

Closed DHS system to prevent dissolved methane emissions as greenhouse gas in anaerobic wastewater treatment by its recovery and biological oxidation

N. Matsuura, M. Hatamoto, H. Sumino, K. Syutsubo, T. Yamaguchi and A. Ohashi

ABSTRACT

Anaerobic wastewater treatment has been focused on its eco-friendly nature in terms of the improved energy conservation and reduction in carbon dioxide emissions. However, the anaerobic process discharges unrecovered methane as dissolved methane. In this study, to prevent the emission of dissolved methane from up-flow anaerobic sludge blanket (UASB) reactors used to treat sewage and to recover it as useful gas, we employed a two-stage down-flow hanging sponge (DHS) reactor as a post-treatment of the UASB reactor. The closed DHS reactor in the first stage was intended for the recovery of dissolved methane from the UASB reactor effluent; the reactor could successfully recover an average of 76.8% of the influent dissolved methane as useful gas (containing methane over 30%) with hydraulic retention time of 2 h. During the experimental period, it was possible to maintain the recovered methane concentrations greater than 30% by adjusting the air supply rate. The remaining dissolved methane after the first stage was treated by the next step. The second closed DHS reactor was operated for oxidation of the residual methane and polishing of the remaining organic carbons. The reactor had a high performance and the influent dissolved methane was mostly eliminated to approximately $0.01 \text{ mgCOD L}^{-1}$. The dissolved methane from the UASB reactor was completely eliminated—by more than 99%—by the post-treatment after the two-stage closed DHS system.

Key words | anaerobic process, closed DHS, dissolved methane, methane oxidation, methane recovery

INTRODUCTION

In recent times, anaerobic wastewater treatment has been focused on its eco-friendly nature in terms of the improved energy conservation and reduction in carbon dioxide emissions. Furthermore, from the viewpoint of depletion of energy and prevention of global warming, the popularization of anaerobic treatment technologies is important. Anaerobic treatment processes have been primarily applied to industrial wastewaters, and today, it is applicable to a wide variety of wastewaters such as low-strength sewage

doi: 10.2166/wst.2010.219

N. Matsuura (corresponding author)

T. Yamaguchi

Department of Environmental System Engineering,
Nagaoka University of Technology,
1603-1 Kamitomioka,
Nagaoka, Niigata 940-2188,
Japan

E-mail: matsuura@stn.nagaokaut.ac.jp;
ecoya@vos.nagaokaut.ac.jp

M. Hatamoto

A. Ohashi

Department of Social and Environmental
Engineering,
Hiroshima University,
1-4-1 Kagamiyama,
Higashihiroshima, Hiroshima 739-8527,
Japan

E-mail: hatamoto@hiroshima-u.ac.jp;
ecoakiyo@hiroshima-u.ac.jp

H. Sumino

Department of Civil Engineering,
Gifu National College of Technology,
2236-2 Kamimakuwa,
Motosu, Gifu 501-0495,
Japan

E-mail: sumino@gifu-nct.ac.jp

K. Syutsubo

Water and Soil Environmental Division,
National Institute for Environmental Studies,
16-2 Onogawa,
Tsukuba, Ibaragi 305-8506,
Japan

E-mail: stubo@nies.go.jp

(Kleerebezem & Macarie 2003; Halalshah *et al.* 2005). However, it has been pointed out that there is a problem even with attractive anaerobic treatment processes (Lettinga *et al.* 1983). The entire amount of methane generated in the anaerobic wastewater treatment cannot be collected as biogas, and a part of the generated methane inherently dissolves in the effluent. Non-recovered methane dissolved in the effluent is discharged and released into the atmosphere as a greenhouse gas.

The concentration of dissolved methane in anaerobic process effluents depends on the methane concentration of produced biogas and is not related to the quantity of methane production. Based on Henry's law, it has been determined that the effluent contains approximately 0.74 mmol L^{-1} (corresponding to $47.3 \text{ mg COD L}^{-1}$) of dissolved methane in general anaerobic processes producing biogas of around 65% methane content at 35°C . When low-strength wastewaters having low methane production potential are anaerobically treated, the ratio of the dissolved methane to recovered methane gas significantly increases with decreasing wastewater strength. This implies that methane recovery efficiency worsens. Cakir & Stenstrom (2005) estimated that the amount of CO_2 emission from anaerobic treatment processes increases as compared to that of activated sludge processes when wastewater strengths less than $700 \text{ mg BOD L}^{-1}$ are applied. Lettinga *et al.* (1983) and Hartley & Lant (2006) also reported problems with dissolved methane, suggesting that new technologies to economically recover or treat dissolved methane in process effluents could make anaerobic wastewater treatment more favorable in reducing greenhouse gas emission for any influent strength.

