flowing carriers changed from white to dark brown after immersion in the tanks of both landfills. The weight of adhering substances to the flowing carriers collected from landfill Y and Z were 96 and 92 mg/carrier, respectively.

Laboratory experiment to estimate an effect of other organic matter on 1,4-dioxane biodegradation by the microbial population collected from the landfill sites

To estimate the effect of other decomposable organic matters on the rates of 1,4-dioxane biodegradation by the microbial population, 1,4-dioxane-removal batch experiments were conducted using the flowing carriers collected from landfills Y and Z. Wastewaters containing different concentrations of organic matter were collected from landfills Y and Z and also used for the experiments. To adjust the 1,4-dioxane concentration to 1.0 to 1.8 mg/L, a standard 1,4-dioxane solution was added to the wastewater. Since the flowing carrier recognized to use by the addition into reactors at 10% v/v of the reactor, a 500 mL glass bottle was filled with 300 mL of the adjusted 1,4-dioxane wastewater and the microorganism-adhered flowing carriers (10% v/v), and closed with a silicone plug. It was then incubated in a thermostat (MIR-554, Panasonic, Osaka, Japan) for two days under darkness and shaking condition (100 rpm) at 25°C. **Table 1** shows the conditions of the batch experiments. As a control (Run 1-A), a flowing carrier with no microorganisms was also used. The wastewater from landfill Z used for Run

Table 1 Conditions of the batch experiments to estimate the effect of the presence of other decomposable organic matters on the rates of 1,4-dioxane biodegradation by the microbial population.

	Microbes	Wastewater	Pre-treatment (aeration)
Run 1-A	×	landfill Z	×
Run 1-B	landfill Y	landfill Y	×
Run 1-C	landfill Y	landfill Z	×
Run 1-D	landfill Y	landfill Z	○
Run 1-E	landfill Z	landfill Z	×
Run 1-F	landfill Z	landfill Z	○

Table 2 Conditions of the batch experiments conducted to estimate the ratio of 1,4-dioxane removal by the microbial population collected from landfill Y.

	Aeration	Sterilization	Addition of flowing carrier	Water temperature
Run 2-A	○	○	○	10°C
Run 2-B	○	○	×	10°C
Run 2-C	○	○	○ (sterilized)	10°C
Run 2-D	○	○	○	20°C
Run 2-E	○	○	×	20°C
Run 2-F	○	×	×	20°C
Run 2-G	○	○	○	30°C
Run 2-H	○	○	×	30°C

1-D and Run 1-F was aerated for seven days to reduce the decomposable organic matter content before its 1,4-dioxane concentration was adjusted (**Table 1**). Each wastewater sample was tested in triplicate. The 1,4-dioxane and DOC of the samples collected before and after the experiments were analyzed by the following methods.

Laboratory experiment to estimate an effect of the water temperature on the rate of 1,4-dioxane biodegradation by the microbial population collected from landfill Y

Batch experiments were conducted to estimate the 1,4-dioxane removal rate by the microbial population collected from landfill Y that exhibited a high removal capacity, and determined the effect of water temperature on the removal rate. Eight test plots were set depending on water temperature and whether the water was sterilized and whether flowing carriers were added (**Table 2**). Phosphorus was added (adjusted to 2.0 mgP/L) to all test plots to modify the balance of TN and TP. The 1,4-dioxane concentration of 1,500 mL of wastewater collected from landfill Y was adjusted to approximately 2.0 mg/L by adding standard 1,4-dioxane reagents, and the wastewater was then treated with aeration

(1.5 L/min) under darkness at different temperatures (10, 20, and 30°C) in a thermostat (**Fig. 2**). These experiments were conducted in duplicate, and 60 mL of the samples were collected for 1,4-dioxane and TOC analysis after 0, 6, 24, 48, and 72 h of incubation. The wastewater was sterilized by filtration through a membrane with a pore size of 0.22 µm (Merck Millipore, Darmstadt, Germany). Additionally, 150 mL of the flowing carriers immersed in wastewater from landfill Y were added to Run 2-A, Run 2-D, Run 2-F, and Run 2-H, and the same amount of the flowing carriers sterilized at 120°C in an autoclave for 30 min were added to Run 2-C.

Field experiment to monitor a long-term change of 1,4-dioxane removals in wastewater treatment plants at landfill sites

The wastewater treatment plant of landfill Y consists of one sedimentation and two aeration tanks. The hydraulic retention time (HRT) of each tank was one to two days, calculated from their volume tanks (18 m³) and discharge flow (200 to 400 mL/s). Because of its low concentration of BOD, there are poor suspended biomass in these aeration tank. The suspended solid of the 1st and 2nd aeration tank were

Fig. 2 Photograph and schematic diagram of the 1,4-dioxane removal experiments in a thermostat.

