Waste Management Bulletin 3 (2025) 58–65

Contents lists available at ScienceDirect

Waste Management Bulletin

journal homepage: www.elsevier.com/locate/wmb

Effect of oxidation reduction potential on methane emission from anaerobic septic systems

Areke Alexander Tiareti [a], Megumi Matsumura [a], Taira Hidaka [a,b,*], Fumitake Nishimura [c], Youhei Nomura [a,b], Taku Fujiwara [a,b]

[a] Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto, Japan
[b] Department of Global Ecology, Graduate School of Global Environmental Studies, Kyoto University, Kyoto, Japan
[c] Research Center for Environmental Quality Management, Graduate School of Engineering, Kyoto University, Kyoto, Japan

ARTICLE INFO

Keywords:
Anaerobic digestion
Dissolved oxygen
Greenhouse gas emission
Nitrate
Sludge

ABSTRACT

Septic systems are major on-site sanitation facilities used in many developing countries to treat domestic wastewater. Climate change concerns have prompted efforts to reduce greenhouse gas (GHG) emissions; nonetheless, septic systems contribute to emissions of GHGs, such as methane. The present study investigated modifications to improve the operating conditions of septic systems to minimize methane emissions by evaluating the oxidation reduction potential (ORP) as an operating parameter using laboratory-scale biodegradation experiments. To investigate the influence of ORP on methane emissions, dog food and potassium nitrate were used as representatives of blackwater and alternative electron acceptors to oxygen, respectively, under various biodegradation conditions. The experimental results suggest that methane emission is suppressed at a critical ORP level (−350 to −450 mV vs. Ag/AgCl). They also showed that ORP can be used as a monitoring signal to better understand methane-producing conditions in septic systems. The proposed modifications to improve septic system operating conditions are to shorten the desludging period and provide sufficient oxygen to the septic tank, considering the critical ORP to prevent anaerobic conditions.

Introduction

Concerns regarding climate change have led to initiatives to minimize greenhouse gas (GHG) emissions. The GHGs include methane, carbon dioxide, and nitrous oxide. Over the last two centuries, human activity has been responsible for significant amounts of methane emitted from both human activities and natural sources, including landfills, oil and natural gas systems, agricultural activities, and coal mining. Wastewater treatment is a major source of human-activity emissions. Decentralized sanitation technologies, such as septic systems, contribute to human-activity GHG emissions (Inc. Metcalf & Eddy et al., 2014). Septic systems are major on-site sanitation facilities used in many developing countries for domestic wastewater treatment, either blackwater alone or both blackwater and greywater (Sotelo et al., 2019). However, the management of such a system is in disorder, which frequently results in poor system performance and functionality. According to the United States Environmental Protection Agency (USEPA) (Doorn et al., 2000), estimated global methane emissions from septic systems account for 10.4 % of CH_4 emissions from domestic wastewater. As an example of on-site study, Diaz-Valbuena et al. (2011) surveyed several septic systems and reported that emission rates of methane, carbon dioxide, and nitrous oxide in the septic vent system were 10.7, 335, and 0.2 g capita^{-1}day^{-1}, respectively.

Desludging is a significant problem faced by most septic system users because most septic tanks are only desludged when they experience serious problems, such as clogging (World Health Organization, 2019). For example, while the average desludging interval of a septic tank in Kiribati is approximately six years, most people do not have their septic tank desludged for more than 20 years (Ministry of Infrastructure and Sustainable Energy, 2015). This is longer than the Japanese personal wastewater treatment system known as Johkasou, which requires annual desludging by law (Tamaki et al., 2021). This infrequent desludging period causes a low settling rate of settleable solids (Harada et al., 2008). Desludging significantly affects biogas production

Abbreviations: GHG, greenhouse gas; ORP, oxidation reduction potential; COD, chemical oxygen demand; DO, dissolved oxygen; DF, dog food; DS, dry solids; TS, total solids; VS, volatile solids.

* Corresponding author at: Graduate School of Engineering, Kyoto University, Kyoto, Japan.
E-mail address: hidaka.taira.4e@kyoto-u.ac.jp (T. Hidaka).

https://doi.org/10.1016/j.wmb.2024.12.003

Available online 17 December 2024

(Boiocchi et al., 2023). These systems can pose health and environmental threats if they are not effectively managed (i.e., regular desludging). Organic concentrations in blackwater septic systems are likely to be higher than those in combined blackwater and graywater systems (Sarac et al., 2001; Beavers and Gardner, 1993). Therefore, regular desludging is critical to prevent sludge from creating additional environmental hazards. Tamaki et al. (2021) proposed more frequent desludging with kitchen garbage to increase methane recovery through anaerobic digestion. More methane recovery means less fossil fuel consumption, which contributes to lower GHG emissions.

Sewage in a septic tank is rich in carbon and nitrogen, and the microbial conversion of these pollutants adds to GHG emissions. Huynh et al. (2021) studied GHG emissions from septic tanks and found that a lower oxidation reduction potential (ORP), higher liquid temperature, and higher biodegradable carbon mass associated with longer storage periods were key conditions for methane emissions. Long storage periods primarily impair organic pollutant removal owing to septage accumulation, which causes settling dysfunction. The stored septage was subjected to anaerobic conditions, resulting in biogas containing methane from methanogens. ORP is a promising indicator for understanding the conditions of methane emissions from septage.

The ORP values in this manuscript are presented as mV vs. Ag/AgCl as a reference electrode, unless otherwise noted. The impact of ORP on various types of biological waste and wastewater treatment has been widely studied. ORP measured in the extracellular environment reflects the net outcome of intracellular metabolism, which is controlled by electron transfer and redox balance (Liu et al., 2013). Anaerobic digestion often results in an ORP of approximately −500 mV (Ács et al., 2015; Nguyen et al., 2019; Chetawan et al., 2020). Micro-aeration, which results in a slightly higher ORP, is advocated for certain benefits in anaerobic digestion. However, ORP regulation at approximately −300 mV to −400 mV may lead to a loss of organic carbon through oxidation and deterioration of methanogens (Chetawan et al., 2020). Nghiem et al. (2014) used micro-oxygen injection into an anaerobic digester to reduce H_2S concentration in biogas, increasing ORP values from the natural baseline value of −485 mV to approximately −300 mV. Nguyen et al. (2019) presented ORP-based micro-aeration as a novel process control tool for heavily loaded anaerobic digestion systems, allowing for partial aerobic oxidation of volatile fatty acids while maintaining anaerobic conditions for methanogens.