Anaerobic wastewater treatments usually require post-treatment processes for polishing effluents to meet water quality levels for discharge. Several post-treatment processes following anaerobic treatments such as activated sludge processes and aerated lagoons have been proposed. However to our knowledge, dissolved methane treatment has not been paid attention in any post treatment process. To date, there is little knowledge of the methods for preventing dissolved methane emissions even though the importance of dissolved methane treatment has been indicated, as mentioned above.

We have been expecting that a closed down-flow hanging sponge (DHS) reactor would be capable of recovering dissolved methane as useful energy gas and to biologically oxidize it. The DHS reactor was originally developed for polishing anaerobic effluents and has been reported to be a promising post-treatment process (Machdar *et al.* 2000; Tandukar *et al.* 2007). Let us assume that air is supplied from the bottom of a closed DHS column, and that the exhaust gas is collected from the top of the column. In the gas phase of the closed DHS

column, methane gas, which is released from a liquid containing dissolved methane by physical gasification based on the gas-liquid equilibrium, is transferred upward by the supplied air and concentrated along the column height. The methane gas concentration of the recovered gas is affected by the air-flow rate and gasification rate. A considerable amount of air-flow causes low methane concentrations in recovered gas, while less air supply increases the methane concentration while lowering the methane recovery efficiency. To obtain the recovery gas as a useful gas that should be burnable, the methane concentration required is more than 30%, and therefore, an appropriate control is needed for the air supply.

In this study, we investigated the performance of our novel post-treatment system consisting of a first closed DHS reactor for dissolved methane recovery and a subsequent second closed DHS reactor for the biological oxidation of non-recovered residual dissolved methane as well as for enhancing water quality. The methane recovery efficiency and recovered gas composition were determined when the first closed DHS reactor was operated to maintain the methane concentrations in the recovered gas at greater than 30% by using the effluents of a pilot scale up-flow anaerobic sludge blanket (UASB) reactor treating an actual municipal sewage. In addition, the treatment performance of the second closed DHS reactor was evaluated.

MATERIAL AND METHODS

Reactors and operational condition

The schematic diagrams of the pilot-scale UASB reactor and two-stage closed DHS reactor are shown in Figure 1. The two-stage closed DHS reactor was employed in the post-treatment of the effluents from the UASB reactor treating an actual municipal sewage in Nagaoka, Japan. The cylindrical UASB reactor had a height of 4.0 m, a diameter of 0.2 m, and a volume of 155 L including the gas-solid separator. The two closed DHS reactors were G2 type of sponge sheets (Machdar *et al.* 2000), but they were closed to the air by a water seal at the bottom. The first and second closed DHS reactors had the same square column structure and size with a height of 2.0 m and square area of 0.2 m.

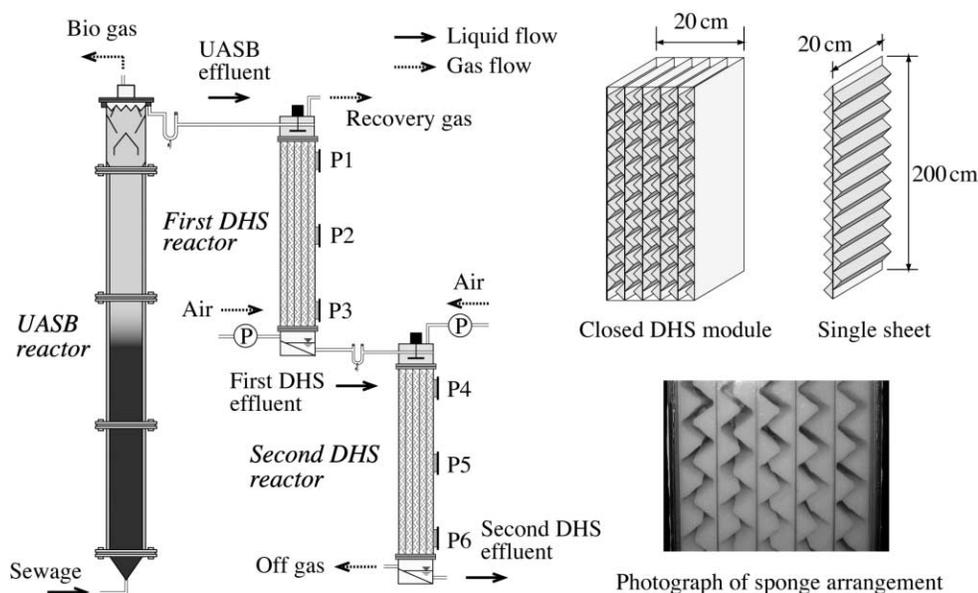


Figure 1 | Schematic diagrams of UASB and two-stage closed-DHS reactor.

