Solid thickening and methane production of livestock wastewater using dissolved carbon dioxide flotation
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ABSTRACT

Dilute manure is classified as wastewater due to the large quantity of water used in livestock production in Korea. Livestock wastewater treatment is required in order to reduce high moisture content and treat fluids discharged from the digestion process. In livestock wastewater treatment plants, large quantities of CO2 gas are produced at combined heat and power facilities as well as in the anaerobic digestion (AD) process. This gas produced during livestock wastewater treatment can be used as a separator of solids from liquid in wastewater. In this study, a flotation system using recycled CO2 gas was used for sludge thickening. An anaerobic toxicity assay (ATA) and a biochemical methane potential assay were used to assess the toxicity impact of recycling CO2 on the methane production potential. ATA experiments confirmed that CO2 toxicity did not impair the AD process. The tests indicated that the cumulative methane yield from influent livestock manure enriched with CO2 was approximately 190 mL-CH4/g-VSadded. The data demonstrated the potential of using dissolved CO2 flotation in the AD of diluted livestock wastewater.

Key words | anaerobic digestion, carbon dioxide, flotation, livestock, manure, methane

INTRODUCTION

Fermentation, or anaerobic digestion (AD), of livestock manure produces biogas containing methane (CH4), carbon dioxide (CO2), and nitrous oxide (N2O) (Knapp et al. 2014). In Korea, livestock manure is considered wastewater rather than a solid waste because of its high water content. According to Oh et al. (2007), piggery wastewater has a water content reaching 98.8 to 99.7%. This high water content is disadvantageous because the low methane gas production rate leads to poor process economics. Therefore, integrating thickening is an important step toward developing an economical process to treat and dilute piggery effluents.

Conventional solid-liquid separation processes utilized in wastewater treatment include filtration, gravity sedimentation, centrifugation, and flotation. Sedimentation is used for both primary and secondary sludge; however, this process is ineffective at concentrating secondary sludge with densities in the range of 1.01 to 1.09 g/cm3 (Vanderhasselt & Verstraete 1999). Several studies have been carried out to apply the dissolved air flotation (DAF) process as a solid thickener (Bratby & Ambrose 1995) in the pre-treatment of wastewater (Manjunath et al. 2000). Float sludge produced by flotation contains approximately 3 percent (w/w) solid concentration. Higher solid levels and fine dewaterability can be achieved using flotation over sedimentation, depending on the sludge characteristics and use of a coagulant. However, residual oxygen in bubbles can be fatal to anaerobic bacteria, which are important in the methane production process. Thus, flotation using CO2 as an alternative to air could be effective in overcoming microbial oxygen toxicity. Another advantage of utilizing CO2 is a reduction in the operational power consumption during the flotation process. Compared with an air flotation system, which requires 4–6 atm, a dissolved carbon dioxide flotation (DCF) system with pressurized CO2 only requires 1.5–2.0 atm. According to Kwak & Kim (2013), treatment efficiency achieved by
CO₂ is approximately the same as that by air. Potential sources of CO₂ for a DAF system can arise from the AD biogas or from biogas combustion utilizing a combined heat and power (CHP) process.

Advantages of using flotation in the treatment of livestock wastewater include reducing an adverse effect on the methane-forming bacteria and separating suspended solids (SS) in water. It is beneficial to improve methane production efficiency in the AD process without harming microbial colonies or causing other adverse biological effects. With this in mind, Burke (1997) developed an anaerobic gas flotation process that recycles methanogens and residual organic matters using CO₂ bubbles in the AD process in order to improve the effluent water quality and enhance the efficiency of methane production. Cizinska et al. (1992) attempted thickening of residual floating matters using the by-product of nitrate-nitrogen without injecting chemicals such as polymer. According to a US patent (Mercier et al. 2007), after coarse particles are removed and a cationic polymer is added, manure emits enough gas (mainly CO₂) to float the solids at the surface, thus providing an economical separation process.