Anaerobic digestion modeling (Batstone et al., 2002) showed that having both methanogens and nitrate reducers in a system may lead to substrate competition. In rice soil, inhibition of methanogenesis by denitrification intermediates was the primary mechanism for reducing methane production by nitrate rather than competing for substrate (Roy and Conrad, 1999). Methanogenesis did not occur until denitrification was completed (Akizuki et al., 2015). Simultaneous denitrification and methanogenesis in a single reactor with ORP variations have been extensively investigated (Chen and Lin, 1993; Tai et al., 2006). Continuous reactors operating in chemical oxygen demand (COD)-rich conditions, such as COD/NOx-N > 8.86 (Akunna et al., 1992) and methanol/NO_3^--N > 2.62 (COD/NOx-N > 3.93), have demonstrated successful denitrification and methanogenesis (Chen et al., 1997). NO_3^- was completely denitrified or reduced to NH_4^+; and barely detected in reactor effluent (Akunna et al., 1992; Chen et al., 1997). Denitrification only occurred at an ORP of approximately 200 mV higher than that of the methanogenic condition (Chen et al., 1997). The importance of the ORP has been assessed in conventional nitrification and denitrification processes (Hidaka et al., 2003). An ORP of less than −200 mV is preferable for denitrification; however, an ORP of less than −300 mV is not recommended for subsequent nitrification reactors (Hidaka et al., 2002).

ORP has been intensively studied to better understand biological reactions in waste and wastewater treatment. However, the primary goal of these studies is to increase treatment performance by enhancing methane production, reducing hydrogen sulfide production, and achieving simultaneous methanogenesis and denitrification. Limited information is available on the ORP's role in mitigating methane emissions from septages. The objective of this study was to assess the relationship between ORP and methane emissions to improve the operation of septic systems, particularly to minimize methane emissions, by using ORP as a monitoring parameter. Laboratory-scale anaerobic digestion batch experiments were performed to investigate the effects of the ORP on methane production. Generally, sludge in septic tanks is stored for a long time; the situation is closer to batch operation, where the concentrations vary with periodic feeding. ORP and methane production may not be in steady states, hence batch experiments are ideal for analyzing general septic tank conditions. Although it is difficult to evaluate the effect of hydraulic retention time (HRT) or organic loading on ORP or methane production in completely mixed septic systems with continuous influent and effluent, like Yu et al. (2020), solids retention time of septage is much longer than HRT calculated by the flow rate and volume of the septic systems, and the trends of changes in ORP and methane production may be applicable.

Materials and methods

Inoculum and substrate

Anaerobically digested sludge cultivated with dog food (DF) was used in the batch experiments. It was originally obtained from an anaerobic digester at a municipal wastewater treatment plant in Japan and was cultivated in previous experiments (Tamaki et al., 2021). Its volatile solids (VS) content was approximately 1.1–1.4 %.

The main objective of this paper is to investigate the relationship between ORP and methane production. This requires stable anaerobic digestion performance. DF (Vita-One; Nippon Pet Food Co., Ltd., Tokyo, Japan) was used as a representative of blackwater (feces and urine) for the batch experiments. The DF components were: total solids (TS) 96.3 %, VS 87.2 %, C 46.3 %dry solids (DS), H 6.5 %DS, N 4.0 %DS, P 1.0 %DS, and S 0.3 %DS (Hidaka et al., 2016). In previous tests, the same dog food served as an effective substrate for anaerobic digestion (Hidaka et al., 2016). The nitrogen and phosphorus concentrations were lower than those found in typical blackwater; however, no nutrients were added because adequate nutrients were available for the biological treatment of organic waste, and stable methane fermentation performance was expected. In all experiments, DF was diluted with ion-exchange water at a 1 g-DF/16 mL-water ratio to achieve a substrate TS of 6 %, assuming an accumulated septage.

At 20 °C, the maximum DO is approximately 9 mg/L, which is lower than average COD concentrations in the influent to septic systems of more than 800 mg/L (Moonkawin et al., 2023). This limits the amount of oxygen supplied to the liquid phase. Continuous aeration makes it difficult to quantify the amount of O_2 supplied and consumed in anaerobic experiments using ORP monitoring. Therefore, in this investigation, nitrate was used instead of oxygen to modulate the ORP in the reactors. Nitrate is easier to be quantitatively measured than oxygen. Facultative bacteria can receive electrons via nitrate instead of oxygen (Inc. Metcalf & Eddy et al., 2014). Although nitrate is not expected to be found in septic systems, oxygen and nitrate are comparable to each other but different from sulfate and carbon dioxide in terms of relative free energy from reduction/oxidation couples (Rittmann and McCarty, 2020). KNO_3 was used as a nitrate in the experiment.

Equipment setup

Laboratory-scale batch reactor experiments were performed in 1 L bottles, as previously described (Tamaki et al., 2019). Each reactor was fitted with a 1 L aluminum gas bag and a magnetic stirrer for mixing. Almost half of the reactors had ORP sensors, whereas the rest did not. In most cases, one reactor with an ORP sensor for ORP monitoring and another without an ORP sensor for periodical water quality analyses were operated under identical conditions. At the end of each 7-day period, the water quality in both reactors was assessed. The results were consistent, which ensured that equipment modification had no effect on the reaction. Pure nitrogen gas was used to flush air out of the headspace of the bottles and create anaerobic conditions.

The reactor was incubated in a mesophilic water bath at 35 °C. Although typical temperatures in the Pacific Islands are 30 °C (Ministry of Infrastructure and Sustainable Energy, 2015), the experiments were performed at 35 °C because this is the temperature at which the major of anaerobic digestion research has been conducted, and the results are comparable. Anaerobic digestion at 30 °C is within the typical range of mesophilic conditions (Speece, 1996), and the difference may not be significant in terms of reaction mechanisms.

Experimental conditions

Four experimental sets were performed, and nine distinct reactor runs (R1–R9) were compared (Table 1). Each experiment lasted 7 days, and the water quality, generated gas volume, and gas composition were measured once every one to three days. These runs were performed in the order of Experiments 1 to 4. In the first experiment (Experiment 1), aeration and mixing were performed in R1 before the start of the experiment, whereas R2 served as the standard anaerobic digestion reactor. In the second experiment (Experiment 2), an excess (2.4 g) of KNO_3 was added to R3 and R4, which were cultivated with and without DF, respectively. In the final experiments (Experiments 3 and 4), adequate or small, varying amounts of KNO_3 were added to R5, R6, R7, R8, and R9, which were cultivated with DF.