Each closed DHS reactor of 80 L volume contained ten sponge sheets occupying 44% of the reactor volume. In each sheet, 46 prisms of an isosceles right triangle ($30 \times 30 \times 200$ mm) made of polyurethane sponge were attached to a plastic rectangular sheet. In the first closed DHS reactor, dissolved methane was recovered by physical gasification. Air was supplied from the bottom of the reactor at $375 \text{ L m}^{-3} \text{ d}^{-1}$ (phase 1) or $250 \text{ L m}^{-3} \text{ d}^{-1}$ (phase 2) based on the reactor volume. The off-gas with methane was recovered from the upper portion. In the second closed DHS reactor, in order to oxidize the residual dissolved methane and organic matter, air was fed from the top at a rate of $2,500 \text{ L m}^{-3} \text{ d}^{-1}$. The exhaust gas was released from the bottom to the atmosphere. The entire system of UASB and two-stage closed DHS reactor was operated at an hydraulic retention time (HRT) of 12.8 h (UASB: 8.8 h, first and second closed DHS: 2.0 h each) with an influent wastewater flow rate of 420 L d^{-1} under ambient conditions ($21^\circ\text{C} \sim 28^\circ\text{C}$) for 131 days.

Measurement of dissolved methane

The dissolved methane concentrations were measured by headspace gas chromatography (GC) using the following conditions. Water samples obtained from the reactors were

gently poured into 122 mL vials with overflow of more than twice the vial volume to decrease the losses of dissolved methane to the atmosphere. One millimeter of 20 mM mercury (II) chloride was added to each vial to inhibit biological methane oxidation. The vial was sealed with a butyl rubber septa and aluminium cap. The headspace of 20 mL was replaced by N_2 gas. The vial was shaken in a water bath at 25°C for 1 h to obtain gas-liquid equilibrium. The gas composition in the headspace was measured with a GC-TCD (Shimadzu GC-8A) as described below. The dissolved methane in the vial was theoretically calculated using the solubility constant of methane (0.0301: Bunsen's constant at 1 atm, 25°C).

Analyses of water and gas

Dissolved oxygen (DO), pH, oxidation-reduction potential (ORP) and temperature were regularly measured to evaluate the performance of the system. BOD, COD, suspended solids (SS), and volatile suspended solids (VSS) were determined according to the [Standard method \(1998\)](#). Ammonium nitrogen, nitrate, nitrite, and sulfate were analyzed by high-performance liquid chromatography (HPLC; Shimadzu LC 20-ADsp). Biogas composition was analyzed with GC-TCD.

Sludge sampling

Sludge samples were taken on day 110 and day 112 from the second and first closed DHS reactors, respectively, when the system performance and temperature were almost stable. The harvested biomass was washed with phosphate buffer (pH 7.2) and resuspended in the same buffer before the measurements of total solids (TS), volatile solids (VS), methane oxidation activity, methane production activity, sulfur oxidation activity, and organic carbon oxidation activity.

Activity tests

Methane oxidation activity test was conducted on the sludges from every sampling port with a nitrate mineral salts medium (ATCC medium 1306). A 122 mL vial containing 22 mL of the medium with each sludge was sealed with a butyl septa and aluminium cap. 20 mL of 100% methane gas was injected into the vial as the substrate. The vial was shaken in a water bath at 25°C, and the methane concentration changes in the headspace were determined with GC-TCD at appropriate time intervals to estimate the activity based on the methane degradation rate.

Methane production activity of the sludge in the first closed DHS reactor was estimated according to previously described procedures (Syutsubo *et al.* 2001). Acetate (200 mg COD L⁻¹) and H₂/CO₂ (80:20, v/v) were used as the substrate. The vials were incubated at 25°C. The gas composition in the vial was analyzed with GC-TCD.

In the sulfur oxidation activity test on the sludge in the first closed DHS reactor, sodium thiosulfite solution (200 mg S L⁻¹) was used as the substrate, and the same medium for the methane production activity were used. The tested sludge in an opened vial was continuously stirred at 25°C and periodically sampled to determine the thiosulfate and sulfate concentrations by HPLC.

