Optimization of bioscrubber systems to simultaneously remove methane and purify wastewater from intensive pig farms

Fang Liu[a,b], Claudia Fiencke[b], Jianbin Guo[a*], Tao Lyu[c*], Renjie Dong[a], Eva-Maria Pfeiffer[b]

[a] *College of Engineering, China Agricultural University, Qinghua East Road 17, 100083, Beijing, China*
[b] *Center for Earth System Research and Sustainability, Institute of Soil Science, Universität Hamburg, Allende-Platz 2, 20146, Hamburg, Germany*
[c] *School of Animal Rural & Environmental Sciences, Nottingham Trent University, Nottinghamshire NG25 0QF, UK*
**Corresponding authors:* jianbinguo@cau.edu.cn (Jianbin Guo); tao.lyu@ntu.ac.uk (Tao Lyu).

Abstract

Use of bioscrubber is attracting increasing attention for exhaust gas treatment in intensive pig farm. However, the challenge is to improve the methane (CH_4) removal efficiency as well as the possibility of pig house wastewater treatment. Three laboratory-scale bioscrubbers, each equipped with different recirculation water types, livestock wastewater (10-times diluted pig house wastewater supernatant), a methanotroph growth medium (10-times diluted) and tap water, were established to evaluate the performance of CH_4 removal and wastewater treatment. The results showed that high CH_4 removal efficiency (25%) can be rapidly achieved with improved methanotrophic activity due to extra nutrient support from the wastewater. The majority of the CH_4 was removed in the middle to end part of the bioscrubbers, which indicated that CH_4 removal could be potentially optimized by extending the length of the reactor. Moreover, 52% - 86% of the ammonium (NH_4^+-N), total organic carbon (TOC) and phosphate (PO_4^{3-}P) removal were simultaneously achieved with CH_4 removal in the present study. Based on these results, this study introduces a low-cost and simple-to-operate method to improve CH_4 removal and simultaneously treat pig farm wastewater in bioscrubbers.

Keywords: Biofiltration; Climate change control; Greenhouse gas; Methanotroph activity; Pig farm wastewater

1. Introduction

The continued increase in greenhouse gas (GHG) concentrations due to anthropogenic activities has led to significant climatic changes (Cox et al., 2000), which have raised the global average temperature by approximately 0.6°C over the past century (Hansen et al., 2012). Carbon dioxide (CO_2) and methane (CH_4) are the two main GHGs in the Earth's atmosphere, but even though CH_4 comprises a lower proportion

(16%) of the total anthropogenic GHG emission compared with CO_2 (76%), CH_4 contributes 28 times the greenhouse effect of CO_2 on a molar basis (IPCC, 2014). Thus, successfully mitigating CH_4 emission could play an important role in global climate change control.

Of all CH_4 emission sources, agriculture and its associated waste is a significant contributor, and the livestock industry is by far the largest emitter (57%) in this category, which estimated at 195 Tg CH_4 y^{-1} (Saunois et al., 2016). Pork is the most widely consumed meat product in the world, and more than half of all pork production is now from intensive pig farms (Philippe & Nicks, 2015), where CH_4 is generated from the pig manure and flows out through the ventilation system (Haeussermann et al., 2006). Currently, pig farms are the second largest contributor (13%) of GHG emissions in the livestock section (McLeod, 2011). Therefore, the treatment of CH_4 from intensive pig farms represents a crucial issue to ensure sustainability in meat production and environmental protection.

Due to the low-cost and easy maintenance of packed-bed air scrubbers (also known as bioscrubbers or biotrickling filters), they have been widely applied as the end-of-pipe technology to treat pig farm exhaust air in many European countries, including Germany, the Netherlands, and Denmark (Liu et al., 2014; Liu et al., 2017a; Melse & Hol, 2017; Van der Heyden et al., 2015). In bioscrubbers, water is sprayed on the top of the packing materials and the exhaust gas enters from beneath the scrubber and flows upwards. These contrasting flow directions can provide intensive contact between the two, enabling the transfer of pollutants from the gas phase to the liquid phase. The packing materials act as the carrier to host methanotrophic bacteria (methanotrophs). As the mixture of exhaust gas and water passes through, CH_4 can be adsorbed onto the surface of the packing material and/or into the attached biofilm and is oxidised by methanotrophs to achieve CH_4 degradation (Aguilar et al., 2010; Liu et al., 2017b; Malhautier et al., 2005; Melse & Timmerman, 2009; Melse & van der Werf, 2005). However, compared to ammonia, the CH_4 removal efficiencies are often relatively low, ranging from 0.9 - 6% (Aguilar et al., 2010; Belzile et al., 2010). Thus, optimization of bioscrubbers to intensify CH_4 removal is required, the relevant study is still lacking.

In field-scale bioscrubber systems, tap water is usually chosen as the spray water (recirculation water) for convenience. However, tap water contains low levels of nutrients and may lead to a long methanotrophic bacteria growth period. It may then cause low CH_4 removal in bioscrubbers, because the biodegradation of CH_4 is heavily reliant on methanotrophic abundance and activity (Yargicoglu & Reddy, 2017). In addition to generating GHGs, pig farms also produce a large amount of wastewater, which need to be treated before discharge (Molina-Moreno et al., 2017). The sustainable concept allows us to consider reusing the high level of nutrients, e.g. nitrogen and

phosphors, in the pig farm wastewater (Luo et al., 2017) to fed the methanotrophs. By doing so, it is hypothesised that the CH_4 removal rate could be improved and the pig farm wastewater could simultaneously be purified in bioscrubbers after using this wastewater as the recirculation water. Moreover, using isolated methanotrophs as the biological additives has been demonstrated to significantly improve CH_4 removal in bioscrubbers (Liu et al., 2017b). Whether the combination of pig farm wastewater and methanotroph addition could further improve bioscrubber performance requires investigation.