Table 1
Experimental conditions.

Experiment set	Reactor condition	Aeration	DF (g-wet)	KNO_3 (g)	COD/N (–)	ORP sensor
Experiment 1	R1-a	Aerated	0.71	–	–	with
Experiment 1	R1-b	Aerated	0.70	–	–	without
Experiment 1	R2-a	–	0.70	–	–	with
Experiment 1	R2-b	–	0.71	–	–	without
Experiment 2	R3-a	–	0.70	2.41	2.8	with
Experiment 2	R3-b	–	0.70	2.40	2.8	without
Experiment 2	R3-c	–	0.70	2.40	2.8	with
Experiment 2	R3-d	–	0.70	2.40	2.8	with
Experiment 2	R4-a	–	–	2.40	0	with
Experiment 2	R4-b	–	–	2.40	0	without
Experiment 4	R5-a	–	0.70	–	–	with
Experiment 4	R5-b	–	0.70	–	–	without
Experiment 4	R6-a	–	0.70	0.45	15	with
Experiment 4	R6-b	–	0.70	0.45	15	without
Experiment 3	R7-a	–	0.70	0.90	7.6	with
Experiment 3	R7-b	–	0.70	0.90	7.6	without
Experiment 4	R8-a	–	0.70	1.50	4.5	with
Experiment 4	R8-b	–	0.70	1.51	4.5	without
Experiment 3	R9-a	–	0.70	1.80	3.8	with
Experiment 3	R9-b	–	0.70	1.80	3.8	without

Experiment 1 (Aeration and mixing)

Four reactors (R1-a, b, and R2-a, b), each containing 0.2 L of sludge and approximately 0.7 g of DF, were prepared. The substrate/inoculum VS ratio was approximately 0.23. Two of the reactors (R1-a and R2-a) had ORP sensors, whereas the other two (R1-b and R2-b) did not. Before the experiment began, aeration at approximately 1 L/min and mixing for 3 h were performed inside the sludge of R1-a and R1-b using aeration stones. The purpose of providing aeration and mixing before the batch operation was to increase the ORP in R1-a and R1-b. Both R2-a and R2-b served as standard anaerobic digestion reactors. The air in the headspace of all reactors was flushed out with pure nitrogen gas, and the systems were incubated in a mesophilic water bath at 35 °C.

Experiment 2 (Addition of excessive amount of KNO_3)

Six reactors containing 0.2 L of sludge were prepared. DF (approximately 0.7 g) was added to four reactors (R3-a, b, c, and d), with a substrate/inoculum VS ratio of approximately 0.22, whereas the other two reactors (R4-a, b) were cultivated without DF. Four reactors were equipped with ORP sensors (R3-a, c, d, and R4-a), and the other two (R3-b and R4-b) were not. KNO_3 was added to increase the ORP before the recording began, and the concentration change was confirmed in three reactors (R3-c, d, and R4-a). The amount of KNO_3 added (approximately 2.4 g) was based on a substrate-COD/NO_3-N ratio of 2.8, which was predicted to result in a higher ORP or fewer methanogens (Goo et al., 2001).

Experiments 3 and 4 (Addition of sufficient amount of KNO_3)

Four and six reactors (R7-a, b, R9-a, b; R5-a, b, R6-a, b, and R8-a, b) containing 0.2 L of sludge were prepared and cultivated with approximately 0.7 g of DF. The substrate/inoculum VS ratio was approximately 0.22–0.28. The reactors R5-a, R6-a, R7-a, R8-a, and R9-a had ORP sensors, whereas the reactors R5-b, R6-b, R7-b, R8-b, and R9-b did not. Adequate or small amounts of KNO_3 (approximately 0, 0.45, 0.90, 1.50, and 1.8 g) were used to ensure the ORP value required for methane production. The amount of KNO_3 added to the ten reactors was calculated using previous experimental data. Because about 1/3 of the added KNO_3 in Experiment 2 remained in the reactors after 7 days, approximately 1.8 g of KNO_3 (corresponding to about 2/3 of 2.4 g) and smaller were considered in these experiments.

Before Experiments 3 and 4, DF with approximately 4 g of VS was added to the inoculum mixture from the six reactors (1.2 L in total) following Experiment 2 to help recover methane fermentation activity. After the addition of KNO_3, the ORP change was continuously monitored as a measure of methane fermentation recovery. Biogas composition analysis after 4 days confirmed the recovery of methane fermentation conditions.

Analyses

The pH, ORP, TS, VS, and COD were measured using standard methods (APHA-AWWA-WEF, 2012). The pH was measured using a pH meter (pH controller NPH-660; Nissinrika; Tokyo, Japan). The ORP was measured using an ORP meter (9300-10D; Horiba, Kyoto, Japan). The measured ORP values served as the reference electrode for Ag/AgCl using a 3.33 mol/L KCl internal solution (mV). Before each experiment, the ORP electrode's condition was checked with an ORP standard solution. The COD was determined using a spectrophotometer (DR2400; Hach, Loveland, CO, USA) and COD reagents (HR; 2125951, Hach). NO_3^--N and NO_2^--N were analyzed using ion chromatography (Dionex ICS-1100; Thermo Fisher Scientific, Waltham, MA, USA). NH_4^+-N was measured using an auto-analyzer (AACS; BL TEC K.K., Osaka, Japan). The samples were filtered using a 0.22 µm filter (PP Syringe Filter; Membrane Solutions, Auburn, WA, USA) for analysis of soluble components.

Daily biogas production in the gas bag was measured using a syringe. All biogas volumes were measured in normal milliliters (NmL) at standard temperature and pressure (STP at 0 °C, 1 atm). The composition of the gas was determined using a gas chromatograph (Agilent 6890; Agilent Technologies, Edinburgh, UK).

Results and discussion

Experiment 1 (Aeration and mixing)

The inoculum sludge had an ORP of −450 mV, while the ORP in R2 remained at approximately −500 mV during the 7-day experiment. Aerating R1 before the experiment resulted in an increase in the initial ORP to −300 mV. During the first few days, the ORP in R1 fluctuated between −350 and −450 mV, which was 50 to 150 mV higher than the ORP in R2, but decreased to −500 mV on day 7. The pH at the start of the experiment was 8.0, while the pH in R1 and R2 at the end was 7.9 and 7.6, respectively. The seed sludge had a VS/TS ratio of 0.64, while on day 7, the VS/TS ratios in R1 and R2 were 0.57 and 0.60, respectively. After 7 days of digestion, R1 and R2 generated 235 and 276 NmL of methane, corresponding to COD-base methane yields of 0.80 and 0.94, respectively. Aeration before the experiment resulted in an increase in ORP at the beginning, a lower VS/TS ratio, and less methane formation in R1, which could be attributed to the higher biodegradation efficiency of aerobic digestion. However, the difference was small, making it difficult to quantify both generated biogas and supplied oxygen simultaneously during digestion. Therefore, nitrate was used instead of oxygen in subsequent experiments.