Organic carbon oxidation activity test on the second closed DHS reactor sludge was performed according to Tandukar *et al.* (2006). Sodium acetate solution (100 mg COD L⁻¹) was used as the substrate and DO concentration was monitored using a YSI 5100 DO meter (YSI/Nanotech Inc., Japan) for the determination of heterotrophic oxygen utilization rate that represents the oxidation activity. All the activity tests were conducted in duplicate.

RESULTS

Biogas and dissolved methane in UASB

The experiment was conducted for 131 days. The average COD concentration of actual municipal sewage fed to the UASB reactor was 352 mg COD L⁻¹. In the start up of 40 days, the COD concentration of the UASB reactor effluent had a tendency to decrease as shown in Figure 2(A); it decreased from approximately 180 to 70 mg COD L⁻¹. Subsequently, the effluent COD concentration was still unstable with considerable fluctuations, which might be accompanied by changes in the influent sewage concentration. At the end of the entire experimental period, the average effluent COD concentration of the UASB reactor was 109 mg L⁻¹, which corresponded to 76% of the COD removal efficiency. The amount of biogas production from the UASB reactor was 16.7 L d⁻¹ in average and the biogas composed CH₄ (72%), CO₂ (5%), and N₂ (23%) (data not shown). The measured dissolved-methane concentration of the UASB reactor effluent increased with improvements in the COD removal and reached 1.08 mmol L⁻¹ (corresponding to 69.1 mg COD L⁻¹) after the operations were conducted for one month (Figure 3(B)). Thereafter, the

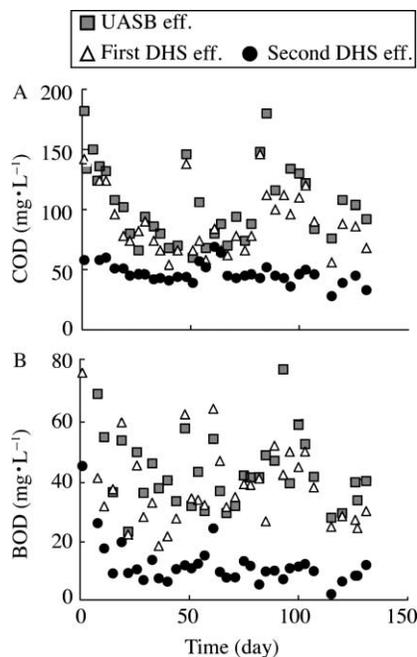


Figure 2 | Time courses of (A) COD and (B) BOD.

dissolved methane concentration slightly decreased in response to the gradual temperature decline. The amount of dissolved methane was evaluated to be almost the same as the methane gas production from the UASB reactor, which indicates that approximately half of the methane generated in the UASB reactor dissolved in the effluent.

Dissolved methane recovery by closed DHS

When the first closed DHS reactor received the UASB reactor effluent, air was supplied to the reactor from the bottom at a flow rate of $375 \text{ L m}^{-3} \text{ d}^{-1}$ until day 89 (phase 1) to primarily recover the methane dissolved in the UASB reactor effluent from the upper exit as methane-containing off-gas. As a result, the recovered methane concentration achieved greater than 30%, which was required as useful gas, except the start-up period (Figure 3(C)). Once the methane concentration decreased to less than 30% on day 89, the air-flow rate was decreased to $250 \text{ L m}^{-3} \text{ d}^{-1}$ until the end of experiment (phase 2), hence, the concentration was maintained above 30%. The influent-dissolved methane concentrations appeared to affect the recovered methane concentrations. The average recovery off-gas composition was CH_4 (37%), CO_2 (7%), and N_2 (58%) over the entire

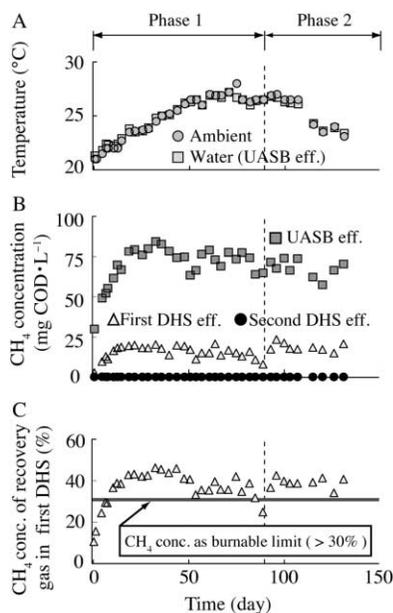


Figure 3 | Time courses of (A) temperature, (B) dissolved methane concentration, and (C) methane concentration of recovery gas in first closed-DHS.

operational period. The oxygen concentration was below the detection limit.

