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Agriculture Residue as Bio-Cover to Inhibit Methane from Slurry Storage

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ABSTRACT: *Animal manure not only produces malodours, but it is also a significant source of methane (CH_4) emission following a microbial-organic material breakdown. The objectives of this study were to measure methane emissions reduction following the uses of agricultural residue as biological cover on the slurry surface during the storage period. The agriculture by-products from paddy husk, rice straw, cocopeat, unfilled grains, and chipped wood were used as a physical cover on a cattle slurry surface at 30 cm thick during 90 days' storage period. Methane emission from stored slurry was measured periodically during the storage period. All residues used were found to enhance further emission during storage thus resulting in higher methane emission compared to an uncovered slurry (Ctrl). This concludes that agriculture residues as covered materials failed to inhibit methane emission from a stored slurry.*

KEYWORDS: agriculture residue, methane emission, slurry cover, slurry storage, greenhouse gas

INTRODUCTION

Animal manures from livestock production provide a source of nutrients to crops when applied to agricultural land. However, animal production has been linked to a number of local and global environmental issues due to their contribution towards greenhouse gases (GHGs) emissions. Gaseous pollutants like ammonia (NH_3), methane (CH_4), and nitrous oxide (N_2O), which make the soil more acidic and contribute to global warming, come mostly from livestock production systems. To lessen the bad effects of these systems, reducing the emissions of these gases should be a top priority, especially since animal production will keep increasing as the world population grows. Methane emission from livestock production is related to enteric fermentation and livestock manures. Methane and N_2O emissions from livestock farms are influenced by the management and usage of manure, particularly when it comes to slurry animal waste, which is commonly produced by swine, dairy, and beef cattle operations. Since manure storage releases up to 18% of all agricultural emissions of GHGs, proper manure management is crucial (Pattey et al., 2005; Chadwick et al., 2011; Sommer et al., 2013). In the year 2022, Malaysia reported 1224.5 and 660.1 Gg carbon dioxide (CO_2) equivalent (eq) of CH_4 from enteric fermentation and manure management with additional 541.9 Gg CO_2 eq of indirect N_2O from livestock manures (NRECC, 2022).

The release of greenhouse gases, mainly CH_4, during slurry manure storage is significant; nevertheless, solutions are being developed and used to decrease these emissions. On average, Malaysian livestock activities have contributed to 1221.3 Gg CO_2 eq emission per year between 2015 till 2019, from manure management and indirect N_2O emission from manure (NRECC, 2022). One way to decrease this emission is to shift from slurry storage to biodigester, which captures CH_4 and converts it to CO_2 by flaring or use to generate renewable energy. This strategy, however, is inapplicable, and uneconomical to small farms because it necessitates a big investment, high maintenance costs, and a large number of animals in order to be economically practical and profitable. As a result, alternative methods are needed to reduce CH_4 and other GHG emissions from slurry storage facilities, especially for Malaysia's small- to medium-scale livestock farmers.

Emissions from slurry storages can be mitigated in several ways, the most common of which involve decreasing the slurry's open surface area by the addition of rooftops or a simple covering approach. Cover can be either both fixed or free floating made of various materials and made to resist the effects of atmospheric agents. Rigid covers are either attached to the tank construction and supported by frames or are self-supporting and form a fixed cover (roof, sealed floor) that is not in direct contact with the slurry. Alternative floating covers can be made from unused waste from agriculture or inexpensive materials such as straw, rice husks, expanded clay granules, vegetable oil or wood chips. Surface cover using agricultural waste not only act as a physical barrier but also retains gaseous emission (Guarino et al., 2006), as a medium for microbes to oxidize methane and as an excellent medium for nitrification-denitrification process (Portejoie et al., 2003; Guarino et al., 2006; Petersen and Ambus, 2006; Hansen et al., 2009). The uses of biological cover from fibrous material which hardens after prolonged undisturbed storage, resulting in the forming of a solid state medium known as a crust.

Methane gas, which is produced by methanogens in anaerobic condition, is 34 times more potent than CO_2 as a greenhouse gas over a 100-year time horizon (Myhre et al., 2013). Since CH_4 emissions from slurry may have no short-term consequences on the local ecosystem, animals, or farmers, and may have no immediate ramifications for the farm's profitability, they were mostly unnoticed in Malaysia. Ammonia volatilisation on the other hand, is the transfer of nitrogen from animal manure into the atmosphere. They imply a loss of vital nitrogen fertilizer in manure. Moreover, anthropogenic NH_3 emissions to the troposphere cause indirect environmental damage such as acidification of soils and eutrophication of waterways (Portejoie et al., 2003; Petersen et al., 2012). Earlier research demonstrated that natural crusts or floating covers can reduce NH_3 emissions from stored slurry by up to 80% (Portejoie et al., 2003; Misselbrook et al., 2005).

