

## Odor from anaerobic digestion of swine slurry: influence of pH, temperature and organic loading

Gerardo Ortiz, Cristina Alejandra Villamar\*, Gladys Vidal

University of Concepción/Environmental Science Faculty and EULA-Chile Center – Environmental and Biotechnology Engineering Group, PO Box 160-C – Concepción – Chile.

\*Corresponding author <cvillamar@udec.cl>

Edited by: Paulo Cesar Sentelhas

Received November 08, 2013

Accepted June 11, 2014

**ABSTRACT:** Farm slurry management from storage and/or treatment is the main source of odors from swine production, which are determined by factors such as operational variations (organic loading), cleaning of facilities and animal diet (pH) or environmental conditions (temperature). The aim of this study was to evaluate the influence of pH, temperature and organic loading on odor generation during anaerobic digestion of swine slurry. The methodology employed batch experimental units under controlled pH (6.0, 6.5, 7.0 and 8.0) and temperature (20, 35 and 55 °C) conditions. Additionally, an Upflow Anaerobic Sludge Blanket (UASB) system was operated under two Organic Loading Rate (OLR) conditions as Chemical Oxygen Demand (COD) (Phase I: 0.4 g L<sup>-1</sup> d<sup>-1</sup> of COD, Phase II: 1.1 g L<sup>-1</sup> d<sup>-1</sup> of COD). Odor (batch and UASB reactor) was evaluated by detection and recognition threshold as Dilution Threshold (D-T). Acidic conditions (pH 6.0) and thermophilic temperatures (55 °C) increased odors (1,358 D-T) and acidified the system (Intermediate/Total Alkalinity ratio (IT/TA): 0.85) in batch experiments. Increasing OLR on UASB reactor reduced odors from 6.3 to 9.6 D-T d<sup>-1</sup> due to an increase in the production of biogas (0.4 to 0.6 g g<sup>-1</sup> COD<sub>removed</sub> of biogas).

**Keywords:** anaerobic treatment/storage, odor threshold, operational factors, swine slurry

### Introduction

Inappropriate management of swine slurry generates odorous volatile compounds that can impact rural and peri-urban zones (Donham et al., 2007). Sulfides (24 - 205 mg L<sup>-1</sup> of H<sub>2</sub>S), Volatile Fatty Acids (VFA) (5-79 mg L<sup>-1</sup> of CH<sub>3</sub>COOH), free ammonia (75 - 152 mg L<sup>-1</sup> of NH<sub>3</sub>) and phenols (12-92 mg L<sup>-1</sup> of phenol) are some of the odorous volatile compounds obtained through incomplete anaerobic degradation processes during storage of slurries, whose composition depends on animal diet (Blanes-Vidal et al., 2009). Carbohydrate-based diets increase VFA production, while protein-based diets form ammonium and sulfur compounds (Le et al., 2005). Therefore, specific bacterial groups from slurries (e.g. genera *Eubacterium*, *Clostridium* and others) as well as temperature and pH have influence on odor production.

The temperature during anaerobic digestion affects microbial growth rates and catalyzes chemical reactions, which volatilize certain compounds (Chae et al., 2008). Under psychrophilic (< 20 °C), mesophilic (25 - 35 °C) and thermophilic (55 - 60 °C) conditions, a microbiological imbalance is likely to occur, which reduces methane production from 13 (mesophilic) to 70 % (psychrophilic and thermophilic) (Kashyap et al., 2003; El-Mashad et al., 2004; Chae et al., 2008). The pH has influence on bacterial growth rates and system buffer capacity (Espinoza-Escalante et al., 2009). It is also a key factor in the formation and characterization of VFA and the ammonium/free ammonia equilibrium.

A pH between acid and neutral (pH 5 - 7) promotes butyric acid production, while basic conditions (about pH 8) favor acetic and propionic acid formation (Horiuchi et al., 2002). Furthermore, anaerobic reactors at pH

above 8 promote free ammonia formation over 0.75 g L<sup>-1</sup>, corresponding to about 13 % of total ammonia or ammonium. However, the transfer to the gaseous phase of part of the ammonium is enhanced with the increased temperature (Hansen et al., 1998).

Operational problems due to loading variations are the main cause of odor generation during swine slurry treatment. UASB systems are anaerobic treatment technologies used in this field, which exhibit optimal removal of organic matter and proteins (over 75 % and close to 80 %, respectively) at temperatures between 30 and 35 °C, pH close to 7 and OLR below 1.8 g L<sup>-1</sup> d<sup>-1</sup> of COD. These conditions are related to biogas production (over 0.2 L g<sup>-1</sup> VS<sub>added</sub> of CH<sub>4</sub> or about 0.1 L g<sup>-1</sup> protein<sub>added</sub> of CH<sub>4</sub>) (Sánchez et al., 2005; Chae et al., 2008; Rodríguez et al., 2011), and decrease of VFA (over 60 %) (Sánchez et al., 2005) and ammonium (about 30 %) (Belmonte et al., 2011). Therefore, the aim of this study was to evaluate the influence of pH, temperature and organic loading on the odor from anaerobic digestion of swine slurry.

### Materials and Methods

#### Effluent sampling

Swine slurries were obtained from a fattening farm (8,000 head) located in south-central Chile (36°33'19.61" S, 71°51'49.64" W). Samples were collected after the primary treatment discharge (equalizer, stationary inclined separator mesh and primary settler) and subsequently stored for no more than 1 day, at 4 °C and under dark conditions to avoid loss of odor.

