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# Study of livestock biogas upgrading using a pilot-scale photocatalytic desulphurizer followed by a hollow fibre carbon dioxide adsorption module

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## Abstract

The objective of this project is to integrate a domestic photocatalytic desulphurization facility with a biogas upgrading module and try to develop a system for biogas desulphurization and upgrading under ambient conditions. Four photocatalytic desulphurization reactors (PDRs) and one activated carbon reactor (ACR) were applied for biogas desulphurization and filtration under ambient conditions. Moreover, a hollow fibre carbon dioxide (CO<sub>2</sub>) adsorption module was applied for biogas upgrading. The operation pressure of the PDR and ACR was under ambient pressure. Results showed that hydrogen sulphide removal efficiency of the photocatalytic desulphurizer was about 0.99–1.00 (v/v) under the inlet biogas flow less than 5 litres/min and the concentration of inlet hydrogen sulphide was lower than 5600 mg/m<sup>3</sup>. For desulphurized biogas upgrading, the removal efficiency of CO<sub>2</sub> was higher than 0.90 (v/v) under the outlet biogas flow was 1 litre/min (i.e. inlet biogas flow was about 2 litres/min). However, the ratio of methane in the upgrading biogas was lower than 0.90 (v/v). Thus, nitrogen gas removal cartridges will be integrated with the biogas upgrading module to promote methane concentration in the upgraded biogas.

## Introduction

The novel photocatalytic wastewater treatment system was developed and applied for dairy cattle wastewater treatment with a simple titanium dioxide (TiO<sub>2</sub>) sol–gel preparation protocol by the research team of National Taiwan University (NTU) (Su *et al.*, 2018). The photocatalytic treatment technique (ultraviolet/titanium dioxide/silicon dioxide (UV/TiO<sub>2</sub>/SiO<sub>2</sub>)) had been applied to treat certain sulphur-containing compounds such as hydrogen sulphide (H<sub>2</sub>S), C<sub>2</sub>H<sub>6</sub>S (dimethyl sulphide, DMS) and C<sub>2</sub>H<sub>6</sub>S<sub>2</sub> (dimethyl disulphide, DMDS) (Canela *et al.*, 1998; Nishikawa and Takahara, 2001). Based on the study of Canela *et al.*, the catalyst, TiO<sub>2</sub>, was coated onto the internal glass surface of the photocatalytic reactor (TiO<sub>2</sub> film thickness = 5.3 µm) using an aqueous slurry, followed by drying with hot air. The photocatalytic reactor with a 30 W black light lamp (wavelength = 365 nm and the irradiation strength = 4.5 mW/cm<sup>2</sup>) was applied and the interior reactor was filled with 0.21 (v/v) oxygen (O<sub>2</sub>) under the humidity ≥0.23 (v/v) for H<sub>2</sub>S removal. Results showed that the H<sub>2</sub>S removal efficiency was higher than 0.99 (v/v) when the inlet H<sub>2</sub>S concentrations of 46.2–1197 mg/m<sup>3</sup> under sufficient O<sub>2</sub> conditions. However, there was about 0.95 (v/v) of sulphate adsorbed on the TiO<sub>2</sub> surface of the reactor and only about 0.0002 (v/v) of sulphate ion was detected in the reactor effluent when the reactor was working under higher H<sub>2</sub>S concentrations (e.g. 840 mg/m<sup>3</sup>) (Canela *et al.*, 1998).

The photocatalytic activity of three semiconductor catalysts (tungsten trioxide (WO<sub>3</sub>), TiO<sub>2</sub> and NiO (nickel oxide)) for the conversion of methane (CH<sub>4</sub>) into methanol at room temperature with an ultraviolet (UV) laser (355 nm) in the aqueous solution has been investigated. The maximum percentage conversions (v/v) of 0.29, 0.21 and 0.20 were observed for WO<sub>3</sub>, TiO<sub>2</sub> and NiO, respectively (Gondal *et al.*, 2004). Moreover, Fourier-transform infrared spectroscopy has been employed to investigate the adsorption and photo-oxidation of CH<sub>4</sub> over powdered TiO<sub>2</sub>. The interaction between the CH<sub>4</sub> and TiO<sub>2</sub> surface is weak. It is found that no CH<sub>4</sub> molecules are adsorbed on the surface at 35 °C in a vacuum. Under UV irradiation, CH<sub>4</sub> decomposes to form carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and formate (HCOO) in the presence of O<sub>2</sub> (Lien *et al.*, 2004). Thus, CH<sub>4</sub> is tough to be completely oxidized to methanol under ambient conditions with TiO<sub>2</sub>/UV light and the photocatalytic desulphurization reactor (PDR) of this study may be applied to the livestock farms.

Biogas produced from anaerobic digestion of animal manure wastewater from Taiwan's livestock farms is comprised of CH<sub>4</sub> (0.60–0.76, v/v), CO<sub>2</sub> (0.18–0.30, v/v), a trace amount of H<sub>2</sub>S and others (Su *et al.*, 2003, 2018). However, some nitrogen was introduced during the biogas desulphurization process (Su *et al.*, 2013, 2014; Su and Chen, 2015; Su and

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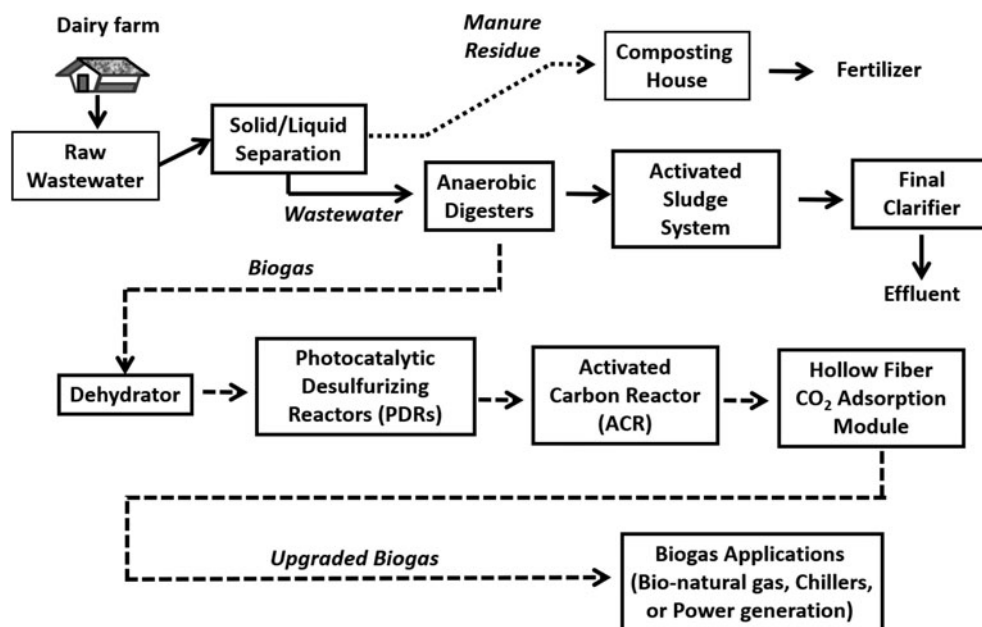


Fig. 1. Flowsheet of all processes for biogas production, desulphurization and upgrading.