This study aims to verify applicability of DCF using CO₂ gas recycled from the AD process of the CHP system for solid thickening required in livestock wastewater treatment. Experiments of AD examined the feasibility of CO₂ gas in flotation in thickening real piggery wastewater and estimated the efficiency of methane formation in the thickened sludge.

**MATERIALS AND METHODS**

**Experimental device and operating conditions**

In this study, an experimental device of DCF was designed for conducting a series of laboratory experiments examining AD for methane production and sludge thickening using CO₂. In order to examine flotation characteristics and treatment efficiency of DCF, comparative experiments between typical DAF and the three thickening processes of flotation (DCF and DAF) and sedimentation (CGS) (conventional gravity sedimentation) were also conducted. A device with a slow mixing speed was installed in the experimental devices of DAF and DCF to inject coagulants and combine the resulting microbubbles and flocs while slowly mixing. The DCF saturator was operated at 1.0–3.0 atm, whereas the DAF saturator was pressurized at 5.0 atm. A pressure gauge was set up at the top of the saturator to ensure correct pressurization, and experiments were also performed with both CO₂ and air bombs.

Figure 1 presents a schematic diagram of the experimental devices for DCF, DAF, and biochemical methane potential (BMP) assay, which included a batchwise livestock manure (treated as livestock wastewater) thickener and a single-phase digester to produce methane. The reactor for methane production was a single-phase anaerobic digester, and tests were conducted in a batch like those on the DCF device.

To examine gas production amounts and response characteristics, the experiment used a typical mesophilic methane production process using livestock wastewater as a substrate. An additional stirring apparatus was omitted, and artificial operation such as pH was applied to comply with the occasional demands of the experimental conditions. To compare methane production under different conditions, 0.5-L serum bottles were set up and installed in an incubator with a constant temperature. Tests were conducted while monitoring for major items, such as pH and gas generation rate, in each serum bottle. The operator measured the generating capacity and methane content after collecting gases every 3 days for a period of time. The gases generated in the serum bottle were collected in a Teflon bag through a discharge pipe installed in the middle of a gas-tight rubber stopper in the serum bottle. Table 1 presents the operating conditions of the experimental equipment for sludge thickening and AD.

**Figure 1** | Schematic diagram of the batchwise manure thickener and single-phase digester.
Sample and analysis methods

This study used piggery wastewater, which was collected from the lower part of retaining facilities for pigsties, as a substrate for the formation of methane. Experiments were conducted to examine changes in the rate of methane production and toxicity by air or CO₂ according to experimental conditions. Measurements were taken from three sludge samples obtained after thickening the wastewater using DAF, DCF, and CGS. To minimize unstable effects by lack of nourishment from essential elements in the AD process, trace elements and water (moisture) controllers were constantly added to all samples. Chaff, an additional mixing substrate to control the moisture content of the wastewater, was smashed and sifted out with a 100-mesh sieve. Only the remaining particles of less than 100 mm in size were used. Tables 2 and 3 present the fundamental properties, including trace elements and inorganic nutrients added for stable operation, of the primary substrate of piggery manure wastewater.

In this study, the standard method of analyzing water quality and solids was used (APHA 2005). Experiments were performed on a prepared immiscible mixture of the wastewater samples from piggy retaining facilities and wastewater from washing the pigsties. This ready-mixed piggery wastewater possessed the typical features of livestock wastewater, including both a high pH (8.7) and alkalinity (5,800 mg/L as CaCO₃). The wastewater included 2,205 mg/L of BOD and 2,221 mg/L of COD₇₅, and the percentage of soluble COD₇₅ was 50.7%. The total solids (TS) concentration was 95% (the percentage of water content, 99.1%), with 35.9% volatile solids (VS) and 64.1% inorganic solids (IS). The ratio of organic matters to nutrient substances (COD:NH₃-N:PO₄³⁻-P) was 51.7: 30.3: 1.0.