In this study, three laboratory-scale bioscrubbers equipped with different recirculation water types (pig farm wastewater (10-times diluted pig farm wastewater supernatant), methanotroph growth medium (10-times diluted) and tap water) were established to evaluate the CH_4 treatment performance. The performance of the bioscrubbers by a stepwise change of the recirculation water to pig farm wastewater were also tested. Then, the methanotrophic activity and spatial variability of CH_4 removal in bioscrubbers were studied to understand the underpinning mechanism. Furthermore, the pollutant (organic matter, nitrogen and phosphorous) removal efficiencies of the pig farm wastewater were investigated. With these results, this study aims to optimise bioscrubber systems to a low-cost and easy-to-operate technology to improve the CH_4 removal and simultaneously treat pig farm wastewater.

2. Materials and Methods

2.1 Experimental setup

The three lab-scale bioscrubbers used in this study were made of identical polyvinyl chloride (PVC) columns with dimensions of 125 x 30 x 30 cm in height, length and width, respectively (Fig. 1). Each column was filled with stacks of coarse plastic square plate from 10 to 120 cm height with a final effective volume of 99 L. This packing material was collected from the field-scale bioscrubbers with an operation time of around 7 years, which were employed at an intensive pig farm in Niedersachsen (Cloppenburg area), northern Germany. The packing material was made of polyethylene with 0.3 m in both length and width and 1.0 cm in thickness. The distance between each plate in the bioscrubbers was around 1 cm. The stack was vertically packed with a 45^{o} tilt to the airflow direction in the columns. In the bottom of the column, 10 cm of recirculation water collection area was connected to the exterior 20 L water tank for water recirculation in the bioscrubber (Figure 1a). The total volume of the recirculation water for each bioscrubber was around 20 L, comprised of 9 L water in the bottom of the bioscrubber and 11 L water in the recirculation tank. To sample from different heights of the bioscrubber, four tubes were placed at 35, 65, 95 and 125 cm height in the column and reached the centre of the column to exclude edge effects. All tubes were equipped with valves for gas sampling. The gas mixer device (HTK Hamburg GmbH, Hamburg, Germany) was used to control the inflow gas composition and flow rate by mixing the

methane and air (Fig. 1a). The mixed air flowed upwards through the packed bed while water was sprayed simultaneously from the top.

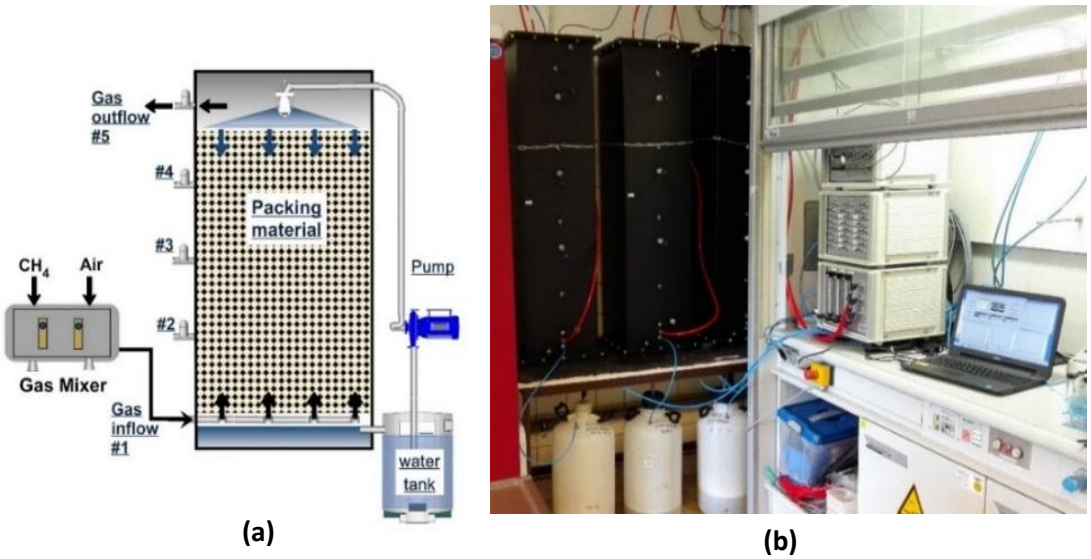

Fig.1 Schematic (a) and photo (b) of the lab-scale bioscrubber.

2.1 Experimental conditions

The experiment was conducted between May and December 2017, with a total duration of approximately 240 days. The experimental bioscrubbers were placed in the indoor laboratory at the Institute of Soil Science, Universität Hamburg, Germany (Fig. 1b). The indoor temperature ranged from 18 to 24°C during this period. Four continuous experimental phases (I, II, III and IV) were involved, based on varying recirculation water types and methanotroph addition (Table 1). To simulate the CH_4 influent loading rate in the field-scale bioscrubber (~100 g/m^3/h), the CH_4 inflow concentration, gas flow rate, empty bed retention time (EBRT), and recirculation water flow rate were kept at approximately 100 mg/m^3, 100 m^3/h, 3.5 s and 0.15 m^3/h, respectively, throughout the experimental phases.