Fig. 3 Schematic diagram of the wastewater treatment plant in landfill Y.

approximately 30 and 15 mg/L, respectively. Samples were collected from the inflows and outflows of the tanks from August 2015 to October 2016. To accelerate the 1,4-dioxane removal rate, 1.8 m³ of the flowing carriers were added to the second aeration tank (Fig. 3) in August 2015. The pH and turbidity of each sample were measured on site using pH meter (D-50, HORIBA, Kyoto, Japan) and turbidity meters (TD-M500, OPTEx, Otsu, Japan). The 1,4-dioxane concentration, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and dissolved organic carbon (DOC) were analyzed by the following methods.

Analytical methods

Fifty milliliters of the samples that had received 50 µL of a 100 mg/L-1,4-dioxane d-8 solution were passed through an Sep-Pak AC-2 Plus cartridge (400 mg/cartridge, Waters, Milford, USA) at a flow rate of 5 mL/min after the cartridge had been conditioned with 10 mL of acetone and 20 mL of pure water in succession. The cartridge was rinsed with 10 mL of pure water and then dried with nitrogen in a vacuum pump for 20 min to remove any residual water. The components retained in the cartridge were eluted with 5 mL of acetone at

a flow rate of 1 mL/min. The eluted components were then evaporated to approximately 1.0 mL under a nitrogen stream, and 10 µL of 100-mg/L 1-Bromo-4-fluorobenzene was then added for gas chromatography-mass spectrometry (GC-MS; 5975B, Agilent, Santa Clara, USA) analysis.

The BOD and COD of the samples were measured following the Japanese Industrial Standard (JIS) method (K 0102: 2013) [20]. The samples were filtrated through 0.7 µm glass fiber filters (GF/F, Whatman, Buckinghamshire, UK) to analyze DOC, dissolved total nitrogen (DTN), and dissolved total phosphorus (DTP). The DOC was measured using a total organic carbon (TOC) analyzer (TOC-L, Shimadzu, Kyoto, Japan), and the DTN and DTP were measured by absorptiometry [20].

RESULTS AND DISCUSSION

Effect of other organic matters on 1,4-dioxane biodegradation by the microbial population collected from two landfills

The BOD, COD, and DOC of the wastewater used in the batch experiments are shown in Table 3. The concentration

Table 3 BOD, COD, and DOC of wastewater used for the batch experiments conducted to estimate the effect of biodegradable organic matter on the 1,4-dioxane removal ratio.

	Wastewater	BOD (mg/L)	COD (mg/L)	DOC (mg/L)
Y landfill	-	4.6	20	16.2
Z landfill	without pre-treatment	20	65	48.2
	with pre-treatment	1.2	53	43.7

Table 4 Removals of 1,4-dioxane and DOC during the batch experiments conducted to estimate the effect of biodegradable organic matter on the 1,4-dioxane removal ratio.

	1,4-dioxane conc. (mg/L)		1,4-dioxane removal (%)		DOC removal		<i>n</i>
	Mean Pre.	Mean Aft.	Mean	± SD	Mean (%)	± SD	
Run 1-A	1.17	1.16	0.7	1.1	0.2	0.9	3
Run 1-B	1.80	0.871	51.5	1.0	33.2	4.0	3
Run 1-C	1.17	1.01	13.5	1.5	11.3	0.5	3
Run 1-D	1.02	0.585	42.8	8.8	2.0	2.6	3
Run 1-E	1.17	1.07	8.6	1.4	18.5	1.1	3
Run 1-F	1.02	0.895	12.5	4.6	0.8	3.1	3

of organic matters in the wastewater from landfill Z was higher than that from landfill Y. Owing to the pretreatment applied to reduce degradable organic matters, the BOD of the wastewater from landfill Z decreased from 20 to 1.2 mg/L.

Table 4 shows the removal results of 1,4-dioxane and DOC from the batch experiments, which were used to estimate the effect of biodegradable organic matters on the 1,4-dioxane removal ratio. The removal ratio for the wastewater collected from landfill Z incubated without the added microorganism population (Run 1-A) was 0.7%. The removal ratios of 1,4-dioxane for the wastewater of landfill Z incubated with microorganisms collected from landfills Y (Run 1-C) and Z (Run 1-E) were 13.5 and 8.6%, respectively. The 1,4-dioxane removal ratio of Run 1-C was higher than that of Run 1-E ($p < 0.01$), which indicated that the 1,4-dioxane removal potential of the microorganisms collected from landfill Y was higher than that of the microorganisms collected from landfill Z.