Hong, 2020). To promote  $\text{CH}_4$  concentration in the desulphurized biogas, a hollow fibre  $\text{CO}_2$  adsorption system was introduced and applied on a livestock farm for biogas upgrading. Some commercial applications were carried out for desulphurized biogas upgrading including (Chen *et al.*, 2015): (1) *absorption*: water scrubbing, organic physical scrubbing, amine scrubbing and inorganic solvent scrubbing; (2) *adsorption*: pressure swing adsorption, vacuum swing adsorption, temperature swing adsorption, electrical swing adsorption; (3) *cryogenic separation*: it is a distillation process operated under very low temperatures (close to  $-170^\circ\text{C}$ ) and high pressure (around 80 bar). Therefore, for the production of very pure  $\text{CH}_4$  this technology can be used; (4) membrane technology (Ibrahim *et al.*, 2018) under various operation pressure (100 mbar–30 bar) and temperature conditions (17–35  $^\circ\text{C}$ ) (Vogler *et al.*, 2013; Falbo *et al.*, 2014; Žák *et al.*, 2018; Tantikhajorngosol *et al.*, 2019).

The objective was to study the feasibility of combining a novel photocatalytic desulphurization facility with a hollow fibre  $\text{CO}_2$  adsorption module for biogas upgrading under ambient conditions for promoting *in situ* livestock biogas applications such as power generation and so on. The acceptable  $\text{H}_2\text{S}$  in the biogas for livestock biogas applications was the lower, the better.

## Materials and methods

### Dairy farm biogas for this study

The conventional method of treating piggery wastewater in Taiwan is the three-step piggery wastewater treatment (TPWT) system, involving (1) solid/liquid separation, (2) anaerobic treatment and (3) aerobic treatment (activated sludge basin with a final clarifier) (Su *et al.*, 1997; Su and Chen, 2018). The TPWT system is also applied to all dairy farms for treating their wastewater. Thus, dairy biogas from the wastewater treatment facility of the NTU dairy farm was used for this study. Analytical data showed that the average COD, BOD and SS of the dairy wastewater after solid/liquid separation were  $4170 \pm 255$ ,  $1650 \pm 910$  and  $3890 \pm 529$  mg/l, respectively.

### PDR design

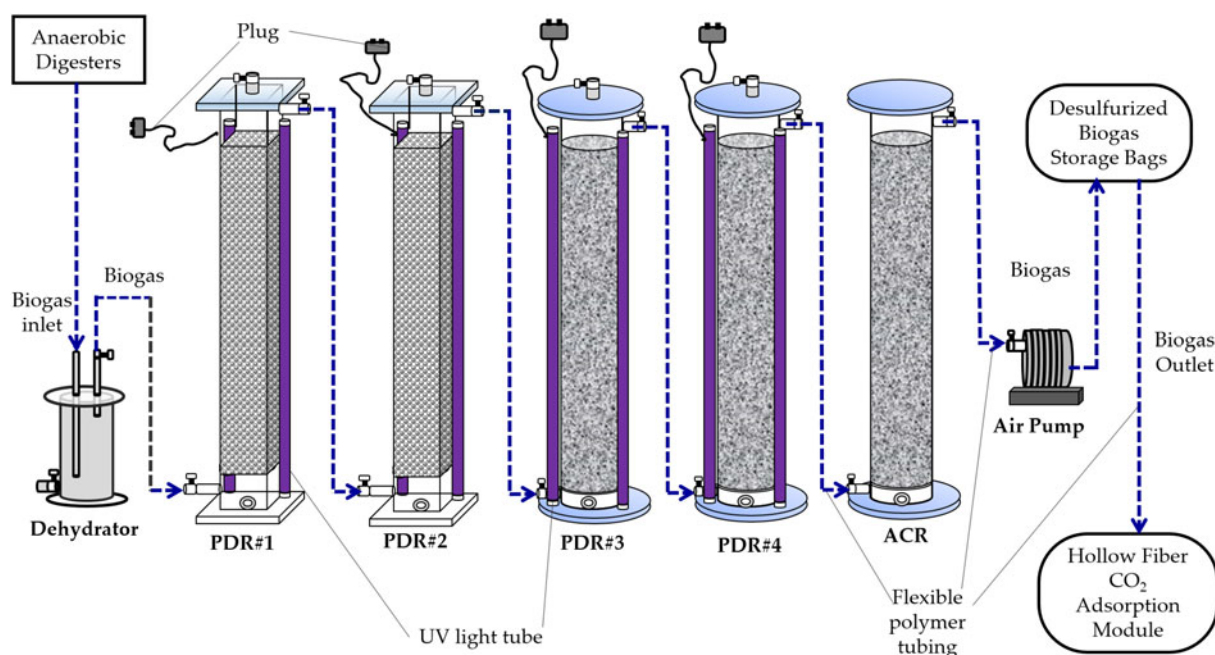
The flowsheet of all processes for biogas production, desulphurization and upgrading is shown in Fig. 1. The PDR was constituted of two acrylic cuboids (130 cm height  $\times$  20 cm width  $\times$  20 cm length, total volume = 52 litres) and two acrylic cylinders (130 cm height  $\times$  20 cm inner diameter, total volume = 41 litres) in series with two UV light tubes (120 cm length, 40 W UV fluorescent blacklight, PULSAR, China) attached to each acrylic cuboid or cylinder (Fig. 2). The aluminium foil sheet was used to cover the surface area of the two acrylic cuboids for reflecting UV light towards the inside of the acrylic cuboids. The two acrylic cuboids were packed with a mixture of Rasching rings (i.e. hollow spherical polypropylene balls) (Sheng-Fa Plastics, Inc., Taiwan) and  $\text{TiO}_2$ -coated light-expanded clay aggregates (LECA) (Su *et al.*, 2013) (Fig. 2). The surface of the LECA beads was coated with a mixture of  $\text{TiO}_2$  anatase powder and concrete. All PDRs used for any time course experiments of this study were packed with Rasching rings and  $\text{TiO}_2$ -coated LECA beads.