Experiment 2 (Addition of excessive amount of KNO_3)

Fig. 1 shows the change in ORP during Experiment 2. The result showed that after adding approximately 2.4 g of KNO_3 and sealing the reactor, the ORP decreased to −430 mV, before increasing dramatically within the first day in both reactors. The ORP in R4 was slightly higher than that in R3 during the first three days, which could be attributed to the absence of biodegradable DF materials. The ORP in both reactors increased from −350 to −150 mV throughout the first five days. After day 6, the ORP stabilized at −150 mV and gradually decreased. The ORP steadily increased before day 5, but as no electron acceptors were added, an increase in ORP was not expected. This increase could imply a time lag in the ORP measurement. VS/TS ratios at the end were 0.48 and 0.47 for R3 and R4, respectively. The pH at the start of the experiment was 8.4, and at the end, it was 8.6 and 8.7 in R3 and R4, respectively.

Fig. 2 shows the nitrate and nitrite concentration changes during Experiment 2. The NO_3^--N persisted in both reactors after the experiment. R4 had a higher NO_3^--N concentration than R3 throughout the experiment due to the lack of biodegradable material (DF) in R3. In both reactors, NO_2^--N concentrations were less than 1 mg N/L. On day 7, the volumes of the generated biogas were 300 and 120 NmL in R3 and R4, respectively. The biogas contained nitrogen and carbon dioxide, but not methane. The nitrogen gas measured after digestion did not differ from the expected value. The addition of 2.41 g KNO_3 resulted in 267 NmL of nitrogen gas, whereas 201 NmL of nitrogen gas was generated in R3, which lacked sufficient biodegradable COD for complete denitrification. Denitrification occurred, while methane production did not occur. These results confirmed that no further NO_3^- addition was required to stop methane fermentation. After denitrification, both reactors showed a color change (i.e., a black to brownish color), which represented inhibiting methanogenic activity.

Experiments 3 and 4 (Addition of sufficient amount of KNO_3)

Fig. 3 shows the ORP changes during Experiments 3 and 4. The ORP in R5 remained constant, ranging between −450 and −550 mV throughout the experiment, similar to the ORP in R2. The addition of KNO_3 increased the initial ORP in R6, R7, R8, and R9 to between −440 and −390 mV, which was 100 mV higher than that in R5, where no KNO_3 was added. The ORP in R7 and R9 increased after one hour, but the ORP in R6 and R8 increased after one day, possibly due to the elimination of reductant substances in digested sludge. After removing the added NO_3^-, the ORP values in R6 and R7 decreased within the first day. Subsequently, the ORP in both R6 and R7 remained constant between −500 and −600 mV, similar to that in R5. In R8 and R9, where more KNO_3 was added, ORP increased to approximately −200 mV over the first 4 to 5 days, then decreased on day 5 and day 6.

VS/TS ratios at the end of incubation in R5, R6, and R8 were 0.50, 0.47, and 0.43, respectively, while those in R7 and R9 were 0.46 and 0.42, respectively. The addition of KNO_3 reduced the VS/TS ratio. This suggests that more organic matter was degraded under anoxic conditions than anaerobic conditions. Throughout the experiment, the pH was maintained between 7.9 and 8.5, with an increase detected following denitrification.

Fig. 4 shows the changes in nitrate concentrations in Experiments 3 and 4. Nitrates were removed, leaving $<$ 1 mg N/L at the end of the experiment. Sufficient COD ensured complete denitrification. Throughout the investigation, NO_2^--N was detected at low levels (usually $<$ 0.2 mg N/L). The NH_4^+-N concentrations ranged from 700 to 1,500 mg N/L. The ammonia needed for microbial growth was present but at lower concentrations than the inhibitory levels (Hidaka et al., 2015). Nitrogen gas generated by denitrification was detected; corresponding to the amount of added KNO_3. Methane was detected in R5, slightly in R6, and R7, but not in R8 or R9. Thus, conditions with and without adequate electron acceptors for methanogenesis were reproduced, leading to a difference in the amount of methane produced.

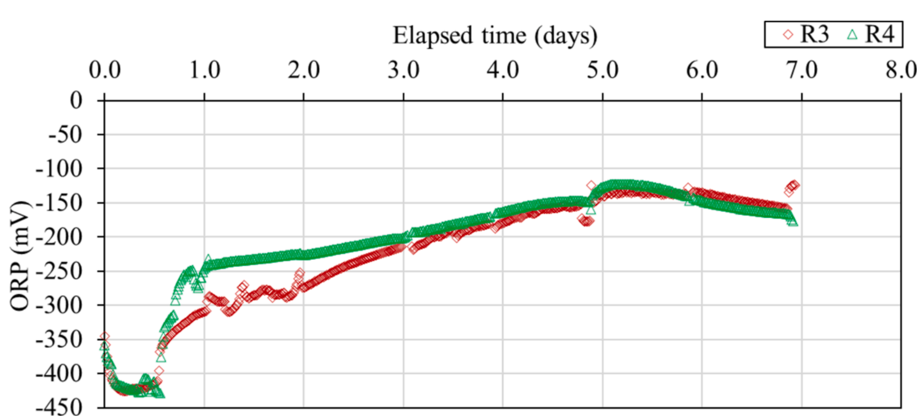

Fig. 1. Change in ORP during Experiment 2.