The entire amount of the influent-dissolved methane could not be collected in the first closed DHS reactor. Dissolved methane was detected in the effluent; its average concentration was 0.25 mmol L^{-1} (corresponding to $16.0 \text{ mg COD L}^{-1}$). This implies that 76.8% of the influent dissolved methane was recovered or biologically oxidized, while the other 23.2% exited the reactor as effluent dissolved methane over the entire period. The BOD removed was very little throughout the experiment and its removal efficiency was only 14.1% (Figure 2(B)); however, a significant sulfur oxidation was observed in the first closed DHS reactor. The sulfate concentration of $5.5 \text{ mg SO}_4 \text{ L}^{-1}$ in the influent increased to $20.8 \text{ mg SO}_4 \text{ L}^{-1}$ in the effluent.

Methane oxidation in closed DHS

In the second closed DHS reactor, which was introduced to oxidize the dissolved methane and organic carbons remaining from the first closed DHS reactor effluent, the air was sufficiently supplied from the top of the reactor at a flow rate of $2,500 \text{ L m}^{-3} \text{ d}^{-1}$. The effluent-dissolved methane concentration was very slight at an average of $0.01 \text{ mg COD L}^{-1}$ even though the exhaust gas contained a very small amount of methane, which was equivalent to $0.22 \text{ mg COD L}^{-1}$ based on the amount of treated wastewater. Consequently, 98% of the dissolved methane was removed by the second closed DHS reactor, and only 0.3% of the dissolved methane in UASB effluent resulted in emissions to the atmosphere (Figure 4).

In the case of the removal of organic carbon in the second DHS reactor, BOD and COD were significantly

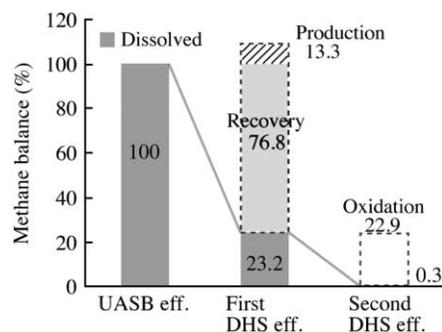


Figure 4 | Methane mass balance within two-stage closed DHS.

removed to 12 mg BOD L⁻¹ and 47 mg COD L⁻¹ in average, respectively, with exception of start up of about 20 days. The reactor had removal efficiencies of 69.0% and 47.3%, respectively, with little effect of the influent concentration (Figure 2(A), (B)).

The oxygen balance during days 93–107, when the performance was stable in the second closed DHS reactor, was constructed using the water quality data to understand the usage of the supplied oxygen. The results showed that 25.7 g d⁻¹ of oxygen was used for COD removal, accounted for 42.8% of the total oxygen consumption, and 13.5% was utilized for the dissolved methane oxidation. Nitrification was observed and 23.8% of the oxygen was consumed for ammonia oxidation by 33.9% of the influent of 27.7 mg NH₄⁺-N L⁻¹.

Microbial activities

To understand the microbial functions and their distributions, sulfur oxidation activity, methane production activity, methane oxidation activity, and organic carbon oxidation activity were evaluated along with the closed DHS reactor height, as shown in Figure 5. The lower portion of Port 3 sludge had the highest sulfur oxidation activity of 0.79 g COD g VS⁻¹ d⁻¹ in the first closed DHS reactor. The sludges of middle Port 2 and upper Port 1 had

activities of 0.35 and 0.40 g COD g VS⁻¹ d⁻¹, respectively, which were approximately half that of Port 3 sludge. On the other hand, relatively low methane production activities were observed in the upper and middle portions. Hydrogen-utilizing methane production activity was higher compared to that of acetate utilization in each portion. In the case of the methane oxidation activity, very low activity was found in each portion of the first closed DHS reactor. However, in the second closed DHS reactor, the highest methane oxidation potential was observed in the upper portion of Port 4. The value of 0.109 g COD g VS⁻¹ d⁻¹ was gradually decreased toward the lower portion of Port 6. The sludge of Port 4 also had the highest organic carbon oxidation activity of 0.104 g COD g VS⁻¹ d⁻¹, which was the same range as that of methane oxidation activity.

DISCUSSION

Methane recovery

In the first closed DHS reactor, the methane concentrations of the recovery gas should be affected by the air-flow rate. In order to investigate the suitable air supply rates for obtaining useful recovery gas comprising more than 30% methane concentrations, we planned to operate the reactor by changing the air supply rates during the experiment.