Untreated biogas entered into the acrylic dehydrator (40 cm height  $\times$  19 cm inner diameter, total volume = 11 litres) and then the biogas inlets of the PDRs in sequencing (Fig. 2). There was a 30 cm inlet tubing inside the dehydrator (Su and Hong, 2020). Biogas was mixed with a trace amount of air inside the dehydrator. The acrylic PDRs are directly connected to the biogas outlet tubing of the dehydrator (Fig. 2).

### Biogas upgrading system design

#### Activated carbon reactor (ACR) design

The ACR was constituted of an acrylic cylinder (130 cm height  $\times$  20 cm inner diameter, total volume = 41 litres). The ACR was packed with a mixture of coconut shell activated carbon pellets (diameter = 5 mm) and Rasching rings (i.e. hollow spherical polypropylene balls) (Sheng-Fa Plastics, Inc., Taoyuan, Taiwan). The ACR was applied to remove impurities and excessive moisture of the desulphurized biogas. It was followed by the four acrylic PDRs (Fig. 2). The operation pressure of the activated carbon filtration reactor was under ambient pressure.



**Fig. 2.** Sketch and flowchart of the photocatalytic desulphurizing reactor (PDR) in coordination with a biogas upgrading system consisting of an activated carbon reactor (ACR) and a hollow fibre carbon dioxide (CO<sub>2</sub>) adsorption module.

#### *Hollow fibre CO<sub>2</sub> adsorption cartridge set for biogas upgrading*

The hollow fibre CO<sub>2</sub> adsorption cartridge set was constituted of one filtration cartridge (47 cm length × 2" outer diameter) (AuraMat-TP-HC-A-B, Aura Material Inc., Hsinchu, Taiwan) and five independent hollow fibre CO<sub>2</sub> adsorption cartridges (47 cm length × 2" outer diameter) (AuraMat-TP-CO<sub>2</sub>-A2, Aura Material Inc., Hsinchu, Taiwan) in parallel. For each time course experiment under various biogas flow rate, only one independent cartridge was used individually for CO<sub>2</sub> adsorption from desulphurized biogas. The operation pressure of the CO<sub>2</sub> adsorption cartridge was under ambient pressure. The size of all biogas tubing including biogas inlet, biogas purging and biogas outlet tubing was 1/4" tubing. Biogas flow meters (Tohama 10B; Yeong Shin Co. Ltd, Hsinchu, Taiwan) were installed at the inlet and outlet of the CO<sub>2</sub> adsorption cartridge set. The pore size of the hollow fibre surface and adsorption interface was less than 1 μm and 0.5–0.8 nm, respectively.

#### *Hollow fibre CO<sub>2</sub> adsorption module for biogas upgrading*

The hollow fibre CO<sub>2</sub> adsorption module (AuraMat-HFDCO<sub>2</sub>-CH4-1L-VC, Aura Material Inc., Hsinchu, Taiwan) (60 cm width × 75 cm length × 115 cm height, power voltage = 220 V/60 Hz) was constituted of two sets, A and B, of hollow fibre CO<sub>2</sub> adsorption cartridges (40 cm length × 3" outer diameter) (AuraMat-HTP-CO<sub>2</sub>-A3, Aura Material Inc., Hsinchu, Taiwan) in parallel. The size of all biogas tubing including biogas inlet, biogas purging and biogas outlet tubing was 1/2" tubing. Each set of adsorption cartridge was constituted of five hollow fibre CO<sub>2</sub> adsorption cartridges in series. Two gas sampling ports were installed at the biogas inlet and outlet tubing for periodical biogas sampling. Desulphurized biogas was introduced into the module through a filtration cartridge (AuraMat-TP-HC-A-B, Aura Material Inc., Hsinchu, Taiwan) and the CO<sub>2</sub> adsorption cartridge sets by an explosion-proof vacuum pump (maximum flow rate = 7.5 litres/min, No. N 87 TTE EX, DRF Corporation, Taipei, Taiwan) inside the module. Another filtration cartridge

(AuraMat-TP-MX1-A-C, Aura Material Inc., Hsinchu, Taiwan) for filtering air was also integrated inside the CO<sub>2</sub> adsorption module. The operation pressure of the CO<sub>2</sub> adsorption cartridge was under ambient pressure.

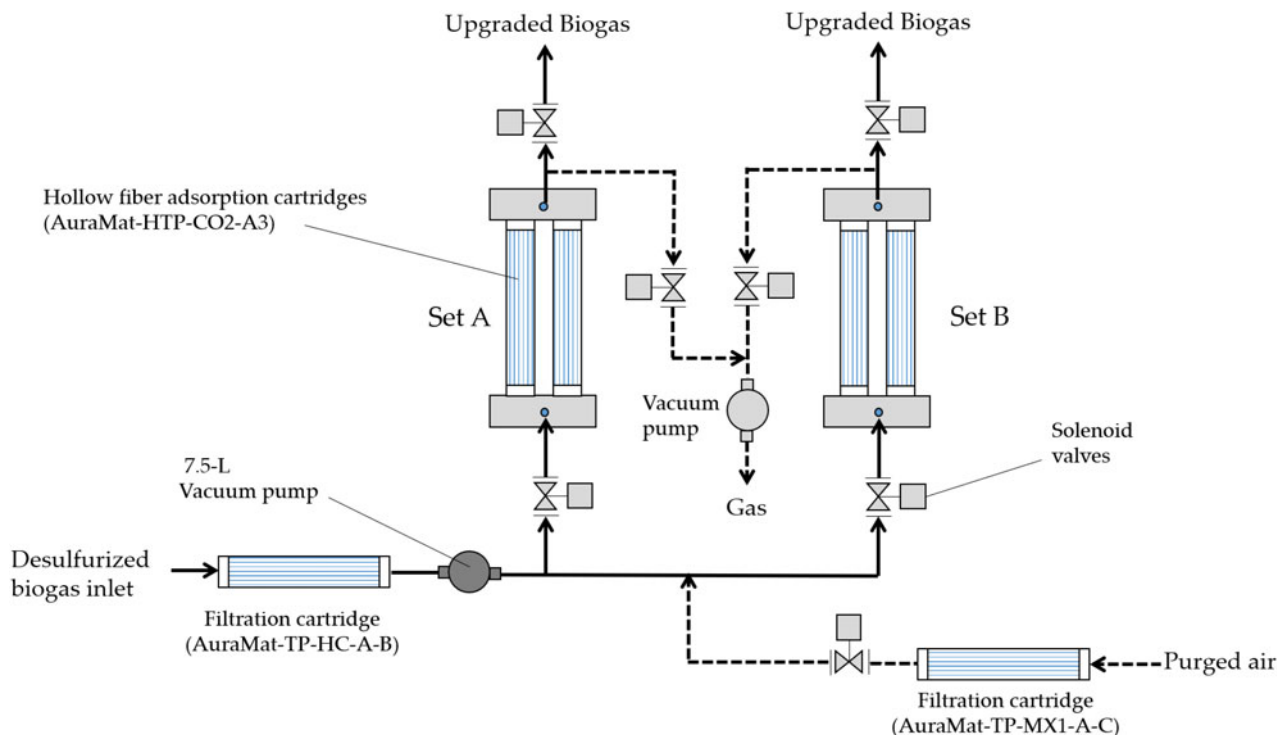
The operation process of the hollow fibre CO<sub>2</sub> adsorption module was as follows in sequence: desulphurized biogas from the storage bags, filtration cartridge (AuraMat-TP-HC-A-B), 7.5 litre vacuum pump, solenoid valves, hollow fibre adsorption cartridges (AuraMat-HTP-CO<sub>2</sub>-A3), solenoid valves and then discharging biogas (Fig. 3). Moreover, the regeneration process of the hollow fibre CO<sub>2</sub> adsorption module was as follows in sequence: purged air, filtration cartridge (AuraMat-TP-MX1-A-C), solenoid valves, hollow fibre adsorption cartridges (AuraMat-HTP-CO<sub>2</sub>-A3), solenoid valves, vacuum pump and then discharging gas (Fig. 3).