To investigate the effect of recirculation water types on the bioscrubbers' performance, tap water-diluted pig farm wastewater supernatant (90:10 by volume), tap water-diluted methanotroph cultivation medium (90:10 by volume) and tap water (100%) were selected as the recirculation waters for bioscrubber 1 (BS1), bioscrubber 2 (BS2) and bioscrubber 3 (BS3), respectively, in phase I (60 days). In phase II (60 days), 2 L (10% of the recirculation water) of methanotrophic solution was added to the recirculation water tanks for all BS recirculation tanks. In phase III (60 days), half the volume (10 L) of the recirculation water in BS2 and BS3 was changed to pig farm wastewater (same preparation as BS1 in phase I). For comparison, 10 L of fresh pig farm wastewater was also used to substitute the recirculation water in BS1. Finally, to confirm the effect of pig farm wastewater, the recirculation water in all the bioscrubbers was changed to fresh pig farm wastewater in phase IV (60 days).

Table 1

Operating conditions of the three bioscrubbers across the experimental phases.

BS	Recirculation water of each experimental phase in 3 BSs				Operating conditions of 3 BSs during the whole experiment					
	Phase I	Phase II	Phase III	Phase IV	Packing Volume (m^3)	CH_4 inflow concentration (mg/m^3)	Air flow rate (m^3/h)	EBRT (s)	CH_4 loading rate ($g/m^3/h$)	Recirculation water flow rate (m^3/h)
BS1	Wastewater (20L)	Wastewater (18L) +Methanotroph (2L)	no change	Wastewater (20L)	0.099	100	100	3.5	101	0.15
BS2	NMS medium (20L)	NMS medium (18L) +Methanotroph (2L)	10 L was replaced with wastewater	Wastewater (20L)						
BS3	Tap Water (20L)	Tap water (18L) +Methanotroph (2L)	10 L was replaced with wastewater	Wastewater (20L)						

BS, EBRT, and NMS medium represent the bioscrubber, empty bed retention time and 10-time diluted methanotroph growth medium;
The wastewater represents 10-times diluted pig farm wastewater supernatant.

The fresh pig farm wastewater supernatant was collected from the intensive pig farm in Niedersachsen (Cloppenburg area), northern Germany. The wastewater was kept in the storage tank after a pre-treatment of solid-liquid separation. The methanotrophic growth medium was prepared in the laboratory, which was a slightly modified nitrate mineral salts (NMS) medium (Whittenbury et al., 1970) and contained a $CuSO_4$ concentration of 1 mg/L.

Methanotrophs were isolated from the biofilm on the packing materials that were obtained from the field scale bioscrubber employed at the intensive pig farm in Niedersachsen. Type I methanotrophs, one species of *Gammaproteobacteria*, was the main methanotrophic bacteria in the biofilm, based on previous detection by an electron microscope (Liu et al., 2017b). The aforementioned NMS medium was used for bacterial enrichment. Enrichment occurred at 28°C under orbital shaking in rubber-stoppered 120 mL bottles, containing 30 mL of NMS medium, 0.3 mL of phosphate buffer solution, and the rest in gas phase. The gas phase was 10% methane synthetic air (80% N_2, 20% O_2, and 0.03% CO_2, Fa. Messer Griesheim) and the gas in the bottle was replaced every week for 2 months. After enrichment, the methanotroph solution was transferred and stored in 1 L amber bottles with 10% methane synthetic air at 4 °C in the dark prior to use.

2.3 Sampling and analysis

2.3.1 Gas sample

In each experimental phase, the first 32 days were run to stabilise the system under the new operation conditions. Triplicated samples were taken every seven days in the last four weeks of each phase for analysis. The gas samples from the inflow, the sample heights of 35, 65 and 95 cm and the outflow (125 cm) of the columns were taken. During sampling, 12 mL of gas was first discarded by a three-way cock, then 10 mL sample volumes were taken by a vacuum glass tubes (10 mL) equipped with single polypropylene fittings for gas analysis. The CH_4 concentration was determined by a gas chromatograph (7890A, Agilent Technologies, US). The injection volume for analysis was 250 µL. Gases were separated on a Porapak Q column (1.8 m length, 2 mm ID) and quantified with a flame ionization detector (FID). The inflow, oven, and detector temperatures were 75°C, 35°C, 280°C (FID), respectively. Helium served as the carrier gas (30 mL/min).

2.3.2 Water sample

Following the gas sampling frequency, the pH and electrical conductivity (EC) of the recirculation water were measured in the recirculation tank, using a pH meter (pH/Cond 340i, WTW, Germany) and a potentiometer (Multi 350i, WTW, Germany), respectively. In experimental phase IV, 50 mL water samples were collected from each recirculation tank for quality analysis every week after the stabilization period. The

analysed parameters included ammonia (NH_4^+-N), nitrate (NO_3^--N), nitrite (NO_2^--N), total organic carbon (TOC) and phosphate (PO_4^{3-}-P). NH_4^+-N concentration was determined by a photometer according to German standard methods (DIN 38406-E5-1). NO_3^--N and NO_2^--N were measured using a High Performance Liquid Chromatograph (HPLC 1200 Series, Agilent Technologies, USA) equipped with a C-18 column (Hypersil ODS, 125 x 4.0 mm, 5 µm, Agilent Technologies, USA) with a UV-Detector (model 430), according to the description by (Sanders et al., 2010). The total nitrogen (TN) content was calculated by the sum concentration of NH_4^+-N, NO_3^--N and NO_2^--N. The TOC content was measured by a C/N analyser (Variomax elementar CNMS). The PO_4^{3-}-P concentration was determined using the colorimetric molybdenum blue reaction (Beermann et al., 2015). All the measurements were conducted in triplicate.