The 1,4-dioxane removal ratios of Run 1-D and Run 1-F, which received aeration as a pretreatment, were 42.8% and 12.5%, respectively. These were 3.2 and 1.5 times higher than those of Run 1-C and Run 1-E, respectively. By pretreating the wastewater of landfill Z, the BOD decreased by 94%, while the COD and DOC decreased by 9% to 18%. These results suggest that reducing the content of biodegradable organic matter through aeration during pretreatment accelerated the 1,4-dioxane removal ratio by microbes. The wastewater of landfill Y contained little biodegradable

organic matter as BOD; therefore, the BOD/COD values of the wastewater were low (4.6 mg/L and approximately 0.5, respectively). Furthermore, the 1,4-dioxane and DOC concentrations of the inflow to the wastewater treatment plant at landfill Y were 1.1 and 14 mg/L when the flowing carriers were immersed, and 1.4 and 17 mg/L when the flowing carriers were collected, respectively. The proportion of organic carbon contained in 1,4-dioxane to DOC was 4.3% to 4.5%, which is significantly higher than the results of past research and studies that reported the proportions of organic carbon contained in 1,4-dioxane to TOC or DOC as 0.01% to 0.3% [21,22]. This particular environmental condition may contribute to the high activity of 1,4-dioxane-degrading microbes in landfill Y. The 1,4-dioxane removal ratio of the wastewater from landfill Y incubated with the added microorganism population collected from Y landfill (Run 1-B) reached 51.5%.

Effect of water temperature on the rate of 1,4-dioxane biodegradation by the microbial population collected from landfill Y

The 1,4-dioxane content, pH, DOC, DTN, and DTP of the wastewater from landfill Y were 1.1 to 1.4 mg/L, 6.9 to 7.5, 14 to 17 mg/L, 17 to 21 mg/L, and <0.1 mg/L, respectively. **Figure 4** shows the changes in the ratio (C/C_0) of the initial 1,4-dioxane concentration (C_0) to the post-treatment concentration (C) at 10°C for Run 2-A, Run 2-B, and Run 2-C;

Fig. 4 Changes in the C/C_0 of 1,4-dioxane for Run 2-A, Run 2-B, Run 2-C, Run 2-D, Run 2-E, Run 2-F, Run 2-G, and Run 2-H. C/C_0 represents the ratio of the post-treatment 1,4-dioxane concentrations to the initial concentrations.

20°C for Run 2-D, Run 2-E, and Run 2-F; and at 30°C for Run 2-G and Run 2-H. The 1,4-dioxane concentration did not significantly decrease in Run 2-B and Run 2-C, which were incubated without a flowing carrier and with sterilized flowing carriers respectively, indicating that the adsorption of 1,4-dioxane by flowing carriers could be ignored. However, the 1,4-dioxane concentration gradually decreased in Run 2-A, which was incubated with microbe-adhered flowing carriers. This indicates that 1,4-dioxane was removed by the microbes-adhered to the flowing carriers. Moreover, the results of the samples incubated with and without sterilized water were similar, which demonstrated the microbes contained in the water could be ignored in the experiments. As samples Run 2-B, Run 2-E, and Run 2-H were incubated without a flowing carrier and sterilized wastewater, the decrease of 1,4-dioxane in these experiments could be caused by stripping. 1,4-Dioxane has high vapor pressure, therefore it could be removed by stripping. The 1,4-dioxane removal ratio of Run 2-G was the highest, followed by Run 2-D and Run 2-A, which could indicate that 1,4-dioxane was removed from Run 2-A, Run 2-D, and Run 2-G by biodegradation and stripping. The removal ratio of 1,4-dioxane at 10°C for two days was approximately 50%, which indicated that the microorganism population collected from landfill Y could degrade 1,4-dioxane under low water temperature conditions.