When hollow fibre CO<sub>2</sub> adsorption cartridges of Set A was saturated, the inlet biogas was automatically shifted to the set B following the operation process for biogas upgrading (i.e. CO<sub>2</sub> adsorption process). Simultaneously, the hollow fibre CO<sub>2</sub> adsorption cartridges of Set A following the regeneration process was automatically regenerated. Similarly, when hollow fibre CO<sub>2</sub> adsorption cartridges of Set B was saturated, the inlet biogas was automatically shifted to Set A for biogas upgrading. Thus, Sets A and B were operated alternatively.

#### *Time-course experiments of photocatalytic biogas desulphurization and hollow fibre CO<sub>2</sub> adsorption for biogas upgrading*

##### *Photocatalytic biogas desulphurization*

The four connected acrylic PDRs under various biogas flow rates carried out photocatalytic desulphurization (0.5, 1, 1.5, 3, 4 and 5 litres/min). The un-desulphurized biogas flew through the inlets and outlets of the PDR#1, #2, #3 and #4, sequentially. Gas samples were taken in triplicates from the inlet of the PDR#1 and the outlet of PDR#4 to perform gas chromatography (GC) analysis and to determine H<sub>2</sub>S, O<sub>2</sub>, NH<sub>3</sub> and SO<sub>2</sub> on-site using a



**Fig. 3.** Flow chart of the hollow fibre carbon dioxide ( $\text{CO}_2$ ) adsorption module including operation process (in solid lines) and regeneration process (in dashed lines).

portable gas detector and detector tubes with a gas-sampling pump. The initial inlet  $\text{H}_2\text{S}$  in biogas was  $4760 \pm 594$ – $5554 \pm 82$  and  $4558 \pm 672$ – $5554 \pm 80$   $\text{mg}/\text{m}^3$  under the flow rate of 0.5–5 litres/min in Tables 1 and 2, respectively. The acrylic PDRs were flushed with water (41 litres/each reactor) from the top of the PDRs and then soaked for a 2 h duration when some sulphur appeared on the surface of  $\text{TiO}_2$ -coated LECA beads after completion of the time course experiments under various biogas flow rates. This process was repeated until most sulphur was washed out from the surface of LECA beads.

#### *Biogas upgrading using independent hollow fibre $\text{CO}_2$ adsorption cartridge set*

Desulphurized biogas was introduced into the biogas filtration cartridge (AuraMat-TP-HC-A-B, Aura Material Inc., Hsinchu, Taiwan) and then the independent hollow fibre  $\text{CO}_2$  adsorption cartridges#1–#5 (AuraMat-TP-CO2-A2, Aura Material Inc., Hsinchu, Taiwan) through a 1/4 HP air pump for time-course experiments of  $\text{CO}_2$  removal from the desulphurized biogas. Biogas samples were taken periodically only from the inlet and outlet of the biogas filtration cartridge as the control set. Moreover, all other biogas samples were taken periodically from the inlet of the biogas filtration cartridge and outlet of the independent hollow fibre  $\text{CO}_2$  adsorption cartridges under various biogas flow rates as the experimental sets. Biogas samples were taken from the sampling ports with 1/8" silicone tubing of the independent hollow fibre  $\text{CO}_2$  adsorption cartridge set using a manual gas sampler (Vac-U-Tube, SKC Inc., PA, USA) connecting with 1 litre gas sampling bags (SKC Cat. No. 232-01, SKC Inc., PA, USA). The operation process of the time course experiments was described as follows: biogas samples were taken at 10 min intervals in an hour using the adsorption  $\text{CO}_2$  cartridge#1 from

the inlet of the filtration cartridge and the outlet of the adsorption cartridge#1 under the outlet biogas flow rate of 1 l/min (i.e. inlet biogas flow rate about 2 litres/min). The rest of the time-course experiments were carried out using the independent adsorption cartridge#2–#5 under the outlet biogas flow rates of 1.5, 2, 2.5 and 3 litres/min, respectively, at 10 min intervals in an hour. The contents,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ , of all biogas samples were determined by using GC with a thermal conductivity detector (GC/TCD).