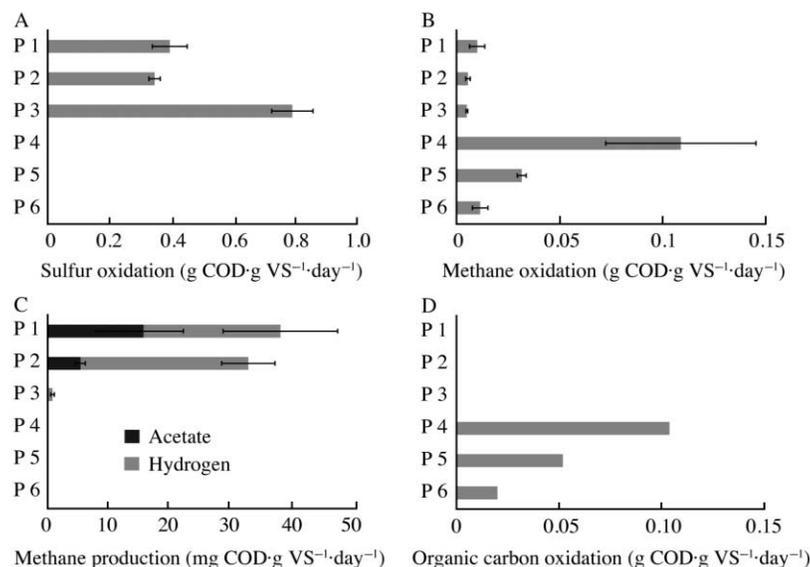


Figure 5 | Microbial activities of (A) sulfur oxidation, (B) methane oxidation, (C) methane production and (D) organic carbon oxidation.

However, fortunately, the starting air-flow rate of $375 \text{ L m}^{-3} \text{ d}^{-1}$ itself met the desired recovery gas concentrations, and hence, we maintained this condition until day 89 at which the methane concentrations became less than 30% once. In order to increase the recovered methane concentrations, the air-flow rate must be reduced theoretically; however, the amount of decrease was unclear. We reduced the air supply rate sensuously to $250 \text{ L m}^{-3} \text{ d}^{-1}$ (approximately 33% reduction), and fortunately, the methane concentration returned to more than 30%. This result suggests that it would be not difficult to recover dissolved methane as a useful gas; however the dissolved methane recovery efficiency is important. Although it is possible to recover the highest methane-concentrated gas near to biogases produced from anaerobic treatment plants with methane concentrations of around 65%, here, the methane recovery efficiency approaches zero in principle. In this experiment using a closed DHS reactor with a height of 2.0 m, the methane recovery efficiency reached approximately 70%, which indicates that the efficiency lies in the range of 0 to 70%; the recovered methane concentrations are between 30 to 65%. If a taller closed DHS reactor is used, the methane recovery efficiency will be enhanced because it is dependent on the reactor height, HRT, and other parameters. These effects must be investigated in future studies.

Oxygen was not detected in the recovery gas from the first closed DHS reactor and even in the gas phase at the middle-height port by GC. 26.1 mg L^{-1} of hydrosulfate was produced, and the oxygen consumption rate required for the oxidation of the influent hydrosulfide was calculated to be $4.3 \text{ g O}_2 \text{ d}^{-1}$, this corresponds to 71.7% of the amount of supplied oxygen. The oxygen consumption rate by sulfur-oxidizing bacteria was evaluated to be $6.6 - 14.5 \text{ g O}_2 \text{ day}^{-1}$ using the measured specific thiosulfate oxidation activity and the amount of retained biomass; this supports the measured sulfate concentrations. On the other hand, methane-oxidation activities were more than two orders of magnitude lower than the sulfur oxidation, implying little effect on the oxygen consumption. In the case of oxygen consumption for organic removal, it is difficult to correctly estimate this consumption; however, the COD reduction might be almost proportional. COD reduction of $19.7 \text{ mg COD L}^{-1}$ corresponded to an oxygen consumption

rate of $8.3 \text{ g O}_2 \text{ day}^{-1}$, which accounted for 138% of the total oxygen consumption. This estimation, which implies a part of the COD reduction, resulted from anaerobic digestion (discussed below). It was reported that the oxygen affinity of biological sulfide-oxidation was higher than that of methane and organic oxidations (David & Jonathan 1990; Shen *et al.* 1996; Rieger *et al.* 2001), which suggests that primarily, sulfide oxidation probably occurs. This result shows that most of the oxygen supplied was utilized for sulfide oxidation in the lower portion. A high air supply rate is not lead to useful recovery gas having methane concentrations greater than 30%, and therefore, the first closed DHS reactor for dissolved methane recovery cannot be expected to have high organic carbon removal because of oxygen deficiency.