2.3.3 Methanotrophic activity

The methanotrophic activities in all bioscrubbers were estimated by measuring the methane removal intensity. Briefly, 150 mL interstitial water samples were collected from the water outlet in each bioscrubber at the end of each experimental phase. The 150 mL samples were placed in 250 mL plasma flasks filled with 50 mL NMS medium. The flasks were then sealed with a rubber-stopper and cultivated under room temperature (~25°C) conditions for 20 days. An initial concentration of about 100 ppm of CH_4 was placed as the overlying gas in the flask. Each treatment was conducted in triplicate. In each flask, 250 µL of the gas sample was taken to analyse the CH_4 concentration by the previously described gas chromatography method (7890A, Agilent Technologies, US) on days 2, 3, 13 and 20, respectively. Thus, the CH_4 degradation rate was used to reflect the potential methanotrophic activity.

2.4 Calculation

Methanotrophic activities were analysed for all the different BSs in each experimental phase. The CH_4 degradation in the flask test was simulated by the first order kinetics model (equation 1):

$$C_t = C_0 * e^{-kt} \quad (1)$$

Where C_t is the CH_4 concentration at time point t in ppm; C_0 is the initial concentration in ppm; k is the reaction rate d^{-1}; t is the reaction time.

After the simulation, the reaction rate (k value) was used to represent the potential methanotrophic activity.

2.5 Statistical analysis

Statistical analyses were carried out using the XLStat Pro® statistical software (XLStat, Paris, France). A one-way ANOVA and post-hoc Tukey's HSD test were used to compare average CH_4 removal efficiencies, the potential methanotrophic activity, and the pollutants' removal abilities in pig farm wastewater between the three bioscrubbers under different experimental phases. All comparisons were assessed at the 95% ($p <$

0.05) and 99% ($p < 0.01$) confidence levels. A linear regression model was used to simulate the methanotrophic activities and CH_4 removal efficiencies in all bioscrubbers.

3. Results

3.1 CH_4 removal

The CH_4 removal efficiencies in different bioscrubbers across the four experimental phases are shown in Fig. 2. After 32 days stabilization, BS1, equipped with the pig farm wastewater, showed significantly higher CH_4 removal (average of 11%) than that of BS2 (average of 6%) and BS3 (average of 5%), which were equipped with the NMS medium and tap water, respectively. In phase II, the CH_4 removal performances in BS1 and BS2 showed significant improvement after adding methanotrophs and reached 23% and 9%, respectively. However, BS3 showed a slight improvement and achieved 6% CH_4 removal. After changing half of the recirculation water to pig farm wastewater in phase III, the CH_4 removal efficiencies in BS2 and BS3 improved significantly to 15% and 12%, respectively. In phase IV, all bioscrubbers showed similar CH_4 removal (25%) after totally

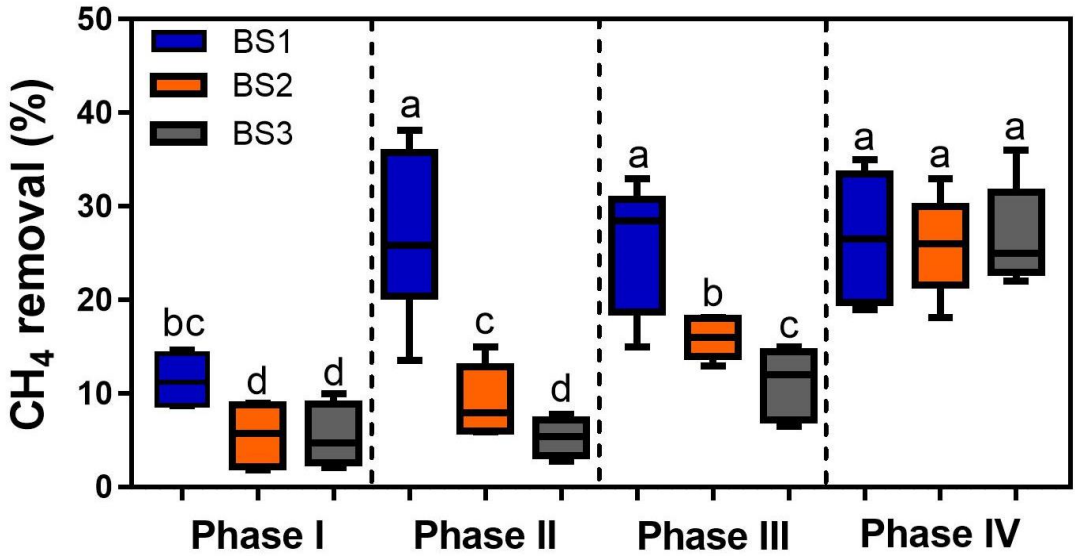

Fig. 2 CH_4 removal performance of the three bioscrubbers (BS) from Phase I to IV.

3.2 CH_4 removal profiles along the bioscrubbers

CH_4 concentrations gradually decreased from the inlet (bottom) to the outlet (top) along the gas flow pathway in all bioscrubbers (Fig. 3). Generally, the CH_4 concentrations in three bioscrubbers did not show a clear difference at the sampling heights of 35 cm and 65 cm in any of the experiment phases. Significantly lower CH_4 concentrations were observed at the sampling heights of 95 cm and 120 cm (out) in BS1 compared with those in BS2 and BS3 in phase I, II and III. When the operations were same in the three bioscrubbers in phase IV, the CH_4 concentration profiles along the depth were similar between themselves (Fig. 3d).