#### *Biogas upgrading using hollow fibre $\text{CO}_2$ adsorption module with automatic regeneration*

The hollow fibre  $\text{CO}_2$  adsorption module had to be warmed up at least 2.5 h and then another 2.5 h for filling up biogas inside the cartridges of the  $\text{CO}_2$  adsorption module before starting any time-course experiments. Desulphurized biogas was introduced into the biogas filtration cartridge (AuraMat-TP-HC-A-B, Aura Material Inc., Hsinchu, Taiwan) and then through three independent hollow fibre  $\text{CO}_2$  adsorption cartridges (AuraMat-HTP-CO2-A3, Aura Material Inc., Hsinchu, Taiwan) of the Set A or B through an explosion-proof vacuum pump (maximum flow rate = 7.5 litres/min, No. N 87 TTE EX, DRF Corporation, Taipei, Taiwan) inside the adsorption module for time-course experiments of  $\text{CO}_2$  removal from the desulphurized biogas. Biogas samples were taken at 10 min intervals in an hour from the inlet and the outlet of the  $\text{CO}_2$  adsorption cartridge module under the outlet biogas flow rates of 1–5 litres/min (i.e. inlet biogas flow rate about 2–10 litres/min). The hollow fibre  $\text{CO}_2$  adsorption cartridges of Sets A and B were operated alternatively and regenerated automatically based on the signals on the control panel. Biogas samples were taken at 10 min intervals in an hour from the inlet and outlet of the adsorption cartridge module under various outlet biogas flow rates. The contents,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ , of all biogas samples were determined by using GC/TCD.

**Table 1.** Data of biogas desulphurization by the photocatalytic desulphurizing reactor (PDR) ( $n = 30$ )

Biogas flow rate (l/min)	Inlet H <sub>2</sub> S (mg/m <sup>3</sup> )	Outlet H <sub>2</sub> S (mg/m <sup>3</sup> )	Removal	CO <sub>2</sub> (v/v)	CH <sub>4</sub> (v/v)	N <sub>2</sub> (v/v)
0.5	4558 ± 672	5 ± 8.5	>0.99	0.30 ± 0.023	0.62 ± 0.028	0.09 ± 0.019
1	5226 ± 647	21 ± 36.0	>0.99	0.30 ± 0.064	0.62 ± 0.023	0.08 ± 0.023
1.5	5320 ± 396	0	1.00	0.32 ± 0.092	0.58 ± 0.016	0.11 ± 0.026
3	5554 ± 80	1 ± 1.7	>0.99	0.27 ± 0.019	0.61 ± 0.033	0.13 ± 0.036
4	5530 ± 140	5 ± 10.1	>0.99	0.27 ± 0.018	0.65 ± 0.017	0.08 ± 0.029
5	5530 ± 99	0	1.00	0.28 ± 0.014	0.66 ± 0.006	0.08 ± 0.085
<i>P</i>				NS	NS	NS

Data presented as mean ± s.d. H<sub>2</sub>S, hydrogen sulphide; CO<sub>2</sub>, carbon dioxide; CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; v/v, proportion of volume of component to volume of sample; Removal, (inlet data-outlet data)/inlet data; *n*, sample size; NS, not significant.

**Table 2.** Continuous data of biogas desulphurization by the regenerated desulphurizing reactor (PDR) ( $n = 45$ )

Biogas flow rate (l/min)	Inlet H <sub>2</sub> S (mg/m <sup>3</sup> )	Outlet H <sub>2</sub> S (mg/m <sup>3</sup> )	Removal	CO <sub>2</sub> (v/v)	CH <sub>4</sub> (v/v)	N <sub>2</sub> (v/v)
0.5	5530 ± 99	1.3 ± 0.00	>0.99	0.28 ± 0.014	0.65 ± 0.006	0.07 ± 0.009
1	5376 ± 234	0.5 ± 0.66	>0.99	0.26 ± 0.002	0.67 ± 0.001	0.07 ± 0.003
1.5	5348 ± 208	1 ± 1.0	>0.99	0.28 ± 0.001	0.65 ± 0.001	0.07 ± 0.001
2	5516 ± 77	0.6 ± 0.77	>0.99	0.27 ± 0.001	0.67 ± 0.001	0.07 ± 0.001
2.5	5460 ± 140	0.6 ± 0.60	>0.99	0.28 ± 0.002	0.64 ± 0.001	0.09 ± 0.003
3	5152 ± 230	3 ± 3.0	>0.99	0.27 ± 0.001	0.62 ± 0.002	0.11 ± 0.001
3.5	5516 ± 125	6 ± 1.9	>0.99	0.26 ± 0.004	0.64 ± 0.006	0.10 ± 0.002
4	5488 ± 117	2.4 ± 0.53	>0.99	0.28 ± 0.005	0.61 ± 0.008	0.12 ± 0.003
4.5	5516 ± 77	0.7 ± 0.97	>0.99	0.27 ± 0.003	0.59 ± 0.001	0.13 ± 0.001
5	5376 ± 212	1.2 ± 0.98	>0.99	0.27 ± 0.001	0.61 ± 0.006	0.12 ± 0.006
<i>P</i>				NS	<0.05	NS

Data presented as mean ± s.d. H<sub>2</sub>S, hydrogen sulphide; CO<sub>2</sub>, carbon dioxide; CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; *n*, sample size; NS, not significant; v/v, proportion of volume of component to volume of sample; Removal, (inlet data-outlet data)/inlet data.

## Analysis

### H<sub>2</sub>S determination in biogas samples

The gas samples were used to measure the concentrations of H<sub>2</sub>S from the inlets and outlets of the PDRs on-site using a portable multi-gas detector (ISC MX series, Industrial Scientific Co., PA, USA). When the concentrations of H<sub>2</sub>S were over the detection limit of the portable multi-gas detector (sensor: H<sub>2</sub>S: 0–697 mg/m<sup>3</sup>, SO<sub>2</sub>: 0–393 mg/m<sup>3</sup>, O<sub>2</sub>: 0–0.30 (v/v), NH<sub>3</sub>: 0–348 mg/m<sup>3</sup>), a gas sampling pump (GV-100C gas sampling pump; Gastec Co., Japan) with H<sub>2</sub>S detector tubes (H<sub>2</sub>S = 14–5575 mg/m<sup>3</sup>) (Gastec Co., Kanagawa, Japan) was applied for H<sub>2</sub>S detection.

### CH<sub>4</sub>, CO<sub>2</sub> and nitrous oxide determination in biogas samples

Biogas samples from the inlets and outlets were collected in 1 litre Tedlar® bags (SKC, PA, USA) with a single polypropylene fitting. This fitting contained a Teflon® syringe port lined septum and a hose connection, which functioned as a shut-off valve for incoming and outgoing gas. Meanwhile, a 500 ml gas collector (GL Sciences Inc., Tokyo, Japan) was used to withdraw gas samples from the inlets and outlets of the PDRs. Biogas samples were analysed for their composition by GC (Master GC, DANI Instruments, Marlborough, MA, USA), which was equipped with a TCD and Carboxen 1010 PLOT capillary column (30 m × 0.53 mm × 0.25 μm film thickness; Supelco Analytical of Sigma-Aldrich Co., PA,

USA) (Su and Chen, 2018). Calibration curves of CH<sub>4</sub>, CO<sub>2</sub> and nitrogen gas were obtained by the external standard method, and the calibration curves correlation coefficient was >0.9974.