Interestingly, the amount of dissolved methane recovered was higher than that of the difference between the influent and effluent, which implies that methane production occurred in the first closed DHS reactor. This phenomenon is supported by the observation of methane production activity particularly in the upper and middle portions, where anaerobic conditions are naturally fabricated. The amount of methane production was equivalent to 14.8% of the recovered methane. The specific methane production activity was extremely low and approximately one order of magnitude lower than that of an UASB reactor sludge treating municipal sewage on both substrates of hydrogen and acetate (Ruiz *et al.* 1998). The amount of calculated methane production based on the activity, $1.49 \text{ g COD-CH}_4 \text{ d}^{-1}$ (Phase 2) did not significantly correspond to the measured one of $3.9 \text{ g COD-CH}_4 \text{ d}^{-1}$, but it was confirmed that a part of the residual organic matter in the UASB reactor effluent was anaerobically decomposed to methane. Strangely, the methane oxidation activity was observed in the upper portion at the same order of magnitude as the methane-production one. Even though the reactor has a methane oxidation potential, methane oxidation would be suppressed because of lack of oxygen. As a result, the oxygen balance, which was constructed using the measurement data of influents and effluents, revealed that out of the expected COD removal, approximately 21% was caused by aerobic oxidation and 47% by anaerobic, with unknown 32%.

Treatment performance

In the second closed DHS reactor, since a large amount of air, which was sufficient to oxidize any possible component such as COD, ammonia, and methane, was supplied into the reactor, we were concerned about exhaust air containing high methane concentrations. This is because gasified dissolved methane in the gas phase would move toward the bottom exit, accompanied by insufficiently oxidized air. However, higher methane-oxidation activities were observed, and the residual dissolved methane introduced from the first closed DHS reactor was almost completely removed to $0.23 \text{ mg COD L}^{-1}$ in average. In addition, some strains of methane-oxidizing bacteria were reported to be active even at very low methane concentrations of around 1.7 ppmv (Conrad 1996), this is the probable reason for the relatively high methane oxidation activity in the lower part. This result suggests that the methane oxidation rate was superior to methane gasification and gas transfer rates in the closed DHS reactor. Although the air supply rate of $2,500 \text{ L m}^{-3} \text{ d}^{-1}$ was set without a firm basis, the methane removal performance was successful, and we maintained the operation conditions. The physical gasification rate has to be determined in future studies for conducting appropriate operations and constructing a well-designed reactor.

The specific methane oxidation activity in the upper portion of the second closed DHS reactor was significantly higher than that in the lower portion of the first closed DHS reactor even though the two portions had almost identical environment conditions, in which oxygen and methane were supplied at similar concentrations, except for hydro-sulfide. As mentioned above, sulfur-oxidizing bacteria are probably predominant and will play important roles in oxygen consumption in the presence of hydrosulfide, whereas methane-oxidizing bacteria would act after sulfide oxidation. Since the knowledge of methane oxidation activity in treatment reactors is little, it is still unclear whether the measured methane oxidation activity was high. By considering the activity of $0.109 \text{ g COD g VS}^{-1} \text{ d}^{-1}$, however, the reactor had the potential to directly accept the UASB reactor effluent for completely oxidizing the dissolved methane of $69.1 \text{ mg COD L}^{-1}$ at only the upper portion if no sulfide is present.

The residual BOD and COD in the final effluent of the second closed-DHS reactor were successfully removed to 12 mg L^{-1} and 47 mg L^{-1} , respectively. This result is reasonable because the organic oxidation activities of 0.02 to $0.104 \text{ g COD g VS}^{-1} \text{ d}^{-1}$ were comparable to the reported values of open DHS reactors treating UASB reactor effluents, which were operated at the same HRT of 2 h (Tandukar *et al.* 2006). Considering the actual amount of removed COD, only 14.2% of the potential organic oxidation activity was evaluated as working. In this study, an important finding is that the organic oxidation and methane oxidation were quite similar with respect to potential activity. This situation is very favorable for preventing methane emissions. In this experiments, the dissolved-methane loading rate of $192 \text{ g COD m}^{-3} \text{ d}^{-1}$ (based on sponge volume) was less than that for COD, $1,068 \text{ g COD m}^{-3} \text{ d}^{-1}$ in the second closed DHS reactor; hence the consumption of dissolved methane would occur in priority to COD removal. It may not be difficult to prevent dissolved-methane emissions if the closed DHS reactor operations are performed at the appropriate HRT to remove organic matters with the air supply required for oxidation.