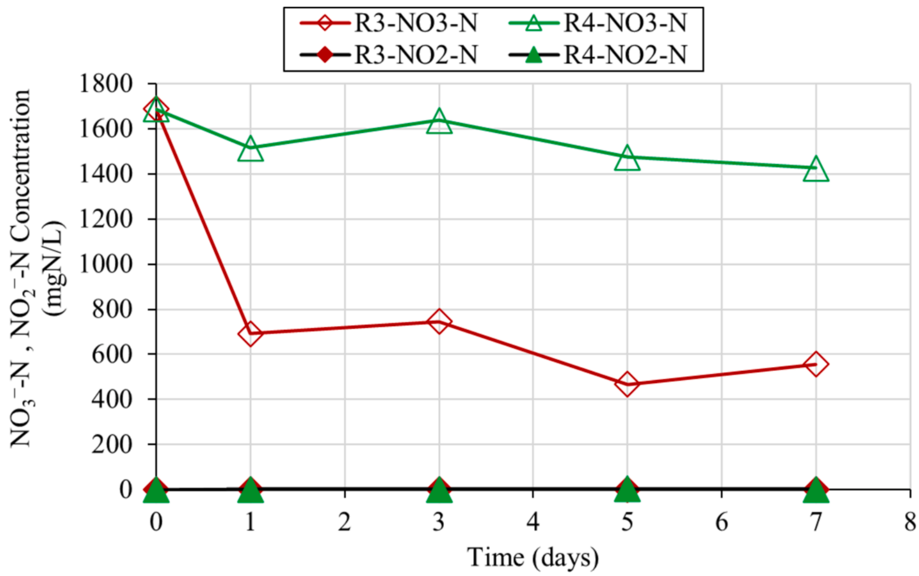

Fig. 2. Changes in nitrate and nitrite concentrations during Experiment 2.

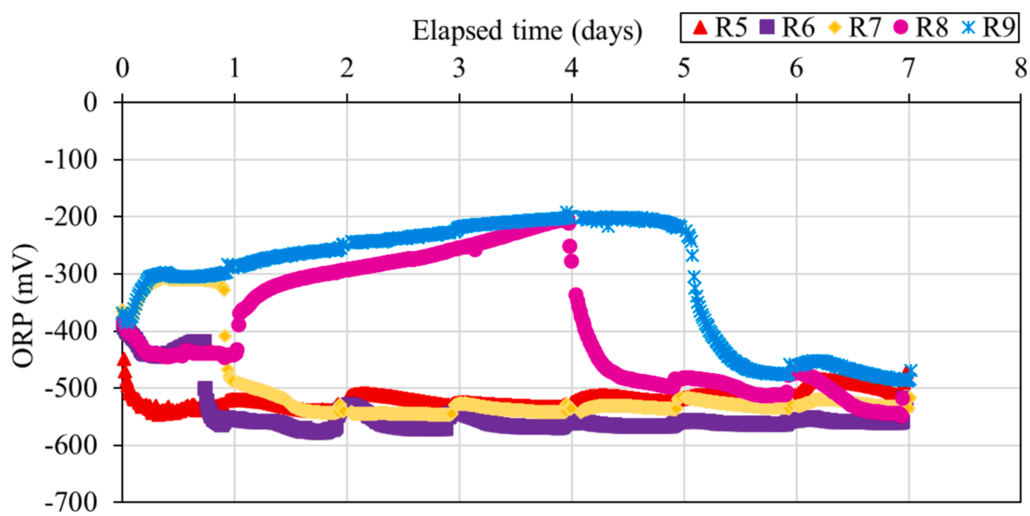

Fig. 3. Changes in ORP during Experiments 3 and 4.

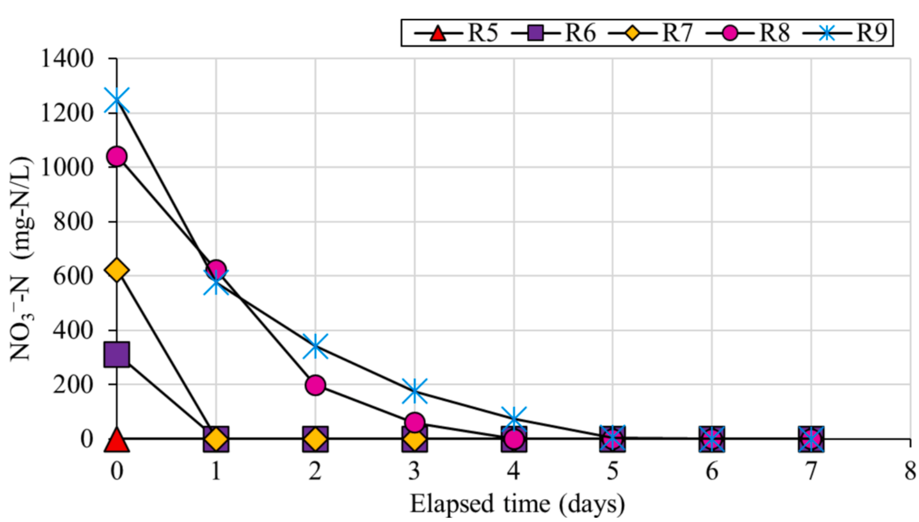

Fig. 4. Changes in nitrate concentrations during Experiments 3 and 4.

Effect of ORP on methane production

Fig. 5 shows the relationship between the average ORP and NO_3^--N concentrations in Experiments 2, 3, and 4 (R3, R4, R5, R6, R7, R8, and R9). In R3 and R4, where denitrification was incomplete, and nitrate remained at > 400 mg N/L, ORP was approximately −400 mV at the start of the experiment and gradually increased to approximately −150 mV at the end. In R5, R6, R7, R8, and R9, the added nitrate was completely denitrified at the end of the experiment. The ORP at the end was different even though there was no nitrate left. ORP decreased to less than −500 mV in R5 and R6, whereas in R7, R8 and R9 it was higher than −400 mV.

Fig. 6 shows the relationship between the average ORP and methane production in Experiments 1, 2, 3, and 4 (R1, R2, R3, R4, R5, R6, R7, R8, and R9). Methane measurements are presented in terms of daily production (NmL/(gVS-added·d)). The average ORP corresponds to each measurement interval. In Experiment 1, R2 exhibited a lower ORP and slightly higher methane production. In R3 (with DF) and R4 (without DF), NO_3^--N concentrations in R3 and R4 were high enough to inhibit methane fermentation. This was confirmed by the absence of methane in the generated biogas. In R5, R6, R7, R8, and R9, the added nitrate was completely denitrified, but methane was not detected in the biogas produced of R8 and R9. The most biodegradable COD appears to have been used for denitrification rather than methane fermentation, although the ORP reached approximately −500 mV.