### Statistical analysis

Time-course experiments were conducted in triplicate. One-way analysis of variance was performed using Origin 9.1 software to compare the results using Tukey's test with a significance level of 0.05. The linear regression analysis was applied between biogas flow rate and removal efficiency of H<sub>2</sub>S or CO<sub>2</sub> in each gas when the removal efficiency was significantly different.

## Results and discussion

### Biogas desulphurization using PDR

The inlet H<sub>2</sub>S in untreated biogas was 4558 ± 672–5554 ± 80 mg/m<sup>3</sup> and the outlet H<sub>2</sub>S in desulphurized biogas was 0–21 ± 36.0 mg/m<sup>3</sup>. Moreover, the H<sub>2</sub>S removal efficiency was about 0.99–1.00 (v/v) under various biogas flow rates (Table 1). Analytical results of biogas samples showed that the gas contents (v/v), CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>, of desulphurized biogas, was 0.58 ± 0.016–0.65 ± 0.017, 0.27 ± 0.019–0.32 ± 0.092 and 0.08 ± 0.085–0.13 ± 0.036, respectively (Table 1). CH<sub>4</sub> content in the desulphurized biogas was >0.69 (v/v) and the

**Table 3.** Carbon dioxide (CO<sub>2</sub>) removal of the desulphurized biogas by independent hollow fibre cartridges (*n* = 30)

Outlet biogas flow rate (l/min)	CH <sub>4</sub> (v/v)			N <sub>2</sub> (v/v)			CO <sub>2</sub> (v/v)		
	Inlet	Outlet	Difference	Inlet	Outlet	Difference	Inlet	Outlet	Removal
1	0.64	0.86 ± 0.011	0.33 ± 0.017	0.10	0.14 ± 0.009	0.35 ± 0.088	0.25	0.01 ± 0.004	0.97 ± 0.014
1.5	0.62	0.76 ± 0.298	0.23 ± 0.048	0.11	0.25 ± 0.172	0.10 ± 0.176	0.27	0.10 ± 0.042	0.63 ± 0.015
2	0.61	0.73 ± 0.046	0.19 ± 0.075	0.11	0.14 ± 0.015	0.25 ± 0.134	0.28	0.13 ± 0.054	0.52 ± 0.196
2.5	0.61	0.71 ± 0.053	0.16 ± 0.087	0.12	0.14 ± 0.011	0.18 ± 0.089	0.27	0.16 ± 0.051	0.43 ± 0.186
3	0.56	0.56 ± 0.006	0.004 ± 0.010	0.16	0.16 ± 0.004	0.003 ± 0.0228	0.28	0.28 ± 0.007	0.01 ± 0.026
<i>P</i>			<0.05			<0.05			<0.05
<i>R</i> <sup>2</sup>			0.475			0.800			0.743

Data presented as mean ± s.d. CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; *n*, sample size; NS, not significant; *R*<sup>2</sup>, coefficient of determination; v/v, proportion of volume of component to volume of sample; Removal or difference, (inlet data–outlet data)/inlet data.

N<sub>2</sub> content was <0.14 (v/v). The desulphurizer (PDR) with over air introduction can result in higher N<sub>2</sub> content but lower CH<sub>4</sub> content. Thus, the operation of the PDRs had to be controlled under low air conditions to assure a certain content of CH<sub>4</sub> in the desulphurized biogas.

Adsorption and photocatalytic decomposition of DMS and DMDS using an improved type of silica bead inner supported with TiO<sub>2</sub> (TiO<sub>2</sub>/SiO<sub>2</sub>) were investigated by Nishikawa and Takahara (2001). Although photocatalytic decomposition of DMDS using the inner-supported bead was below 0.53 (v/v) for the same condition as DMS, the removal of DMDS in the lighting up condition from the start using the bead was about 1.00 (v/v) for 50 h. It was suggested that DMDS was treated completely by the composite effects of adsorption and photocatalytic decomposition (Nishikawa and Takahara, 2001). The LECA bead of the PDR was proven without any H<sub>2</sub>S adsorption characterization (Su *et al.*, 2013, 2014; Su and Chen, 2015; Su and Hong, 2020). Thus, H<sub>2</sub>S removal of the biogas was completely photocatalytic oxidation without any adsorption.

### Biogas desulphurization using regenerated PDR

When the concentrations of outlet H<sub>2</sub>S increased, some yellowish elemental sulphur was observed on the surface of some TiO<sub>2</sub>-coated LECA beads inside the PDRs. In the meantime, inlet biogas was switched off, and tap water (41 litres/reactor) was introduced from the top of the PDRs soaking for a 2 h duration before draining the soaking water. This process was repeated until the sulphur was washed out from the surface of LECA beads. Comparison of the H<sub>2</sub>S removal efficiency from biogas before (Table 1) and after PDR regeneration (Table 2) was made to achieve optimal operation parameters. The data of statistical analysis showed that there was no significant difference in the contents of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> in the desulphurized biogas by using the PDR for desulphurization under the biogas flow less than 5 litres/min (Table 1). The PDR is only applied to remove H<sub>2</sub>S, thus, the contents of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> should remain constant.

After PDR regeneration, inlet H<sub>2</sub>S in untreated biogas was 5152 ± 230–5530 ± 99 mg/m<sup>3</sup> and the outlet H<sub>2</sub>S in desulphurized biogas was 0.48 ± 0.66–6.27 ± 1.86 mg/m<sup>3</sup>. Moreover, H<sub>2</sub>S removal efficiency was higher than 0.99 (v/v) under various biogas flow rates, i.e. 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 litre/min (Table 2). Analytical results of biogas samples showed that the gas contents (v/v), CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>, of desulphurized biogas,

were 0.59 ± 0.001–0.67 ± 0.001, 0.26 ± 0.002–0.28 ± 0.014 and 0.07 ± 0.001–0.13 ± 0.001, respectively (Table 2). Thus, sulphur on the surface of LECA beads might be dissolved in the tap water in the form of elemental sulphur or sulphate ion (Su and Hong, 2020). The photocatalytic oxidation of H<sub>2</sub>S at the gas/solid interface was investigated using TiO<sub>2</sub> as the photocatalyst and *in situ* Fourier transform infrared spectroscopy analysis by Kataoka *et al.* (2005). A malodorous compound, H<sub>2</sub>S was removed via a photocatalytic process under ambient conditions. H<sub>2</sub>S was oxidized to sulphate species on the surface of TiO<sub>2</sub> without producing a noticeable gaseous intermediate, e.g. sulphur dioxide (SO<sub>2</sub>) (Kataoka *et al.*, 2005). The results of this study showed that there was no SO<sub>2</sub> detected in the outlet biogas of the PDR. Thus, the results of this study were consistent with the finding of the study of Kataoka *et al.* (2005). However, the data of statistical analysis showed that there was a significant difference in the contents of CH<sub>4</sub> in the desulphurized biogas by using the regenerated PDR under the biogas flow less than 5 litres/min (*P* < 0.05) (Table 2). The results implied that some sampling or analysing errors may occur in those gas samples.