As a slurry cover, additional substrate or synthetic cover is considered an additional expense. In this way, reusing agricultural by-products decrease farmers expenses. The goal of this project was to get an early look at how agricultural waste and by-products could be used to reduce CH_4 emission during slurry storage. It was expected that the use of agriculture waste residues and by-products as a physical barrier will minimize the amount of CH_4 emitted from the slurry surface.

MATERIALS AND METHODS

Slurry Agriculture Biomass as Physical Cover

Fresh slurry (FS) was obtained from a reception pit and slurry handling pond of a private farm located at Pedas, Negeri Sembilan. The slurry, derived from different breed of cattle and buffalo were pooled. The cattle were at the range of 1-4 years old and weighed around 50-300 kg. These animals were fed with total mixed ration (TMR) at 3% dry matter (DM) basis of bodyweight, which comprises of 60% concentrates and 40% fresh grass / pastures (% dry matter basis). The concentrates contain mainly palm kernel expeller (PKE), grinded corn, soya bean meal, soya bean hull, grinded rice hull, crude palm oil (CPO), molasses, and limestone with an addition of less than 0.002% minerals and trace elements for the animal growth requirement. The slurry obtained were kept in a 130 L drum container and stored under cover for 48-92 hr prior to use. The slurry physicochemical composition (pH; oxidation redox potential, ORP; dry matter, DM; volatile solid, VS; carbon and nitrogen was characterized before the experimental design was carried out. Initial slurry characteristics were 2.0 ±0.3% dry matter Kg^{-1} slurry (DM), 65.9 ±1.96% volatile solid Kg^{-1} DM (VS), total carbon (C) 321.5 ±62.70 mg Kg^{-1} slurry, total nitrogen (N) 51.2 ±25.14 mg Kg^{-1} slurry, C:N ratio 6.28:1, and pH 7.0±0.03.

Cattle slurry was transferred into 130 L *high-density polyethylene* (HDPE), such that each pail received 40 Kg cattle slurry with and without agriculture residue by products as biological cover (30 cm thickness). There were 5 types of agriculture residue by-products used; i) slurry + chipped wood (CW); ii) slurry + paddy husk (SE); iii) slurry

+ rice straw at 3- 5cm length (JE); iv) slurry + cocopeat (CP); v) slurry + unfilled grains (PH); and untreated control as Ctrl. The experiment was carried out from September 2021 until December 2021 for a period of 91 days.

Moisture loss, temperature, pH and oxidation redox potential (ORP)

The slurry moisture loss was weighted using digital weighing scale FX5000i (AND Company Limited, Japan). While, slurry temperature, pH and ORP were measured using a Hanna pH electrode probe (model HI 991003; Hanna Instrument, USA). Those measurement was conducted only on Ctrl treatment slurry to avoid disturbances of the slurry surface. Meanwhile, the ambient temperature and humidity was recorded using EasyLog EL-USB-2-LCD (Lascar Electronic, United Kingdom).

Slurry dry matter (DM) and volatile solids (VS) content

Slurry dry matter (DM) and volatile solids (VS)were determined by drying 10 g slurry samples at 80°-105°C to constant weight (16 hr) and as loss-on ignition at 450°C for 16 hr in muffle furnace Carbolite CWF 1200 (Carbolite Ltd, UK).

Total carbon (C) and nitrogen (N)

The total C and N of fresh slurry were measured using Elementar Analyzer (CHNOS) model Vario Macro Cube (Elementar, Germany).

Methane gas measurement

Methane gas fluxes were sampled using a steady state static chamber technique from the barrel headspace through a butyl rubber septum during closed system. Headspace gas samples were taken immediately (T0) after securing the lid in place, after 30 (T30) and 60 minutes (T60). Gas samples were placed in 20 mL pre-evacuated gas vials and analysed using Agilent 7890B gas chromatogram (GC). The GC was equipped with J &W Scientific CS- Gaspro 45 m X 0.320 µm capillary columns, and equipped with a flame ionized detector (FID). The GC setup was; injector at 200°C with flow 24ml min^{-1} (13.18 PSI), oven and FID temperature 40°C and 150°C respectively, column flowrate 4ml $min^{-1}$and total run time of 5.5 min. Gas fluxes were calculated based on the linear increase in gas concentration between the T0 and T60 samples over the one-hour period, headspace volume and slurry weight. Cumulative gas emissions for the storage period were calculated by interpolating the measurements between adjacent sampling points using the trapezoidal rule (Cardenas et al., 2010).