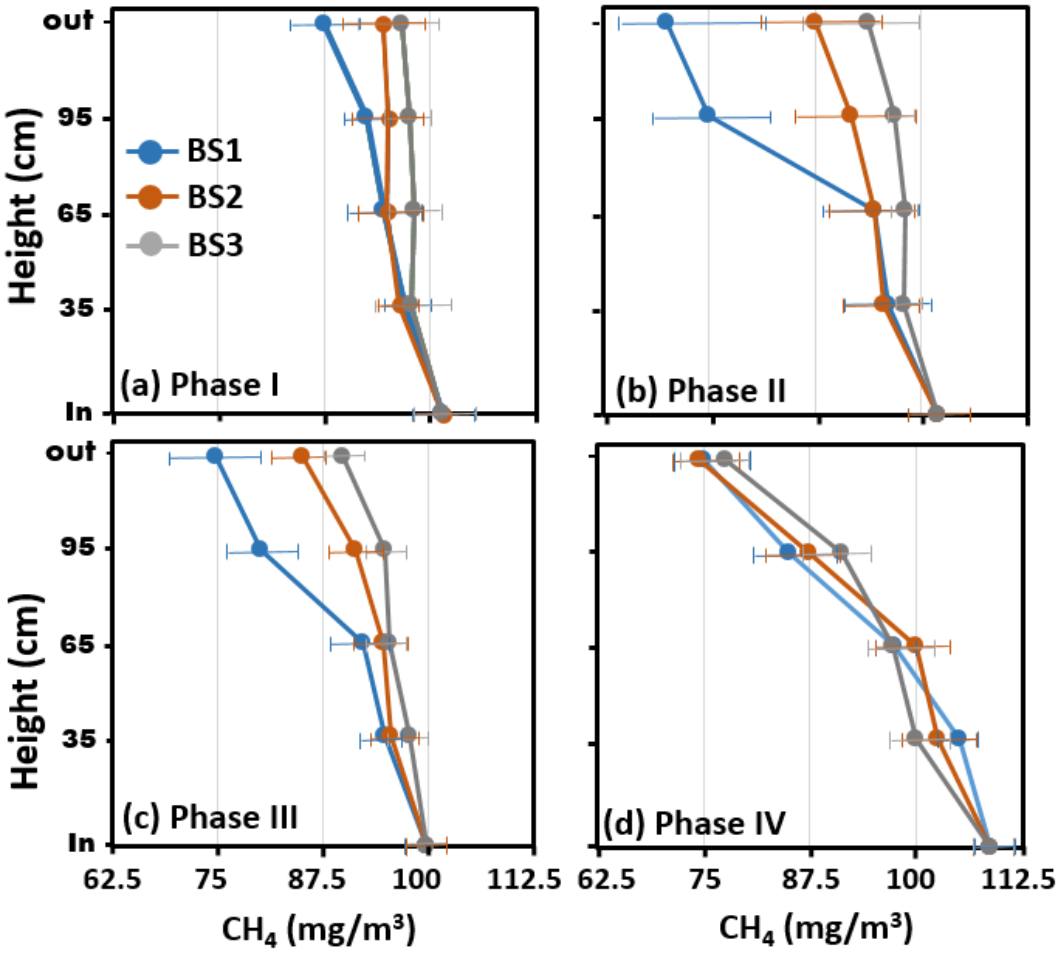

Fig. 3 Concentrations of CH_4 at different depths in the three bioscrubbers (BS) from Phase I to phase IV.

3.3 Methanotrophic activity

In order to better understand the effect of pig farm wastewater and methanotroph addition on CH_4 removal in bioscrubbers, the activities of methanotrophs were measured in the four experimental phases (Fig. 4). The experimental process was simulated using the first order kinetics model and the reaction rates (*k* values) were calculated to represent the methanotrophic activity. In phase I, the methanotrophic activity (k of 0.21 d^{-1}) in BS1 was around 1~3 times higher than that of BS2 (k of 0.07 d^{-1}) and two orders of magnitude higher than that in BS3 (k of 0.003 d^{-1}). After adding methanotrophs from Phase II, BS1 kept a relatively stable methanotrophic activity (k of 0.34 d^{-1}) until phase IV. Methanotrophic activity slightly increased in BS2 (k of 0.09 d^{-1}) and BS3 (k of 0.05 d^{-1}) in phase II. Nevertheless, after the replacement of the recirculation water in phase III and IV, methanotrophic activity in BS2 and BS3 continually improved and achieved a similar level (k of 0.31 d^{-1}) to that of BS1.