The linear regression analysis was not applied between biogas flow rate and removal efficiency of H<sub>2</sub>S in each gas (Tables 1 and 2) because the removal efficiency was not significantly different.

### Biogas upgrading using independent hollow fibre CO<sub>2</sub> adsorption cartridge set

The higher the CH<sub>4</sub> content, the higher the heat value of biogas. In other words, the lower the CO<sub>2</sub> content, the higher the CH<sub>4</sub> content in biogas. Analytical data showed that the inlet and outlet CH<sub>4</sub> contents (v/v) in the desulphurized biogas under various outlet biogas flow rates (1 to 3 litre/min) were 0.56–0.64 and 0.56 ± 0.006–0.86 ± 0.011, respectively (Table 3). The highest CH<sub>4</sub> content (v/v) in the outlet biogas was 0.86 ± 0.011. The inlet and outlet N<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.10–0.16 and 0.14 ± 0.009–0.25 ± 0.172, respectively (Table 3). The lowest N<sub>2</sub> content (v/v) in the outlet biogas was 0.14 ± 0.009. The amount of introducing air might be reduced through an opening of the dehydrator. Moreover, the inlet and outlet CO<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.25–0.28 and 0.01 ± 0.004–0.28 ± 0.007, respectively (*P* < 0.05) (Table 3). The data of statistical analysis showed that there was a significant difference in the difference of CH<sub>4</sub>/N<sub>2</sub> or removal of CO<sub>2</sub> in the upgraded biogas by using the independent hollow fibre cartridges under the biogas flow less

**Table 4.** Carbon dioxide (CO<sub>2</sub>) removal of the desulphurized biogas by a hollow fibre CO<sub>2</sub> adsorption module (*n* = 30)

Outlet biogas Flow rate (l/min)	CH <sub>4</sub> (v/v)			N <sub>2</sub> (v/v)			CO <sub>2</sub> (v/v)		
	Inlet	Outlet	Difference	Inlet	Outlet	Difference	Inlet	Outlet	Removal
1	0.62	0.84 ± 0.006	0.35 ± 0.010	0.09	0.14 ± 0.005	0.40 ± 0.047	0.29	0.03 ± 0.005	0.90 ± 0.018
2	0.61	0.77 ± 0.008	0.26 ± 0.014	0.11	0.14 ± 0.002	0.30 ± 0.018	0.28	0.09 ± 0.008	0.68 ± 0.027
3	0.63	0.76 ± 0.024	0.21 ± 0.038	0.10	0.13 ± 0.005	0.22 ± 0.045	0.27	0.11 ± 0.024	0.57 ± 0.077
4	0.62	0.74 ± 0.046	0.19 ± 0.075	0.11	0.14 ± 0.007	0.24 ± 0.068	0.27	0.13 ± 0.046	0.51 ± 0.158
5	0.62	0.70 ± 0.045	0.13 ± 0.072	0.11	0.13 ± 0.014	0.20 ± 0.129	0.28	0.18 ± 0.057	0.36 ± 0.205
<i>P</i>			<0.05			<0.05			<0.05
<i>R</i> <sup>2</sup>			0.407			0.697			0.702

Data presented as mean ± s.d. CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; *n*, sample size; NS, not significant; *R*<sup>2</sup>, coefficient of determination; v/v, proportion of volume of component to volume of sample; Removal or difference, (inlet data–outlet data)/inlet data.

than 3 litres/min (Table 3). The results implied that different biogas flow rates affect the removal efficiency of CO<sub>2</sub>, which was related to the removal efficiency of CH<sub>4</sub> and N<sub>2</sub> by using simple hollow fibres CO<sub>2</sub> adsorption cartridges.

The highest removal efficiency (v/v) of CO<sub>2</sub> was 0.97 ± 0.014 under the outlet biogas flow rate of 1 litre/min (Table 4). The removal efficiency of CO<sub>2</sub> decreased with increased desulphurized biogas flow rates (*P* < 0.05). Experimental results showed that the hollow fibre adsorption cartridge was capable of removing CO<sub>2</sub> from the desulphurized biogas and promote CH<sub>4</sub> concentrations, however, the cartridge had to be regenerated once an hour after the CO<sub>2</sub> adsorption process. Thus, an integrated hollow fibre CO<sub>2</sub> adsorption module significantly removed CO<sub>2</sub> in biogas and was more feasible for commercial pig farm use.

#### Biogas upgrading using a hollow fibre CO<sub>2</sub> adsorption module

The hollow fibre CO<sub>2</sub> adsorption module comes with an automatic regeneration function. Analytical data showed that the inlet and outlet CH<sub>4</sub> contents (v/v) in the desulphurized biogas under various outlet biogas flow rates (1 to 5 litre/min) were 0.61–0.63 and 0.70 ± 0.045–0.84 ± 0.006, respectively (Table 4). The highest CH<sub>4</sub> content (v/v) in the outlet biogas was 0.84 ± 0.006. The inlet and outlet N<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.09–0.11 and 0.13 ± 0.005–0.14 ± 0.007, respectively (Table 4). The lowest N<sub>2</sub> content (v/v) in the outlet biogas was 0.13 ± 0.005. Moreover, the inlet and outlet CO<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.27–0.29 and 0.03 ± 0.005–0.18 ± 0.057, respectively (Table 4). The highest removal efficiency (v/v) of CO<sub>2</sub> was 0.90 ± 0.018 under the outlet biogas flow rate of 1 litre/min (Table 4). The removal efficiency of CO<sub>2</sub> decreased with increased desulphurized biogas flow rates (*P* < 0.05). Experimental results showed that the hollow fibre adsorption module was capable of removing CO<sub>2</sub> from the desulphurized biogas and promote CH<sub>4</sub> concentrations, however, the module was automatically regenerated once an hour after the CO<sub>2</sub> adsorption process.