Methane was found in the biogas from R6 and R7. The methane production in R7 was higher than that in R6, and the ORP in R7 was slightly higher than that in R6, although the difference was slight. This could be because the seed sludge in R6 (Experiment 4) was exposed to nitrate in the previous experiments of R7 and R9 (Experiment 3), where less methane production was observed with nitrate addition. The conditions in R5 were similar to those in R2, and both had similar ORPs, but R5 produced less methane than R2. The seed sludge for R5 (Experiment 4) was exposed to nitrate in the previous experiments of R7 and R9 (Experiment 3). Each experiment was limited to 7 days of operation, and the total amount of methane generated was limited. Although the methane production ability recovered after exposure, the activity may have been lower than before. Methane production was lower in R5 and R6 than R2 and R7, respectively, but the trends of changes in ORP and methane production were consistent. More methane generation was expected, if more time or biodegradable COD were available.

These results are consistent with previous research (Chen et al., 1997), which indicates that nitrate in anaerobic digestion inhibits methane fermentation at an ORP approximately 200 mV higher than the methanogenic condition without nitrate, and that methanogenesis does not occur until denitrification is complete (Akizuki et al., 2015). Yu et al. (2020) showed that low-dose micro-aeration improved methane recovery, whereas high oxygen dose resulted in reduced methane synthesis and increased accumulation of volatile fatty acids, primarily due to the oxygen inhibition, in blackwater treatment. Although ORP in the effluent remained constant regardless of micro-aeration, aeration increased ORP by 120 to 220 mV prior to the methane fermentation reaction (Yu et al., 2020). R1 in the present study showed a 15 % decrease in methane generation compared to R2 because of the oxygen addition before the experiment. ORP in R1 increased by 50 to 100 mV during methane generation compared to R2 without aeration. Thus, slight oxygen injection to raise ORP before entering septic systems may partially decrease methane generation.

Applicability of ORP in monitoring septic systems

Aerobic conditions in septic systems can be achieved by agitating the influent water flow, surface aeration, or mechanical aeration. Although intentionally maintaining aerobic conditions may be impractical, avoiding excessive anaerobic conditions may limit methane emissions from septic systems. ORP values of −96 mV and −495 mV indicate to dissolved oxygen (DO) concentrations of 0.1 mg/L and 1 × 10^{-8} mg/L, respectively (Nguyen et al., 2019). However, measuring DO at values less than 0.1 mg/L on-site using practical DO sensors is challenging. This is one reason why ORP is preferable to DO under anaerobic conditions, even though ORP measurements might be somewhat unstable. In the present experiments, the ORP was able to capture the difference that could not be distinguished by low DO concentrations between a situation where the denitrification reaction was in progress, that is, near aerobic conditions, and a situation where methane was produced. This confirms that methane production occurred at ORP levels below −350 mV, particularly around −500 mV. Keeping ORP higher than −350 to −450 mV prevents organic matter from being released as CH_4 from septic systems. Shortening the desludging interval can help to prevent lowering ORP.

If suspended organic materials settle in septic systems, they are retained until sludge is withdrawn, although self-degradation proceeds

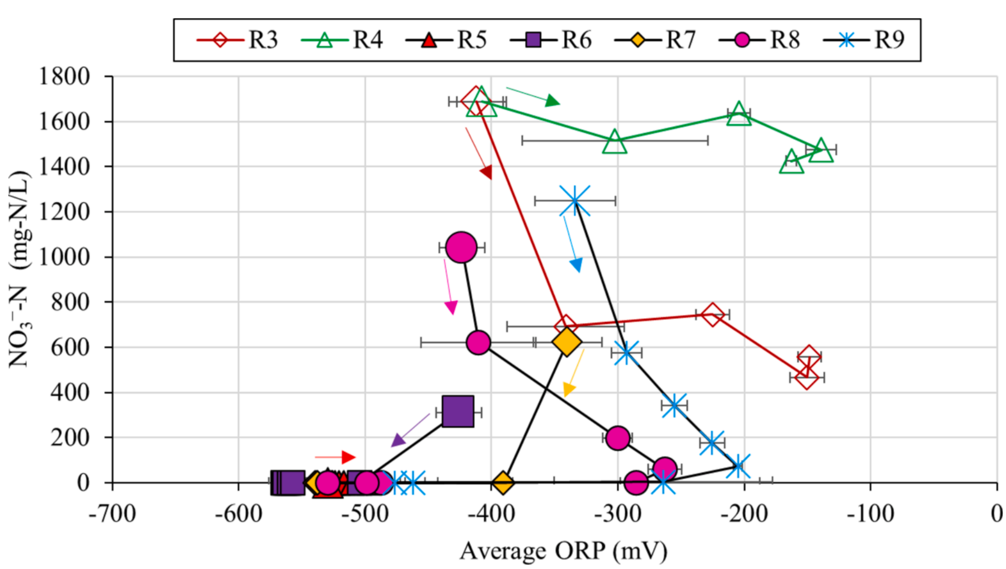

Fig. 5. Relationship between the average ORP and NO_3^--N concentration. Each marker represents the average ORP value, with the standard deviation (SD) corresponding to each measurement interval. The value at the beginning is depicted as a large marker with an arrow, and the markers that follow are connected with lines for each procedure.

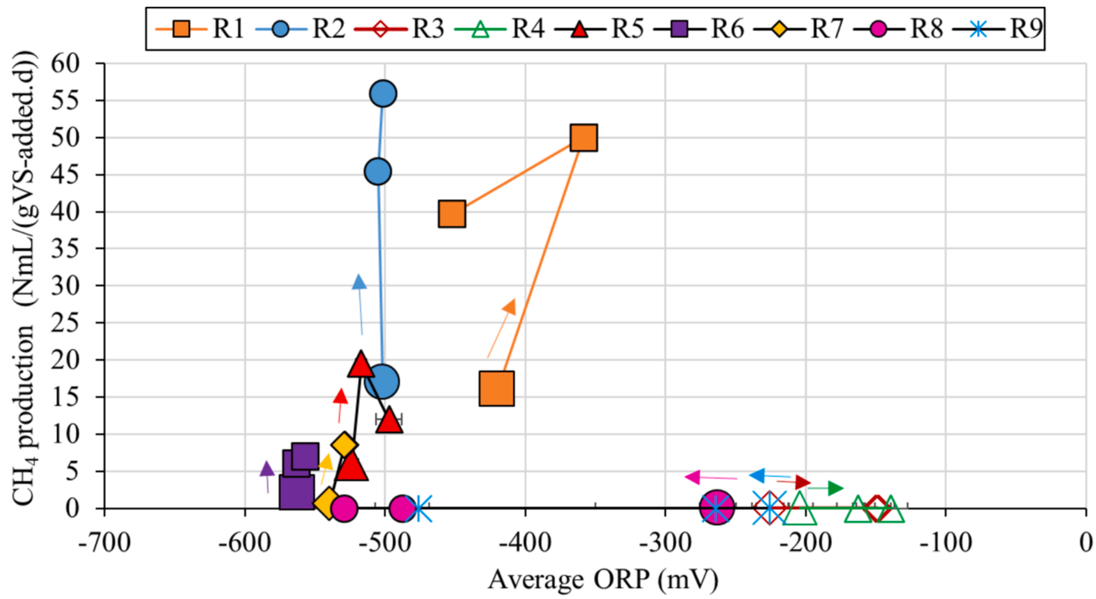

Fig. 6. Relationship between the average ORP and methane production in Experiments 1, 2, 3, and 4. Each marker represents the average ORP value with the standard deviation (SD) corresponding to each measurement interval.