RESULTS AND DISCUSSION

Slurry Agriculture Bio-Cover

Slurry characteristic and general observation

Agricultural residues utilization in livestock farm is not a new idea. One of the important benefits of recycling crop residues is that they are available on farm at a low cost (English et al., 2006). Many of the agricultural by-products has been used as permeable cover to reduce odour and NH_3 from the storage pond (Sommer et al., 1993; Portejoie et al., 2003; Guarino et al., 2006). Utilization of these agricultural residue by-products were seen as another approach to lower CH_4 emissions by hardening to become a crust on the slurry surface (Petersen and Ambus, 2006). Straw, (either rice straw or barley straw) is the most used by-products for this matter. Yet, other materials such as cornstalks, corn cobs, alfalfa, sugarcane waste, rice hulls and husk have also been examined. These materials have low buoyancy and are prone to damage from wind and precipitation. Some studies found these materials sank rapidly into the slurry, typically in low DM slurry such as from pig waste (Portejoie et al., 2003; English et al., 2006). In this study, there was no crust observed as most of the agriculture residues used partially or fully sank into the slurries.

As the by-product sank into the slurry, this would represent adding organic matter and volatile solid materials. The DM and VS content of the slurries among treatments were obviously different due to fermentable characteristics depending on the amount of substrate that sank as sediment to the bottom of slurries, while the increase of the DM and VS on Ctrl was due to water evaporation in which slurries become thicker (Table 1). Water evaporation and loss in Ctrl indicated 39% loss, significantly differ as compared to the treated slurry at a range 5.7 to 10.4%. The high-water loss is reflected from the ambient temperature and humidity conditions. Although the average temperature during study was recorded at 28.5°C, the maximum temperature at noon was higher and reached 40°C due to the usage of zinc material rooftop. As the agriculture residue covers blocked water evaporation, this resulted in lower moisture loss in treated slurries (Figure 1: iv). In addition, covered surface by agriculture by-products may resulted in the accumulation of slurry volume during rainfall (Guarino et al., 2006).

Observation on Ctrl slurry pH showed that the slurry's pH gradually increased to alkaline level during storage (pH 7.5 to pH 8.3) (Figure 1: i). This occurrence is due to high loss of CO_2 rather than NH_3 as the solubility of CO_2 is 200 times lower than NH_3 (Portejoie et al., 2003). The pH recorded on other treatments was not measured as this may disturbed the biomass on slurry surface resulting in false positive GHG emission. However, the pH measured at the end of the experiment for the covered slurries (SE, CP, JE, CW and PH) showed a neutral pH (Table 1) due to the breakdown of organic matter producing organic acid and volatile fatty acid (VFA) (Portejoie et al., 2003). On the other hand, ORP level of the Ctrl indicated that the slurries ORP increase to the highest level, which is at 327 mV on day 30 and nearly constant at -16 to -76.6 mV