Biochemical methane potential and anaerobic toxicity assay

Owen et al. (1979) developed a BMP assay and an anaerobic toxicity assay (ATA) to analyze the conversion concentration of organic matter to CH₄ gas in the anaerobic reaction condition and to evaluate potential efficiency and toxicity of the anaerobic process. The experimental procedure of this study began with putting the target sample into the serum bottle, blocking the opening with a butyl rubber septum with a low gas permeability rate, and sealing the bottle with a reinforced...
plastic top. Anaerobic degradation occurred in an incubator maintaining a constant temperature. After analysis of the gas volume and composition over a fixed period, CH$_4$ production yield was recorded. To determine the degree to which the experimental target sample for the ATA affected the gas amount and other factors, a control experiment was conducted under the same conditions without the addition of elements composed of mineral salts and trace metals. The gas production yield was measured using a glass syringe for a fixed period, and the gas concentration was analyzed with a mass spectrometer (GC-MS 6890N Network GC System, USA) for estimating the CH$_4$ production yield.

RESULTS AND DISCUSSION

Particle separation and thickening characteristics

While the process of sedimentation is simple, its construction requires a large, wide space. Flotation, however, can be set up with a smaller space. The latter does need power to supply bubbles, but DCF in particular consumes less electricity than DAF does. Because AD produces methane gas, a substance used in producing electric power, flotation may be more useful than sedimentation in wastewater treatment plants using AD. To verify the feasibility of DCF, we concentrated the sample collected from the pigsty and analyzed changes in chemical properties. These experiments compared flotation thickening and solid change characteristics between DAF and DCF.

Figure 2 presents the change in the interface of the sludge (thickened livestock wastewater) with thickening time. The dynamic range of the sludge interface by the gravitational sedimentation decreased over 90 minutes and almost disappeared after 2 hours. The ultimate thickening percentage by the sedimentation was 50.8%, while the interfaces formed with the layer that was quickly separated by DAF and DCF increased. The first rise of the interface rapidly progressed over 7–10 minutes with an increase in the bubble-floc agglomerates, which were initially formed by the rise of the milky water injected into the batch column. As shown in section B of Figure 2, the re-ascent of the interface was observed with slight thickening between 10 and 20 minutes after the fine bubbles combined with flocs remaining in the batch column.

The solid components of water treated by flotation thickening (DAF and DCF) and the raw wastewater were analyzed, and their changes were observed as shown in Table 4. For the raw wastewater with 16,260 mg/L of TSs,
the TS concentration of thickened sludge was detected at 44,030 mg/L for DAF, 40,120 mg/L for DCF, and 37,840 mg/L for CGS. DCF also had a slightly lower efficiency than that of DAF, and the difference in bubble diameter distribution was considered the cause of the separation efficiency of particles. The average diameter of bubbles in DCF trials was about 100 μm at 2 atm of pressure (Kwak & Kim 2013), a size relatively larger than the diameter of bubbles in DAF trials in the range of 20–100 μm (Han et al. 2002).

The next step was to investigate the chemical composition distribution of solid particles in the sludge. The TS concentration in the raw livestock wastewater was 26,260 mg/L, and it consisted of 45% dissolved solids (DSs) and 55% (SSs and/or 72% VS and 28% IS. The composition difference of sludge thickened among the three processes of DAF, DCF, and CGS was not great. The sludge thickened by sedimentation contained only 32% fixed suspended solids, about 5–7% higher than those in the flotation sludge.

**AD of thickened sludge**

For the mesophilic AD experiments, the generated gas amount was measured, and the methane content was analyzed for the digestion operation period of 30 days. The summarized results are shown in Table 5. As shown in Figure 3(a), the gas production yield from the CGS sludge rapidly increased before peaking at 24 days, but that from the DCF peaked after 24 days. The slowest yield was from the DAF sludge. The time to produce the cumulative gas production (200 mL) was 16 days for the CGS sludge, 18 days for the DCF sludge, and 23 days for the DAF sludge. Figure 3(b) indicates the change in gas generation over the 3-day interval, with the peak of gas production yield at 14 days for the CGS sludge, 18 days for the DCF sludge, and 21 days for the DAF sludge. The lag phase for the residual sludge including air and CO₂ showed the phenomena to be slightly long. The overall gas production yield per injected VS was the highest in the DCF sludge, followed by the CGS sludge and then the DAF sludge. The VS removal fractions of the DCF sludge and the CGS sludge were slightly higher than in the previous study at 0.61 (Riaño et al. 2011).