slightly. In the case of ordinary anaerobic digestion of sewage sludge at wastewater treatment plants, methane gas generation is nearly complete after a HRT of approximately 30 days (Inc. Metcalf & Eddy et al., 2014), and further methane gas generation is unlikely even if the HRT is extended. The batch anaerobic digestion of dewatered sewage sludge showed that biodegradation is limited even if the storage period is extended to a few months because not all components are biodegradable (Hidaka et al., 2019). The maximum generating potential of methane gas is unlikely to differ significantly from septic systems if the sludge is removed after a few months or if the sludge is stored for 1–6 years or more. However, when the amount of settled sludge in septic systems increases, resuspension becomes more likely, and suspended solids are discharged, resulting in the decreased effluent quality. Water quality control in septic systems necessitates preventing sedimented sludge overflow.

By transferring the septage to an anaerobic digestion facility, methane, a GHG that would otherwise be discharged into the environment can be collected and used as an energy source from decentralized wastewater treatment systems (Ansari et al., 2024; Guo et al., 2023; Sun et al., 2017). Although septage has a lower methane yield than biodegradable substrates such as kitchen garbage, it can help balance the nutritional burden when co-digested with other biomass (Lu et al., 2019). Frequent desludging is expected to reduce overall GHG emissions. When ORP is reduced, and methane production begins, it is difficult to stop, and ORP can be used as a monitoring signal for desludging.

Conclusions

Laboratory-scale biodegradation experiments with DF and potassium nitrate, representing blackwater and an alternative electron acceptor to oxygen, showed that methane emission is suppressed at a critical ORP level (−350 to −450 mV vs. Ag/AgCl). These results demonstrate that ORP can be used as a monitoring signal to better understand methane-producing conditions. This helps to prevent methane gas emissions from septic systems as much as possible, for example, by shortening the desludging period and providing sufficient oxygen in a septic tank, taking into account the critical ORP required to control anaerobic conditions.

CRediT authorship contribution statement

Areke Alexander Tiareti: Writing – original draft, Methodology, Investigation. **Megumi Matsumura:** Methodology, Investigation, Writing – original draft. **Taira Hidaka:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Fumitake Nishimura:** Validation, Supervision. **Youhei Nomura:** Writing – review & editing, Validation. **Taku Fujiwara:** Writing – review & editing, Supervision.

Acknowledgement

This research was supported by the Osaka Bay Regional Offshore Environmental Improvement Center (Grant No. 030005) and by the Japan Society for the Promotion of Science (KAKENHI, Grant No. 20H04386).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Ács, N., Bagi, Z., Rákhely, G., Minárovics, J., Nagy, K., Kovács, K.L., 2015. Bioaugmentation of biogas production by a hydrogen-producing bacterium. Bioresour. Technol. 186, 286–293.

Akizuki, S., Wong, T.K., Aoki, Y., Rodríguez, G.-C., Niwa, C., Toda, T., 2015. Effects of substrate COD/NO_2^--N ratio on simultaneous methanogenesis and short-cut denitrification in the treatment of blue mussel using acclimated sludge. Biochem. Eng. J. 99, 16–23.

Akunna, J.C., Bizeau, C., Moletta, R., 1992. Denitrification in anaerobic digesters: possibilities and influence of wastewater COD/N-NO_X ratio. Environ. Technol. 13, 825–836.

Ansari, A., Dutt, D., Kumar, V., 2024. Catalyzing paradigm shifts in global waste Management: a case study of Saharanpur Smart city. Waste Manage. Bull. 2, 29–38.

APHA-AWWA-WEF, 2012. Standard methods for the examination of water and wastewater, 22nd ed., American Public Health Association/American Water Works Association/Water Environment Federation, New York, USA.

Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A., 2002. The IWA Anaerobic Digestion Model No 1 (ADM1). Water Sci. Technol. 45, 65–73.

Beavers, P.D., Gardner, E.A., 1993. Prediction of virus transport through soils. In: 15th AWWA Federal Convention'. Gold Coast, Qld, pp. 530–535.