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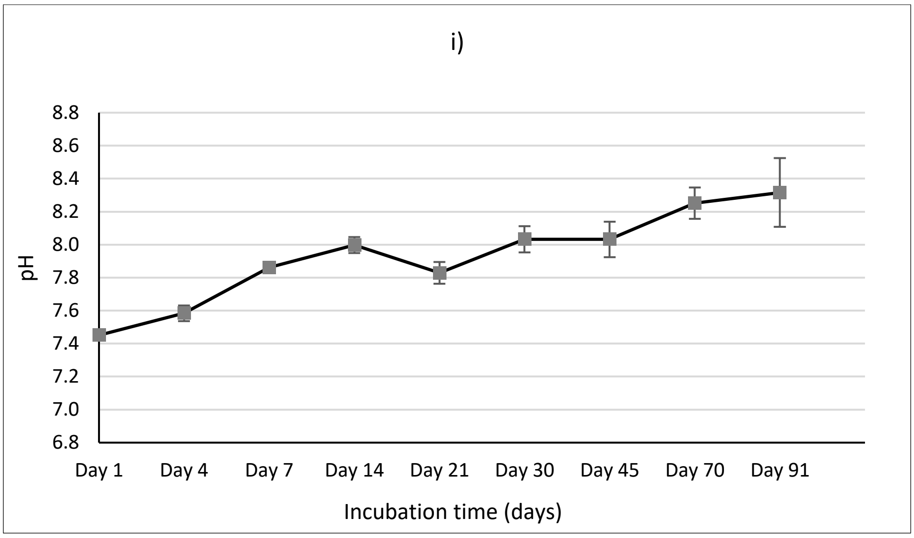
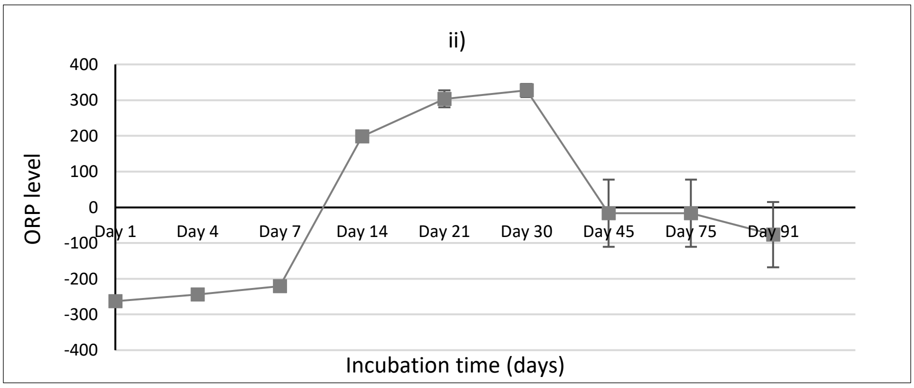
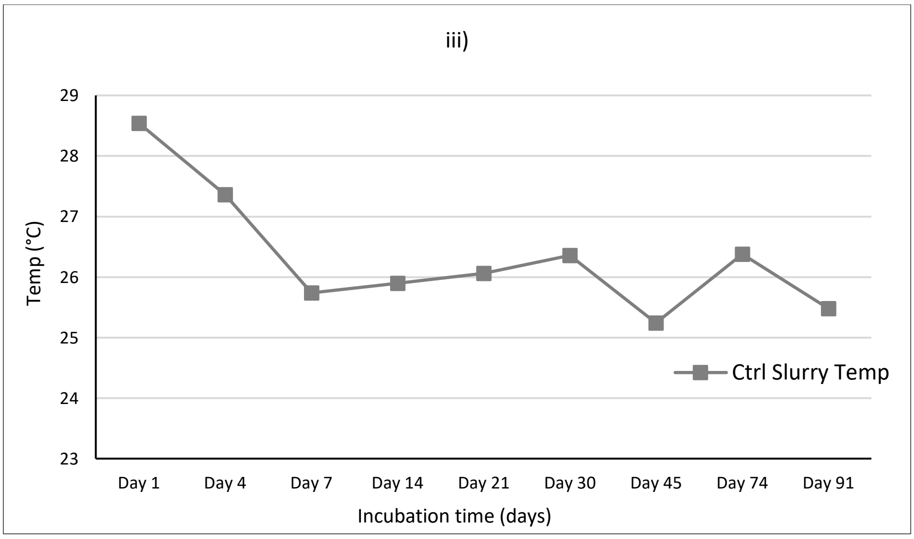
between day 45 to day 91 (Figure 1: ii). The ORP level increased to positive value indicating that the slurry is in highly oxidizing agent and probably oxygen is absorbed into the slurry as it is low in organic matter. Table 1 showed that ORP of treated slurries is significantly different compared to Ctrl due to the presence of organic matters in slurries, anaerobic microbial activities, and organic breakdown.