CONCLUSION

To prevent the emission of greenhouse methane gas from anaerobic wastewater treatment plants, we have proposed a post-treatment system consisting of two closed DHS reactors for the recovery and oxidation of dissolved methane from effluents after anaerobic treatment processes. In the first closed DHS reactor, $69.1 \text{ mg COD L}^{-1}$ (corresponding to 1.08 mmol L^{-1}) of dissolved methane could be successfully recovered as burnable gas; it contained methane concentrations over 30% and no oxygen, and the high methane recovery coefficient was around 76.8%. In the second closed DHS reactor, the residual dissolved methane of approximately 0.25 mmol L^{-1} was almost oxidized to $3.8 \mu\text{mol L}^{-1}$ mostly in the upper portion where a higher methane oxidation potential exists. As a result, the dissolved methane of the UASB reactor effluent was completely removed—by more than 99%—by the two-stage system. With regard to water quality, the first closed DHS reactor has only slight COD removal capacity because the air supply is

not sufficient to obtain useful recovery gas. However, high COD and BOD removals can be expected in the second closed DHS reactor since the air supply is sufficient; this is possible because the residual dissolved methane will be quickly oxidized in the upper portion before being emitted to the atmosphere as off-gas.

ACKNOWLEDGEMENTS

A part of this study was supported by Assistance of Research and Development of Construction Technology from the Ministry of Land, Infrastructure, Transport and Tourism of Japan and by New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES

- Cakir, F. Y. & Stenstrom, M. K. 2005 Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology. *Water Res.* **39**, 4197–4203.
- Conrad, R. 1996 Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O, and NO). *Microbiol. Rev.* **60**(4), 609–640.
- David, W. K. & Jonathan, B. W. 1990 Hemoglobins of the *Lucina pectinatu*/Bacteria Symbiosis. *Biol. Chem.* **265**(27), 16043–16053.
- Halalshah, M., Sawajneh, Z., ZuÖbi, M., Zeeman, G., Lier, J., Fayyad, M. & Lettinga, G. 2005 Treatment of strong domestic sewage in a 96 m³ UASB reactor operated at ambient temperatures: two-stage versus single-stage reactor. *Bioresour. Technol.* **96**, 577–585.
- Hartley, K. & Lant, P. 2006 Eliminating non-renewable CO₂ emissions from sewage treatment: An anaerobic migrating bed reactor pilot plant study. *Biotechnol. Bioeng.* **95**(3), 384–398.
- Kleerebezem, R. & Macarie, H. 2003 Treating industrial wastewater: anaerobic digestion comes of age. *Chem. Eng.* **110**(4), 56–64.
- Lettinga, G., Roersma, R. & Grin, P. 1983 Anaerobic treatment of raw domestic sewage at ambient treatment using a granular bed UASB reactor. *Biotechnol. Bioeng.* **25**(7), 1701–1723.
- Machdar, I., Sekiguchi, Y., Sumino, H., Ohashi, A. & Harada, H. 2000 Combination of a UASB reactor and a curtain type DHS (downflow hanging sponge) reactor as a cost-effective sewage treatment system for developing countries. *Water Sci. Technol.* **42**(3–4), 83–88.
- Rieger, L., Koch, G., Kühni, M., Gujer, W. & Siegrist, H. 2001 The EAWAG Bio-P module for activated sludge model No. 3. *Water Res.* **35**(16), 3887–3903.
- Ruiz, I., Soto, M., Veiga, M. C., Ligeró, P., Vega, A. & Blázquez, R. 1998 Performance of and biomass characterization in a UASB reactor treating domestic waste water at ambient temperature. *Water SA* **24**(3), 215–222.
- Standard Methods for the Examination of Water and Wastewater 1998 20th edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Shen, C. F., Miguez, C. B., Bourque, D., Groleau, D. & Guiot, S. R. 1996 Methanotroph and methanogen coupling in granular biofilm under O₂-limited conditions. *Biotechnol. Lett.* **18**(5), 495–500.
- Syutsubo, K., Sinthurat, N., Ohashi, A. & Harada, H. 2001 Population dynamics of anaerobic microbial consortia in thermophilic granular sludge in response to feed composition change. *Water Sci. Technol.* **43**(1), 59–66.
- Tandukar, M., Uemura, S., Ohashi, A. & Harada, H. 2006 Combining UASB and the “fourth generation” down-flow hanging sponge reactor for municipal wastewater treatment. *Water Sci. Technol.* **53**(3), 209–218.
- Tandukar, M., Ohashi, A. & Harada, H. 2007 Performance comparison of a pilot-scale UASB and DHS system and activated sludge process for the treatment of municipal wastewater. *Water Res.* **41**, 2697–2705.