Boiocchi, R., Mainardis, M., Rada, E.C., Ragazzi, M., Salvati, S.C., 2023. Carbon footprint and energy recovery potential of primary wastewater treatment in decentralized areas: a critical review on Septic and Imhoff Tanks. Energies 16, 7938.
Chen, K.-C., Lin, Y.-F., 1993. The relationship between denitrifying bacteria and methanogenic bacteria in a mixed culture system of acclimated sludges. Water Res. 27, 1749–1759.
Chen, K.-C., Lin, Y.-F., Houng, J.-Y., 1997. Performance of a continuous stirred tank reactor with immobilized denitrifiers and methanogens. Water Environ. Res. 69, 233–239.
Chetawan, W., Saritpongteeraka, K., Chaiprapat, S., et al., 2020. Influence of temperature and oxidation-reduction potential on hydrolysis of swine manure wastewater. Int. J. Environ. Sc. Develop. 11, 143–147.
Diaz-Valbuena, L.R., Leverenz, H.L., Cappa, C.D., Tchobanoglous, G., Horwath, W.R., Darby, J.L., 2011. Methane, carbon dioxide, and nitrous oxide emissions from septic tank systems. Environ. Sci. Technol. 45, 2741–2747.
Doorn, M., Liles, D., Thorneloe, S., 2000. Quantification of methane emissions from latrines, septic tanks, and stagnant, open sewers in the world. In: van Ham, J., Baede, A.P.M., Meyer, L.A., Ybema, R. (Eds.), Non-CO_2 Greenhouse Gases: Scientific Understanding, Control and Implementation: Proceedings of the Second International Symposium, Noordwijkerhout, The Netherlands, 8–10 September 1999, Springer Netherlands, Dordrecht, 2000, pp. 83–88.
Goo, S., Miyahara, T., Noike, T., 2001. Behavior of nitrate in anaerobic digestion. Doboku Gakkai Ronbunshu (in Japanese) 61–68.
Guo, G., Zhou, S., Chen, Y., Wang, W., Qin, Y., Li, Y.-Y., 2023. Evaluation of bioenergy production and material flow in treating Japanese concentrated Johkasou sludge using high-solid anaerobic membrane bioreactor based on one-year operation. Chem. Eng. J. 469, 143918.
Harada, H., Dong, N.T., Matsui, S., 2008. A measure for provisional-and-urgent sanitary improvement in developing countries: septic-tank performance improvement. Water Sci. Technol. 58, 1305–1311.
Hidaka, T., Nishimura, F., Tsuno, H., 2002. Importance of ORP Control in Influent to Nitrification Tank. Adv. Asian Environ. Eng. 2, 19–24.
Hidaka, T., Tsuno, H., Kishimoto, N., 2003. Advanced treatment of sewage by pre-coagulation and biological filtration process. Water Res. 37. https://doi.org/10.1016/S0043-1354(03)00353-1.
Hidaka, T., Sawahara, H., Togari, T., Tsumori, J., 2015. Anaerobic digestion of sewage sludge with high solid content and its use as fertilizer. J. Water Environ. Technol. 13, 349–358. https://doi.org/10.2965/jwet.2015.349.
Hidaka, T., Sano, S., Nishimura, F., Fujiwara, M., 2016. Applicability of dewatered sewage sludge from oxidation ditch processes to anaerobic digestion with simple operation. J. Japan Soc. Civil Engineers, Ser. G (Environmental Research) 72, III_135–III_144.
Hidaka, T., Nakamura, M., Oritate, F., Nishimura, F., 2019. Utilization of high solid waste activated sludge from small facilities by anaerobic digestion and application as fertilizer. Water Sci. Technol. 80, 2320–2327.
Huynh, L.T., Harada, H., Fujii, S., Nguyen, L.P.H., Hoang, T.-H.-T., Huynh, H.T., 2021. Greenhouse gas emissions from blackwater septic systems. Environ. Sci. Technol. 55, 1209–1217.
Inc. Metcalf & Eddy, Abu-Orf, M., Bowden, G., Burton, F.L., Pfrang, W., Stensel, H.D., Tchobanoglous, G., Tsuchihashi, R., Aecom, 2014. Wastewater engineering: treatment and resource recovery. McGraw Hill Education.
Liu, C.-G., Xue, C., Lin, Y.-H., Bai, F.-W., 2013. Redox potential control and applications in microaerobic and anaerobic fermentations. Biotechnol. Adv. 31, 257–265.
Lu, D., Liu, X., Apul, O.G., Zhang, L., Ryan, D.K., Zhang, X., 2019. Optimization of biomethane production from anaerobic Co-digestion of microalgae and septic tank sludge. Biomass Bioenergy 127, 105266.
Ministry of Infrastructure and Sustainable Energy, 2015. Kiribati, The Kiribati National Building Code, Betio.
Moonkawin, J., Huynh, L.T., Schneider, M.Y., Fujii, S., Echigo, S., Nguyen, L.P.H., Hoang, T.-H.-T., Huynh, H.T., Harada, H., 2023. Challenges to accurate estimation of methane emission from septic tanks with long emptying intervals. Environ. Sci. Technol. 57, 16575–16584.
Nghiem, L.D., Manassa, P., Dawson, M., Fitzgerald, S.K., 2014. Oxidation reduction potential as a parameter to regulate micro-oxygen injection into anaerobic digester for reducing hydrogen sulphide concentration in biogas. Bioresour. Technol. 173, 443–447.
Nguyen, D., Wu, Z., Shrestha, S., Lee, P.-H., Raskin, L., Khanal, S.K., 2019. Intermittent micro-aeration: New strategy to control volatile fatty acid accumulation in high organic loading anaerobic digestion. Water Res. 166, 115080.
Rittmann, B.E., McCarty, P.L., 2020. Environmental Biotechnology: Principles and Applications, second ed. McGraw-Hill Education.
Roy, R., Conrad, R., 1999. Effect of methanogenic precursors (acetate, hydrogen, propionate) on the suppression of methane production by nitrate in anoxic rice field soil. FEMS Microbiol. Ecol. 28, 49–61.
Sarac, K., Kohlenberg, T., Davison, L., Bruce, J.J., White, S., 2001. Septic system performance: a study at Dunoon, northern NSW'. In: On-Site, cfsites1.uts.edu.au. http://cfsites1.uts.edu.au/find/isf/publications/saracetal2001septicsystemdunoon.pdf.
Sotelo, T.J., Satoh, H., Mino, T., 2019. Assessing wastewater management in the developing countries of Southeast Asia: underlining flexibility in appropriateness. J. Water Environ. Technol. 17, 287–301.
Speece, R.E., 1996. Anaerobic Biotechnology for Industrial Wastewaters. Archae Press.
Sun, Z.-Y., Liu, K., Tan, L., Tang, Y.-Q., Kida, K., 2017. Development of an efficient anaerobic co-digestion process for garbage, excreta, and septic tank sludge to create a resource recycling-oriented society. Waste Manag. 61, 188–194.
Tai, C.S., Singh, K.S., Grant, S.R., 2006. Combined removal of carbon and nitrogen in an integrated UASB-jet loop reactor bioreactor system. J. Environ. Eng. 132, 624–637.
Tamaki, S., Hidaka, T., Mizuno, T., Kusuda, Y., Nishimura, F., 2019. Anaerobic digestion of oxidation ditch sludge at low temperatures with hyperthermophilic pretreatment. J. Water Environ. Technol. 17, 67–75.
Tamaki, S., Hidaka, T., Nishimura, F., 2021. Effects of using lactic acid bacteria in the storage and subsequent anaerobic co-digestion of crushed kitchen garbage. Bioresour. Technol. Rep. 13, 100640.
World Health Organization, 2019. Progress on household drinking water, sanitation and hygiene 2000-2017: special focus on inequalities. World Health Organization.
Yu, N., Guo, B., Zhang, Y., Zhang, L., Zhou, Y., Liu, Y., 2020. Different micro-aeration rates facilitate production of different end-products from source-diverted blackwater. Water Res. 177, 115783.