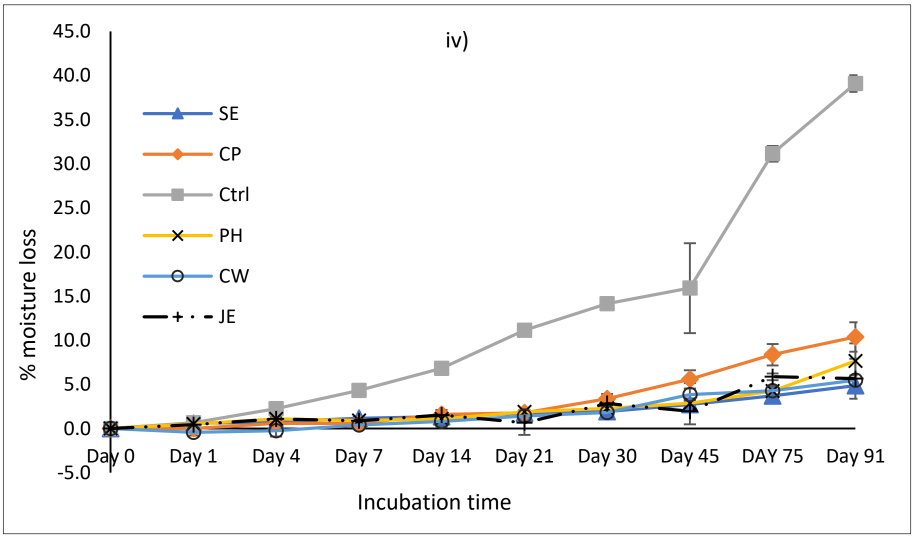
Table 1: Slurry characteristic after 91 days storage.

Treatment	End Observation			
	pH	ORP (*mV*)	Dry Matter Kg^{-1} Fresh Slurry % DM (±SEM)	Volatile solid Kg^{-1} DM % VS (±SEM)
Paddy Husk (SE)	6.9±0.02	-121.0 ±19.36	2.0 ±0.22	72.0 ±1.12
Cocopeat (CP)	7.3±0.02	-239.8 ±15.58	6.9 ±0.25	74.7 ±1.12
Ricestraw (JE)	7.0±0.04	-200.2 ±38.62	2.1 ±0.37	66.5 ±2.47
Chipwood (CW)	7.3±0.03	-95.4 ±10.22	1.0 ±0.32	74.0 ±7.94
Unfilled grains (PH)	6.9±0.02	-150.8 ±24.79	3.0 ±0.67	71.8 ±2.48
Untreated (Ctrl)	8.3±0.21	32.6 ±132.48	2.8 ±0.72	64.5 ±3.80




ii)
ORP level
400
300
200
100
0
-100
-200
-300
-400
Day 1
Day 4
Day 7
Day 14
Day 21
Day 30
Day 45
Day 75
Day 91
Incubation time (days)


iii)
Temp (°C)
29
28
27
26
25
24
23
Ctrl Slurry Temp
Day 1
Day 4
Day 7
Day 14
Day 21
Day 30
Day 45
Day 74
Day 91
Incubation time (days)


iv)
% moisture loss
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
SE
CP
Ctrl
PH
CW
JE
Day 0
Day 1
Day 4
Day 7
Day 14
Day 21
Day 30
Day 45
DAY 75
Day 91
Incubation time