As shown in Figure 4, the methane content increased as time passed. After 30 days, the methane content of the DAF sludge, the DCF sludge, and the CGS sludge was 53.6%, 63.4%, and 68.6% on average, respectively. These values for the three processes are in the typical range found by previous studies (Hellwing et al. 2014; Hidalgo & Martín-Marroquín 2015). The results show that the DAF sludge had a high content of CO₂ and other gases for the whole period, and the final amount of methane production was similar in both the DCF sludge and the CGS sludge. Based on these results, we may presume that the adverse effect of

| Table 4 | Results of solid composition analysis on livestock wastewater taken from pigsty |
|---|---|---|
| Solid concentration (mg/L) | Raw wastewater | Floated sludge by DAF |
| Description | Total | Volatile | Fixed | Total | Volatile | Fixed |
| TS | 16,260 | 11,620 | 4,640 | 44,030 | 29,710 | 14,320 |
| SS | 8,900 | 6,140 | 2,760 | 34,910 | 22,740 | 12,170 |
| DS | 7,360 | 5,480 | 1,880 | 9,120 | 6,970 | 2,150 |
| Floated sludge by DCF | Precipitated sludge by CGS |
| Description | Total | Volatile | Fixed | Total | Volatile | Fixed |
| TS | 40,120 | 27,750 | 12,370 | 37,840 | 23,820 | 14,020 |
| SS | 29,450 | 19,520 | 9,930 | 28,550 | 16,660 | 11,950 |
| DS | 10,670 | 8,230 | 2,440 | 9,290 | 7,220 | 2,070 |

Thickening time of DAF and DCF is 40 minutes, while CGS is 2 hours.
the residual air in the sludge thickened by air bubbles on methane production is long-lasting.

**ATA assay of bubbles**

An ATA was performed on the air and CO₂ to understand the effects of the sludge thickened by flotation during AD. To determine whether the toxicity of air and CO₂ was present or not, the ATA used the sludge thickened by DAF and DCF as the substrate of methane production. The G/S (gas to solid) ratio was divided into three steps as 0.1, 0.01, and 0.001. According to previous research (Chung & Kim 1997), the G/S ratio should be maintained at more than 0.009 in order to concentrate the activated sludge and obtain reliable thickening efficiency. The G/S ratio is the same concept as the A/S (air to solid) ratio during the flotation process. To conduct the ATA, AD of the sludge occurred for 30 days to produce methane. The sludge was obtained from three types of solid thickenings, DAF, DCF, and CGS, under the ideal temperature and nutrient make up for methane production. As shown in Figure 5, the methane yield of the DCF sludge was greatly reduced as the G/S ratio increased, while the methane yield of the DAF sludge was slightly reduced as the G/S ratio increased. For the DAF sludge, the methane production yield was reduced down to 150.55 mL/g-VS_{added}, corresponding to 61.4% compared to the control sample. Thus, the ATA evaluated that CO₂ had no toxicity on the methane formation process, but air demonstrated toxicity at a G/S ratio of both 0.01 and 0.1 for the DAF sludge. For a similar previous case, stable operation could not be achieved using the DAF sludge as a substrate (Creamer et al. 2010).