Removal rate of 1,4-dioxane and its dependence on water temperature

In order to estimate an effect of water temperature in the removal of 1,4-dioxane, removal constants at 10, 20, and 30°C were calculated. When the decline in 1,4-dioxane caused by microbes or stripping is a first-order reaction, the equation can be described as

$$dC/dt = -kC \quad (1)$$

where C is the concentration of 1,4-dioxane (mg/L) and k is its removal rate constant (1/h). Equation (1) can be transformed as

$$C = C_0 e^{-kt} \quad (2)$$

where C_0 is the initial concentration of 1,4-dioxane (mg/L) and t is the treatment time (h). Equation (2) can be transformed as follows.

$$\ln(C/C_0) = -kt \quad (3)$$

The values of $\ln(C/C_0)$ calculated from the data obtained in the batch experiment with regard to the effect of temperature of this study were plotted on a graph at $t = 6, 24, 48$, and 72 h, and then each k value was calculated from the slopes between $\ln(C/C_0)$ and t (Table 5). The k values tended to vary with the presence of microbes. For example, the k values were 2.80×10^{-2} 1/h (Run 2-D) and 0.604×10^{-2} 1/h (Run 2-E) at 20°C, demonstrating that the k of samples incubated

Table 5 Values of k (removal rate constant) obtained in the laboratory experiments, and the k_1 (removal rate constant by stripping) and k_2 (removal rate constant by biodegradation) values calculated by equation (4).

	$k(=k_1+k_2)$ (1/h $\times 10^{-2}$)	k_1 (1/h $\times 10^{-2}$)	k_2 (1/h $\times 10^{-2}$)
Run 2-A	1.13	0.183	0.952
Run 2-B	0.183	0.183	0.00
Run 2-C	0.0837	-	-
Run 2-D	2.80	0.643	2.16
Run 2-E	0.643	0.643	0.00
Run 2-F	0.517	-	-
Run 2-G	6.23	1.62	4.60
Run 2-H	1.62	1.62	0.00

Table 6 Values of k (removal rate constant), $-Ea/R$ (activation energy/universal gas constant) and A (pre-exponential factor) calculated by the Arrhenius equation.

	experimental value (1/h $\times 10^{-2}$)			predicted value (1/h $\times 10^{-2}$)			$k = A \times \exp(-Ea/R)$		r^2
	10°C	20°C	30°C	10°C	20°C	30°C	A	$-Ea/R$	
k	1.14	2.80	6.22	1.14	2.74	6.31	1.83×10^9	-7.30×10^3	1.00
k_1	0.183	0.643	1.62	0.191	0.590	1.70	4.66×10^{11}	-9.38×10^3	1.00
k_2	0.952	2.16	4.60	0.953	2.15	4.61	2.23×10^8	-6.76×10^3	1.00

with microbe-adhered flowing carriers were higher than those incubated without flowing carriers. Similar tendencies were observed at 10°C and 30°C.

As the decline in 1,4-dioxane in this study was due to stripping and microbial biodegradation, k can be described as

$$k = k_1 + k_2 \quad (4)$$

where k_1 is the removal rate constant by stripping, and k_2 is the removal rate constant by biodegradation.

As the wastewater was sterilized and there were no microbes in sample Run 2-B, the decrease in 1,4-dioxane by biodegradation can be ignored. Therefore, the k value obtained from this experiment can be considered as the removal rate constant by stripping at 10°C, and the k_2 of Run 2-A can then be calculated by $k - k_1$. Similarly, the k values of experiments Run 2-E and Run 2-H can be considered as the k_2 at 20°C and 30°C, respectively, and the k_1 at 20°C and 30°C were then determined using the data from experiments Run 2-D and Run 2-G. Both k_1 and k_2 increased with increasing water temperature, which can be explained as the biodegradation and stripping rates increasing with increases in water temperature.

The Arrhenius equation was used to determine the effect

of water temperature on the removal rate of 1,4-dioxane. The equation can be described as follows:

$$k = A \exp(-Ea/(R \cdot T)) \quad (5)$$

where A is a constant known as the pre-exponential factor (1/d), Ea is the activation energy (J/mol), R is the universal gas constant (J/(mol·K)), and T is the absolute temperature in K. Equation (5) can be transformed as

$$\ln k = \ln A + (-Ea/R)/T \quad (6)$$

The coefficient $-Ea/R$ and A were determined from the slope of the correlation line and the intercept of equation (6). Furthermore, the limited removal ratio of 1,4-dioxane in the field under any HRT and water temperature conditions can be predicted by equation (5) using the $-Ea/R$ and A described in **Table 6**. The effect of water temperature on k_1 and k_2 is calculated from the intercept and slope of equation (6). **Table 6** shows the experimental k , k_1 , and k_2 values obtained by this study, and the predicted k , k_1 , and k_2 values calculated by equation (5) using the $-Ea/R$ and $\ln A$ obtained from equation (6). As R is the universal gas constant, the apparent activation energy for biological 1,4-dioxane removal within the temperature range of 10 to 30°C was calculated as 56.2 kJ/

Fig. 5 Changes in the 1,4-dioxane removals of the first and second aeration tanks, and from the sedimentation tank to the effluent (after the third tank).

mol. Recent studies reported that the activation energy of the 1,4-dioxane-degrading bacteria *Pseudonocadia* sp. D17 and *Afipia* sp. D1 were 51.9 and 47.3 kJ/mol, respectively [12,23]. These results suggested that 1,4-dioxane degradation activation energy of the microbes in landfill Y were similar to that of other 1,4-dioxane-degrading bacterium reactions in the earlier reports.