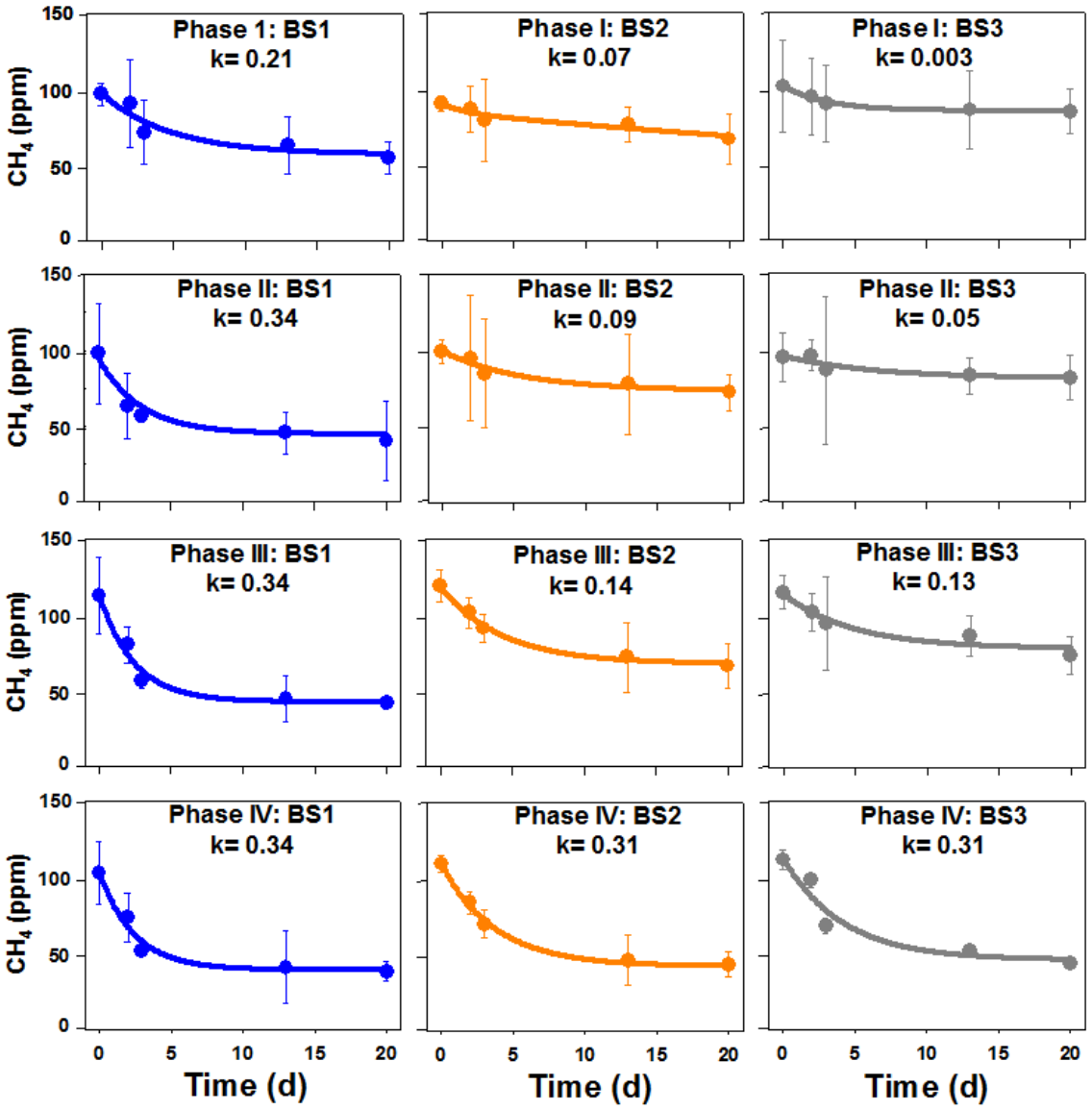

Fig. 4 Simulated methanotrophic activity in all bioscrubbers (BS) from Phase I to IV.

3.4 Wastewater treatment performance

To evaluate whether the pig farm wastewater can be purified during CH_4 removal in bioscrubbers (BS), the water quality, pH and EC, and concentrations of pollutants (NH_4^+-N, NO_3^--N, NO_2^--N, TOC and PO_4^{3-}-P) were tested in phase IV (Table 2). The total nitrogen (TN) was calculated by the sum concentration of NH_4^+-N, NO_3^--N and NO_2^--N. At the beginning of phase IV, all bioscrubbers were equipped with fresh pig farm wastewater as their recirculation water. Generally, the bioscrubbers did not show significant differences for all the measured parameters. When compared with the initial 10-time diluted pig farm wastewater, the EC values significantly increased from around 2.4 mS/cm to 5.2-5.9 mS/cm in the three bioscrubbers. The pH values did not show significant changes (6.2 - 7.3) compared with the initial wastewater (7.9).

The initial pig farm wastewater contained high levels of PO_4^{3-}-P (11 ± 3 mg/L), TOC (152 ± 11 mg/L), TN (39.4 ± 5.3 mg/L), and NH_4^+-N (36 ± 5 mg/L). The removal of PO_4^{3-}-P reached 73 ± 3%, 64 ± 3% and 64 ± 4% in BS1, BS2 and BS3, respectively. The removal of TOC in the three bioscrubbers was found to be in the range of 74 - 86%. The bioscrubbers provided removed 29 ± 3%, 29 ± 7%, and 52 ± 11% of the TN in BS1, BS2 and BS3, respectively. For different species comprising the TN, NH_4^+-N removal was 64 ± 4%, 52 ± 8%, and 73 ± 15% in BS1, BS2 and BS3, respectively, while concentrations of NO_3^--N (2.3 ± 0.2 mg/L) and NO_2^--N (1.1 ± 0.1 mg/L) increased to 13 ± 0.1 and 3 ± 0.2 mg/L in BS1, 9 ± 1 and 2 ± 0.2 mg/L in BS2, and 8 ± 1 and 1 ± 0.1 mg/L in BS3, respectively.