**BMP assay**

A BMP assay was conducted under the same conditions as the ATA tests. The methane yield was compared using two sets of data collected from the experiment and modeled using the modified Gompertz model (MGM). The

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**Table 5** Measurement results of methane yield for three types of thickening processes

<table>
<thead>
<tr>
<th>Descriptions</th>
<th>DAF</th>
<th>DCF</th>
<th>CGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative volume of biogas yield</td>
<td>0.238</td>
<td>0.301</td>
<td>0.288</td>
</tr>
<tr>
<td>(L/g-VS_{added})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average daily biogas yield</td>
<td>0.039</td>
<td>0.055</td>
<td>0.061</td>
</tr>
<tr>
<td>(L/g-VS_{added} \cdot \text{day})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum daily biogas yield</td>
<td>0.079</td>
<td>0.100</td>
<td>0.096</td>
</tr>
<tr>
<td>(L/g-VS_{added} \cdot \text{day})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average methane fraction in biogas (%)</td>
<td>53.6</td>
<td>63.4</td>
<td>68.8</td>
</tr>
<tr>
<td>Maximum methane fraction in biogas (%)</td>
<td>67.0</td>
<td>76.0</td>
<td>79.0</td>
</tr>
<tr>
<td>VS (added) (g)</td>
<td>10.70</td>
<td>9.99</td>
<td>8.58</td>
</tr>
<tr>
<td>VS removal fraction (–)</td>
<td>0.555</td>
<td>0.683</td>
<td>0.623</td>
</tr>
<tr>
<td>Terminate duration of methane yield (days)</td>
<td>37–40</td>
<td>34–37</td>
<td>37–40</td>
</tr>
</tbody>
</table>
cumulative methane yield per injected VS in the mesophilic-dry AD experiment was measured in the range of 120.52 mL/g to 214.35 mL/g and generated from the DCF sludge, the CGS sludge, and the DAF sludge in order of the overall gas yield for 30 days. The BMP assay estimated that air adversely affected methane production, as found in the ATA test, as well. The difference in the cumulative methane yields between the DCF sludge and CGS sludge was not significant at 23.64 mL, while the difference between the DAF sludge and the other sludge was great at 70.19 to 93.83 mL. The greatest cumulative methane yield per injected VS was 220.03 mL/g in the DCF sludge, which is not high compared with previous studies (Kaparaju & Rintala 2008; Rico et al. 2012).

Figure 6 presents the result of the BMP assay based on the MGM and indicates three patterns of methane production, which were highly correlated with the determination coefficient, $R^2$, of 0.93 to 0.95. The MGM estimated the methane
production characteristics of sludge thickened by flotation as well as gravity sedimentation. The cumulative methane yield for the DCF sludge showed a pattern especially similar to that of the CGS sludge, but the DAF sludge presented a lower quantity of methane production than the others.

CONCLUSIONS

This study aimed to verify the applicability of flotation using CO₂ generated from the AD process of the CHP system for solid thickening required in livestock wastewater treatment, as well as to promote an enhancement in methane production efficiency.

1. The thickening efficiency of DCF was slightly lower than that of DAF, but the difference between DCF and DAF was not significant. The difference in thickening efficiency may be due to the distribution of bubble sizes. Additionally, the sludge composition did not show any differences between CGS.

2. The maximum gas yield was recorded at 14 days in the CGS sludge, 18 days in the DCF sludge, and 21 days in the DAF sludge as time passed.

3. For the DCF sludge, the methane gas production rate did not change noticeably, depending on the G/S ratio, but the methane production yield of the DAF sludge decreased dramatically. The residual CO₂ gas in the DCF sludge had no toxicity effects on the methane formation process, but air in the DAF sludge did show toxicity.

4. For the mesophilic-dry AD, the cumulative methane yield per injected VS was in the range of 120.5–214.4 mL/g. The amount of methane yield was the lowest in the DAF sludge. The cumulative methane yields of the DCF sludge and the CGS sludge were similar.

In conclusion, the experimental results demonstrated that improvements in the treatment of piggery wastewater containing high water content in sludge might be achieved using CO₂. Additionally, CO₂ remaining in the thickened sludge, unlike air, did not have any toxicity on AD. Therefore, the feasibility of a flotation system using CO₂ emitted from the AD process in livestock wastewater treatment plants was verified, solving the problem of high water content in livestock wastewater.

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