Long-term monitoring of 1,4-dioxane removals at wastewater treatment plants in landfill sites

The 1,4-dioxane, pH, turbidity, BOD, COD, and TOC of the inflow in the wastewater treatment plant at landfill Y ranged from 0.91 to 1.2 mg/L, 7.3 to 7.9, 15 to 57 mg/L, 5.8 to 15 mg/L, 18 to 23 mg/L, and 16 to 21 mg/L, respectively. The DTN of the inflow ranged from 17 to 21 mg/L, and the DTP was approximately 0.1 mg/L. These water quality data of the outlet of the 1st tank, 2nd tank, and effluent of the wastewater treatment plant at landfill Y can be found in the supplemental file (Table S1). The phosphate was insufficient for the ideal balance of BOD: N: P in activated sludge processes [24]. However, no phosphate was added to our samples as we observed no effect on 1,4-dioxane removal in our laboratory experiment (see Table S2, S3 and Fig. S1 in the supplemental file).

Figure 5 shows the changes in the removals of 1,4-dioxane in the first and second aeration tanks, and in the

sedimentation tank with an adjoining small aeration tank (approximately 2 m³) before elution, which were measured from August 2015 to October 2016. The 1,4-dioxane removals of each tank were 9.1%, 6.0%, and 7.4%, respectively, in August 2015. The 1,4-dioxane removals in the first and sedimentation tanks ranged from -3.7% to 13.7%, with an average of 3.6%, and from -4.7% to 21.6%, with an average of 6.8%, respectively. The maximum and minimum values were observed in May and January 2016, respectively. Microbe-attached flowing carriers were added to the second tank in August 2016, and the 1,4-dioxane removals ranged from 20.3% to 57.1% with an average of 32.9% after treatment. The maximum and minimum values were observed in October 2015, with a water temperature of 17.1°C, and March 2016, with a water temperature of 8.4°C, respectively. These results demonstrated that 1,4-dioxane was mainly removed in the second tank with flowing carriers. This indicated that the microbes attached to the flowing carriers may have accelerated the removal of 1,4-dioxane. Furthermore, the result also suggested that microbes may take approximately two months to effectively remove 1,4-dioxane. Figure 6 shows the correlation between the removal of 1,4-dioxane and water temperature. Over 40% of 1,4-dioxane was removed at water temperatures above 15°C, and over 20% of removal was observed at 3°C (January 2016).

Fig. 6 Correlation between the 1,4-dioxane removal ratio and water temperature.

CONCLUSIONS

The results of the laboratory and field experiments revealed that the indigenous microbes attached to flowing carriers can remove 1,4-dioxane, a recalcitrant substance, from wastewater at landfill sites, and also indicated that 1,4-dioxane can be removed from contaminated sites by biological processes with a simple treatment, such as the addition of flowing carriers. Moreover, this is also the first reporting of 1,4-dioxane removal by accelerating the activity of the indigenous microbes in the field.

Microbes collected from landfill Y exhibited higher 1,4-dioxane biodegradation activity than those from landfill Z. The wastewater of landfill Y contained low amounts of biodegradable organic matter as the BOD/COD ratio was low, and contained a significantly higher proportion of organic carbon in 1,4-dioxane than that in DOC ($> 4.0\%$). These environmental conditions may have contributed to the high 1,4-dioxane degradation activity of the microbes from landfill Y. Furthermore, the results of the batch experiments suggested that reducing biodegradable organic matter by aeration during pretreatment can accelerate biodegradation. The results also showed that both the removal rate constant by stripping and biodegradation tended to increase with increasing water temperature, yet the field investigation at landfill Y showed

that over 20% of 1,4-dioxane was removed in the aeration tank with flowing carriers at a water temperature of 3°C , and 57% removal was observed at 17°C . To further investigate the effectiveness of biological 1,4-dioxane degradation, it is necessary to isolate the microorganisms involved in 1,4-dioxane biodegradation to evaluate the process characteristics and apply the treatment to other contaminated sites.

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SUPPLEMENTARY MATERIALS

Supplementary Tables and figure for this article can be accessed at the journal website as a separate file.

https://www.jstage.jst.go.jp/article/jwet/16/6/16_18-032/_supplement/_download/16_18-032_1.pdf

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