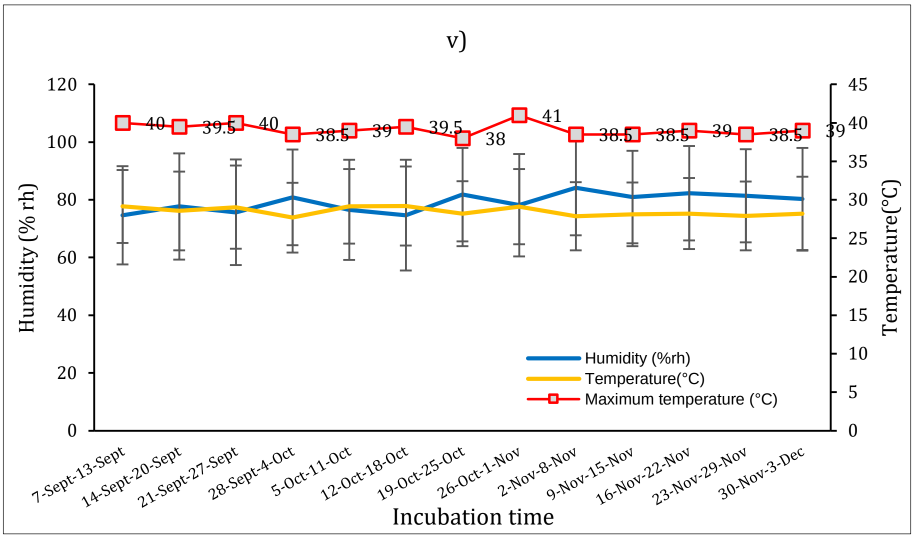


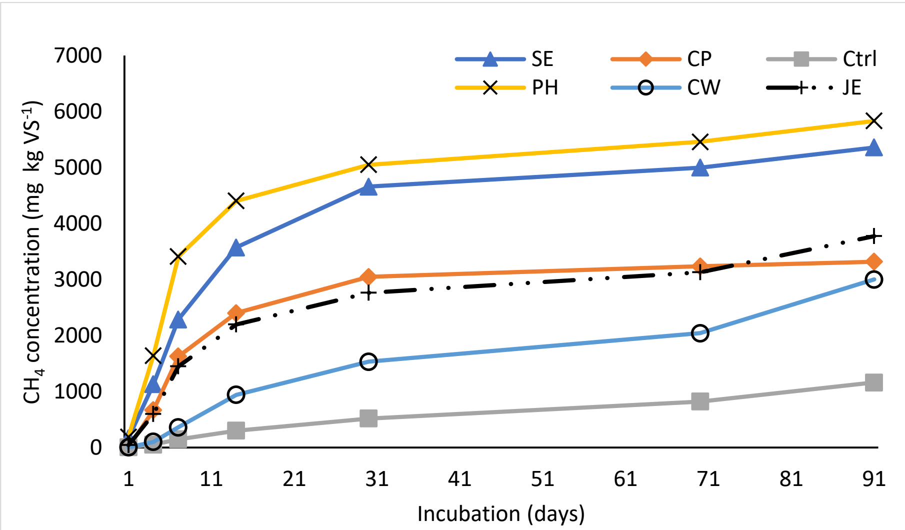
Figure 1 : Observation on i) slurry pH, ii) ORP iii) slurry temperature iv) slurry moisture losses and v) environment temperatures during storage period.

Methane Carbon Emission.

In this study, organic biological waste from agriculture by-products were used to cover slurry surface. Figure 2 revealed that none of the covered slurry have showed a reduction in CH_4 emissions. Those agriculture waste did not act as a physical bio-cover to inhibit CH_4 but do stimulate microbial activities through organic degradation thus resulting in higher cumulative CH_4 emission observed during storage. This finding is similar to a study conducted by Berg et al., 2006 in which the slurries were stored at 25°C. During the study, it was observed that the agriculture waste used as cover partially sank into the slurries. The sinking of this residue act as organic matter addition to the slurries. As a result, utilization of PH, SE, JE, CP and WC contributes more CH_4 emission rather than reduction. The highest in CH_4 emission was from PH, at 401% followed by SE, JE, CP and WC at 361%, 225%, 186% and 158% respectively as compared to Ctrl. The high emission from PH is probably due to its high proportional contents of some fermentable carbohydrates.

Although our study objective is not achieved, some studies had reported a potential use of sawdust, straw and peat as a slurry surface cover to mitigate CH_4. Sawdust were able to block CH_4 emission completely while peat is reported to reduce emission by 88.5% (Matulaitis et al., 2015). Meanwhile, the use of Straw was reported to inhibited CH_4 emission at a range between 24 to 28%. (Pelletier et al., 2005; Guarino et al., 2006; VanderZaag et al., 2009). Higher reduction rate of up to 90% can be achieved if a thicker cover is applied (Pelletier et al., 2005). However, Guarino et al., (2006) claimed the uses of straw is only efficient in a short-term application, such as 1 week. In this study, JE utilization which increases CH_4 emission was similar to a study by Berg et al., (2006) in which CH_4 emission were found to increase by 47% and may increase to up to 67% if used with saccharose. Guarino et al., (2006) on the other hand, found the uses of woodchipped reduced CH_4 emission by 31% in cattle slurry, which also opposes the current findings. Guarino et al., (2006) also reported that the utilization of corn stalk may increase CH_4 emission between 8 to 31% during storage. Pelletier et al., (2005), suggested that bio-cover may remain to float and will not sink if the slurry DM content is higher, resulting in good permeable cover, especially for NH_3 reduction (Pelletier et al., 2005). Although, reports showed slurry covers had an inconsistent impact on CH_4 gas emissions, it generally still be useful to decrease odour, NH_3, H_2S, and CO_2 emissions (Portejoie et al., 2003; English and Fleming, 2006; Zhang et al., 2013; Matulaitis et al., 2015).

Figure 2: Cumulative methane emission during slurry storage with agriculture residue bio-cover.



CONCLUSION

The covering methods by the uses of agriculture by-products investigated in this study were found to stimulate more emission of a potent CH_4. In this case, higher GHG is emitted with the use of organic agricultural waste thus it is concluded that this strategy is not practicable and may increase atmospheric carbon level. Other mitigation approach is needed and shall be further evaluated.

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