Table 2
Pig farm wastewater treatment performance from the three bioscrubbers (BS) in phase IV.

Parameters	Initial	BS1		BS2		BS3	
	Value	Value	Removal (%)	Value	Removal (%)	Value	Removal (%)
pH	7.9±0.1	7.3±0.2	-	6.2±0.4	-	6.9±0.3	-
EC (mS/cm)	2.4±0.5	5.7±0.9*	-	5.2±1.2*	-	5.9±0.8*	-
PO_4^{3-}-P (mg/L)	11±3	3±1*	73±3	4±2*	64±3	4±3*	64±4
TOC (mg/L)	152±11	21±4*	86±5	32±2*	79±6	39±6*	74±7
TN (mg/L)	39.4±5.3	28±0.8*	29±3	28±4.2*	29±7	19±7.1*	52±11
NH_4^+-N (mg/L)	36±5	12±0.5*	66±4	17±3*	52±8	10±6*	73±15
NO_3^--N (mg/L)	2.3±0.2	13±0.1*	-	9±1*	-	8±1*	-
NO_2^--N (mg/L)	1.1±0.1	3±0.2*	-	2±0.2*	-	1±0.1*	-

* these values represent significant differences compared with the original 10-times diluted pig farm wastewater supernatant.

4. Discussion

According to the 2018 Global Report on Food Crises from the WFP (World Food Programme) (WFP, 2018), an estimated 124 million people in 51 countries are currently facing food insecurity and shortages. In order to produce more meat to fulfil the world consumption, livestock production has shifted from traditional, extensive, decentralized family farms to intensive livestock farms (Ilea, 2009). As a result, the livestock sector is now becoming one of the most significant contributors to environmental problems, including greenhouse gases emissions (Dennehy et al., 2017; Melse & Mosquera, 2014), and water pollution (Mallin et al., 2015).

Traditionally, exhaust gases and wastewater from the intensive pig farms are treated separately by different technologies. Ecologically friendly biodegradation technologies, e.g. bioscrubbers and biofilters, are mainly equipped to purify the exhaust gases (Melse & Timmerman, 2009). Pig farm wastewater, characterized by high concentrations of nutrients, e.g. organic matter and nitrogen, are usually treated by anaerobic digestion (Ni et al., 2017) which is followed by post-treatment for nitrogen removal, such as ammonia stripping (Wu et al., 2018). However, a previous study has

demonstrated the simultaneous removal of nitrogen from the swine wastewater and H_2S from the exhaust gas using a bubble column reactor (Deng et al., 2009). The present study uses an integrated approach to achieve simultaneous CH_4 mitigation and wastewater treatment, which could provide a new insight for the future application of this technology.

The biodegradation of the pollutants from either the gas or water phase is heavily dependent on the bacterial growth in bioreactors, such as membrane bioreactors (Lebrero et al., 2014), anaerobic digesters (Zhang et al., 2012), constructed wetlands (Kizito et al., 2017), and bioscrubbers (Melse & Hol, 2017). Thus, substances, such as activated sludge and livestock manure, with relative high concentrations of nutrients, are commonly used to prime the systems for bacteria growth. Based on the same concept, significantly higher CH_4 removal in BS1 (11%), compared with BS2 (6%) and BS3 (5%) in phase I (Fig. 2), could be due to the extra nutrients from pig farm wastewater for methanotroph growth. The CH_4 removal in BS2 is higher than that in BS3 but lower than BS1, which may be because the 10-times diluted NMS medium contained less available nutrients for methanotroph growth compared with pig farm wastewater. Increasing the concentration of the NMS medium may improve the CH_4 removal ability, however, the cost will also dramatically rise to affect the scalability.

Coupled with recirculating pig farm wastewater in the bioscrubber, extra methanotroph addition could further improve the CH_4 removal from an average of 11% to 25% (Fig. 2). BS1 presented significantly higher CH_4 removal percentages than BS2 and BS3 after the addition of methanotrophs, which may due to the nutrients from wastewater that can be utilized by the added bacteria to form a biofilm on the packing materials. This hypothesis was supported by the results of the potential methanotrophic activity, which had its highest value in BS1 after methanotroph addition (Fig. 4). The methanotroph activity was significantly positively correlated with the amount of CH_4 removed (Fig. 5), which indicated that the methanotrophic activity in the recirculation water could be used to diagnose the CH_4 removal ability of a bioscrubber.

To understand the CH_4 removal processes inside bioscrubbers, the dynamics of the CH_4 concentrations profile along the depth of the bioscrubbers though the four experimental phases were investigated (Fig. 3). The CH_4 concentration changed the least at the bottom of the columns, however, the amount of CH_4 heavily decreased (increased CH_4 removal) from the middle to the outlet of the bioscrubbers. This increase in CH_4 removal may be caused by an increased methanotrophic presence and activity at the middle to end part of the system. Recirculation water flows from the top to the bottom in bioscrubbers, thus, the nutrients may accumulate at the top first and to be easily and quickly utilized by methanotrophs. Previous studies have also demonstrated that the middle and top part of the biofilter system contained 1.1–2.5 fold methanotrophic

activity compared with the bottom part when treating CH_4 emissions from landfill (Pawłowska & Stępniewski, 2006). The higher contact time between CH_4 and the microbial community could also be contributing to the significant increase in CH_4 removal along the length of the column (Gómez-Cuervo et al., 2016). However, more research is required to quantify the proportion and activity of the methanotrophs along the length of the bioscrubbers.