#### Biogas upgrading using a regenerated hollow fibre CO<sub>2</sub> adsorption module

The hollow fibre CO<sub>2</sub> adsorption module was automatically regenerated for 3 h before performing the continuous time-course experiments. Analytical data showed that the inlet and outlet CH<sub>4</sub>

contents (v/v) in the desulphurized biogas under various outlet biogas flow rates (1–5 litre/min) were 0.63–0.65 and 0.70 ± 0.045–0.86 ± 0.005, respectively (Table 5). The highest CH<sub>4</sub> content (v/v) in the outlet biogas was 0.86 ± 0.005. The inlet and outlet N<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.10–0.11 and 0.12 ± 0.002–0.13 ± 0.006, respectively (Table 5). The lowest N<sub>2</sub> content (v/v) in the outlet biogas was 0.12 ± 0.002. Moreover, the inlet and outlet CO<sub>2</sub> contents (v/v) in the desulphurized biogas were 0.25–0.27 and 0.01 ± 0.002–0.18 ± 0.054, respectively (Table 5). The highest removal efficiency (v/v) of CO<sub>2</sub> was 0.94 ± 0.028 under the outlet biogas flow rate of 1 litre/min (Table 5). The removal efficiency of CO<sub>2</sub> decreased with increased desulphurized biogas flow rates (*P* < 0.05). Experimental results showed that the hollow fibre adsorption module was capable of achieving more than 0.90 (v/v) of CO<sub>2</sub> removal efficiency (i.e. 0.90 ± 0.018–0.94 ± 0.028) from the desulphurized biogas and promote CH<sub>4</sub> content (v/v), however, the CH<sub>4</sub> content (i.e. 0.84 ± 0.006–0.86 ± 0.005) was still less than 0.90 after CO<sub>2</sub> adsorption process. The N<sub>2</sub> adsorption cartridge might be needed to remove N<sub>2</sub> (i.e. 0.13 ± 0.006–0.14 ± 0.005, v/v) in the desulphurized biogas and significantly promote CH<sub>4</sub> content. The hollow fibre CO<sub>2</sub> adsorption module has to be modified for enlarging module size by installing more cartridges, i.e. increase the desulphurized biogas loading volume, or rest the automatic regeneration intervals to achieve more than 0.95 (v/v) of CH<sub>4</sub> in the upgrading biogas.

The data of statistical analysis showed that there was a significant difference in the removal of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> in the upgraded biogas by using the hollow fibre module under the biogas flow less than 5 litres/min (*P* < 0.05) (Tables 4 and 5). The results implied that different biogas flow rates affect the removal efficiency of CO<sub>2</sub>, which was related to the removal efficiency of CH<sub>4</sub> and N<sub>2</sub> by using simple hollow fibres CO<sub>2</sub> adsorption module. Also, the automatic hollow fibre CO<sub>2</sub> adsorption module significantly removed the CO<sub>2</sub> in biogas without manual regeneration and operation.

The linear regression analysis was applied between biogas flow rate and removal efficiency of CO<sub>2</sub> in each gas (Tables 3–5) because the removal efficiency was significantly different. Since the maximum adsorption limit was set at 1 litre/min of outlet biogas flow rate, the removal efficiency of CO<sub>2</sub> for all sets under the outlet biogas flow rate of more than 1 litre/min declined rapidly right after saturation of the hollow fibre adsorption. Results of linear regression analysis showed that the *R*<sup>2</sup> value of Tables 3–5 was

**Table 5.** Carbon dioxide (CO<sub>2</sub>) removal of the desulphurized biogas by a regenerated hollow fibre CO<sub>2</sub> adsorption module ( $n = 30$ )

Outlet biogas flow rate (l/min)	CH <sub>4</sub> (v/v)			N <sub>2</sub> (v/v)			CO <sub>2</sub> (v/v)		
	Inlet	Outlet	Difference	Inlet	Outlet	Difference	Inlet	Outlet	Removal
1	0.64	0.86 ± 0.005	0.34 ± 0.008	0.10	0.13 ± 0.006	0.36 ± 0.061	0.27	0.01 ± 0.002	0.94 ± 0.028
2	0.64	0.79 ± 0.009	0.23 ± 0.014	0.10	0.13 ± 0.003	0.31 ± 0.027	0.27	0.09 ± 0.008	0.68 ± 0.023
3	0.64	0.77 ± 0.021	0.21 ± 0.034	0.10	0.12 ± 0.002	0.26 ± 0.016	0.27	0.11 ± 0.021	0.58 ± 0.065
4	0.65	0.74 ± 0.038	0.15 ± 0.058	0.10	0.13 ± 0.001	0.24 ± 0.010	0.25	0.13 ± 0.046	0.44 ± 0.153
5	0.63	0.70 ± 0.045	0.11 ± 0.072	0.11	0.12 ± 0.012	0.13 ± 0.011	0.26	0.18 ± 0.054	0.30 ± 0.190
<i>P</i>			<0.05			<0.05			<0.05
<i>R</i> <sup>2</sup>			0.520			0.769			0.746

Data presented as mean ± s.d. CH<sub>4</sub>, methane; N<sub>2</sub>, nitrogen; *n*, sample size; NS, not significant; *R*<sup>2</sup>, coefficient of determination; v/v, proportion of volume of component to volume of sample; Removal or difference, (inlet data-outlet data)/inlet data.

0.74282, 0.70246 and 0.74621, respectively, when the *y*-axis was CO<sub>2</sub> removal efficiency and the *x*-axis was outlet biogas flow rate.

## Conclusions

The purpose of developing the PDR was intended to desulphurize livestock biogas under ambient conditions and applied with the various biogas applications such as power generation, absorption chillers, or kitchen stoves. The higher the heat value, the more efficient the biogas applications. For onsite application, the loading volume of biogas must be increased with the enlargement of the size of the biogas desulphurization facility and the hollow fibre CO<sub>2</sub> adsorption module. Thus, nitrogen gas adsorption cartridges might be needed and installed next to the hollow fibre CO<sub>2</sub> adsorption cartridge inside the new hollow fibre CO<sub>2</sub> adsorption module for promoting CH<sub>4</sub> concentration in the upgraded biogas.

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**Conflict of interest.** None.

**Ethical standards.** Not applicable.

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