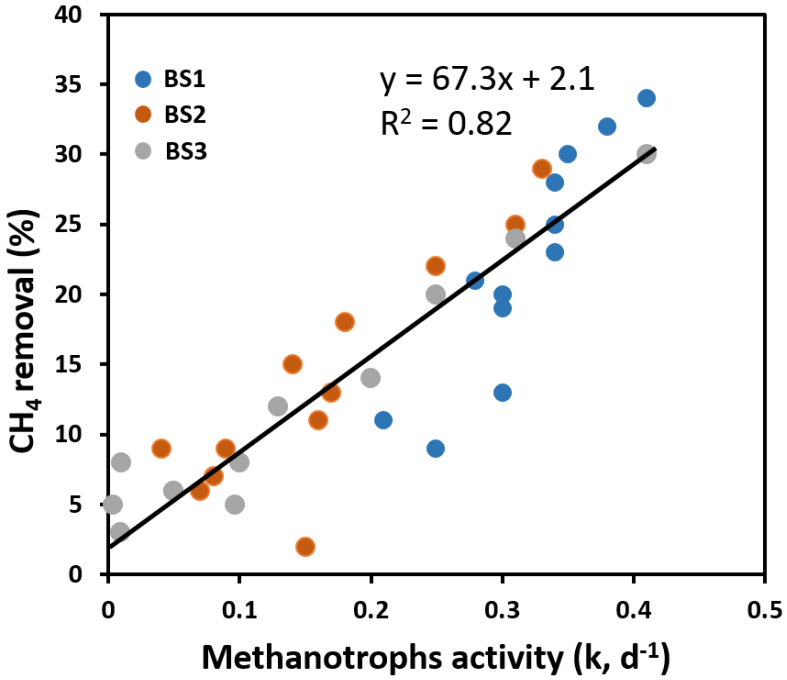

Fig. 5 The correlation between methanotrophic activity and CH_4 removal efficiency

Under the present optimization methods, the bioscrubbers removed 52 - 86% of the PO_4^{3-}-P, TOC, and NH_4^+-N from the wastewater (Table 2), when associated with CH_4 removal. PO_4^{3-}-P, as an important nutrient, can be assimilated by numerous bacterial cells and supports their basic metabolisms (Liu et al., 2001; Smith & Prairie, 2004). It can potentially support different bacteria, e.g. methanotrophs, organic degradation bacteria, nitrification/denitrification bacteria, which grow on the packing materials in bioscrubbers after introduced by wastewater. In addition to the oxidation of CH_4, methanotrophic bacterial could also co-metabolise and degrade organic pollutants (Benner et al., 2015; Lyew & Guiot, 2003), which may support TOC removal in bioscrubbers. The potential organic degradation bacteria may also contribute to the TOC removal (Li et al., 2018; Yamashita et al., 2015), however, the quantity and activity of this bacteria needs to be determined in future studies.

Methanotrophs has been demonstrated to be able to oxidize both CH_4 and NH_4^+-N (Bodelier & Frenzel, 1999; Su et al., 2017), thus, the considerable NH_4^+-N removal in the bioscrubbers may be partly due to methanotrophic nitrification (Sutka et al., 2003).

Moreover, the significantly increased concentrations of NO_3^--N and NO_2^--N (Table 2) supports the idea that the potential nitrification process (Kizito et al., 2017; Melse & Hol, 2017), which was not measured in the present study, occurred in the bioscrubbers. Nevertheless, the TN removal was in the range of 29 - 52% in the three bioscrubbers (Table 2), which relatively low compared with other bioreactor systems for wastewater treatment (Yu et al., 2007). This may due to the preparation of artificial gas by mixing pure CH_4 and air, which could aerate the bioscrubbers and result in aerobic conditions. The denitrification process, which could convert NO_3^--N and NO_2^--N to N_2 for final nitrogen removal, would be heavily prohibited under these aerobic conditions. Real pig house exhaust gases could also contain other substances, such as CO_2, N_2O, NH_3 (Melse & Mol, 2004; Melse & Mosquera, 2014), which could consume oxygen in the bioscrubber to reduce the aerobic condition. Thus, the TN removal may be improved when used in the real pig house exhaust gas treatment plant, however, this requires further study.

Theoretically, once the EC of the recirculation water exceeds 22 mS/cm in bioscrubber systems, the water needs to be refreshed to avoid the inhibition of the CH_4 removal ability due to the high concentration of ions, e.g. NH_3^+, in the water. However, the EC in the present study, for all systems, only reached 5.9 mS/cm in phase IV when using 10-times diluted pig farm wastewater, making the implementation of this system feasible. However, it should be noted that the original pig farm wastewater may contain a high concentration solid particles and other pollutants, such as heavy metals (Shen et al., 2016), that may influence the bioscrubber efficiency. Thus, appropriate wastewater pre-treatments should be considered before applying these optimisations.

5. Conclusions

The proposed optimization methods for bioscrubbers, selecting pig farm wastewater as the recirculation water combined with isolated methanotroph addition, was demonstrated to be a promising strategy to simultaneously remove CH_4 and purify pig farm wastewater. High CH_4 removal efficiency (25%) can be rapidly achieved with improved methanotrophic activity due to the extra nutrient support from the wastewater. The majority of the CH_4 was removed in the middle to end part of the bioscrubbers. For the wastewater, removal of 52 - 86% of the NH_4^+-N, TOC and PO_4^{3-}-P can be achieved in the present study.

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