An average organic matter content was observed as chemical oxygen demand of 22.6 g L<sup>-1</sup>, biochemical oxygen demand of 9.9 g L<sup>-1</sup> and nutrient concentration

as total nitrogen of 5.4 g L<sup>-1</sup>, ammonium of 4.7 g L<sup>-1</sup>, total phosphorous of 0.4 g L<sup>-1</sup>. NO<sub>3</sub><sup>-</sup> values were lower than 10 mg L<sup>-1</sup> (Table 1). Moreover, slurries exhibited alkalinity ratios (IA TA<sup>-1</sup>) ranging from 6.2 to 6.8. The detection/recognition threshold of odor varied from 64 to 112 D-T and between 32 and 64 D-T, respectively.

### Experiment types

Odor was evaluated under batch and continuous conditions. The batch reactors were used to measure the effects of pH and temperature under storage conditions (incomplete anaerobic digestion). Meanwhile, a continuous reactor was used to evaluate the effects of organic matter loading on anaerobic treatment of swine slurry.

### Batch reactors

The experimental assay (Table 2) employed duplicate polyethylene bottles of 1.37 L (0.5 L used volume, 9.5 × 8 cm cross-section, 18 cm high) subjected to three temperature conditions by water bath with a thermostat and four pH values adjusted with acidic/basic solutions (10, 5 and 1M of HCl and NaOH). The temperature was modified to certain conditions: psychrophilic (20 °C), mesophilic (35 °C) and thermophilic (55 °C) (El-Mashad et al., 2004). The pH was modified to optimize free ammonia production (pH 8.0), acidification (pH 6.0), neutral conditions (pH 7.0) and the normal slurry state (pH 6.5) (Espinoza-Escalante et al., 2009).

Each experimental unit was monitored considering a storage time of ten days. Odor sampling and physico-chemical parameters were made on aliquots of 5 mL of slurry from each batch reactor. Thus, volume taken during the sampling period (ten days) was not more than

Table 1 – Physicochemical characterization of swine slurries.

Parameter	Unit	Value	
		Mean	Range
pH	-	6.4	6.2 to 6.8
EC	mS cm <sup>-1</sup>	17.8	15.9 to 19.7
Eh	mV	304.1	-301.1 to -307.0
COD	g L <sup>-1</sup> O <sub>2</sub>	22.6	22.1 to 23.1
BOD <sub>5</sub>	g L <sup>-1</sup> O <sub>2</sub>	10	9 to 10
TA	g L <sup>-1</sup> CaCO <sub>3</sub>	8.9	7.1 to 12.1
IA	g L <sup>-1</sup> CaCO <sub>3</sub>	4.6	3.1 to 8.3
TN	g L <sup>-1</sup>	5.4	5.3 to 5.5
NH <sub>4</sub> <sup>+</sup>	g L <sup>-1</sup>	4.7	2.8 to 5.6
TP	g L <sup>-1</sup>	0.4	0.3 to 0.4
Odor detection threshold	D-T	84.7	64.0 to 112.0
Odor recognition threshold	D-T	45.3	32.0 to 64.0

Table 2 – Experimental design of batch reactors.

Variable	pH <sub>1</sub> (6.0)	pH <sub>2</sub> (6.5)	pH <sub>3</sub> (7.0)	pH <sub>4</sub> (8.0)
T <sub>1</sub> (20 °C)	T <sub>1</sub> pH <sub>1</sub>	T <sub>1</sub> pH <sub>2</sub>	T <sub>1</sub> pH <sub>3</sub>	T <sub>1</sub> pH <sub>4</sub>
T <sub>2</sub> (35 °C)	T <sub>2</sub> pH <sub>1</sub>	T <sub>2</sub> pH <sub>2</sub>	T <sub>2</sub> pH <sub>3</sub>	T <sub>2</sub> pH <sub>4</sub>
T <sub>3</sub> (55 °C)	T <sub>3</sub> pH <sub>1</sub>	T <sub>3</sub> pH <sub>2</sub>	T <sub>3</sub> pH <sub>3</sub>	T <sub>3</sub> pH <sub>4</sub>

10 % of the total volume. The 10 days-time period was chosen because in previous experiments an odor detection threshold below 2.0 D-T (minimum detection limit of the olfactometer) was observed. Odor monitoring measurements considered the determination of ammonium (total ammonia), free ammonia and Total and Intermediate Alkalinity (TA and IA).

### UASB reactor

A tubular glass reactor UASB with 2.75 L capacity (2.5 L used volume, 58 cm high, and 8.4 cm diameter) was employed. The system was maintained under mesophilic conditions (35 °C) using heated water recirculated by peristaltic pumping from a thermostat. The upflow-feeding was continuous though a peristaltic pump for 141 days. The system worked in two phases, which considered average Hydraulic Retention Times (HRT) of 9 (Phase I) and 10 days (Phase II). The biological granule concentration in the reactor was about 11.5 g L<sup>-1</sup> of VSS.

The UASB system was fed with an average loading of 0.4 ± 0.1 g L<sup>-1</sup> d<sup>-1</sup> of COD (Phase I) and 1.1 ± 0.2 g L<sup>-1</sup> d<sup>-1</sup> of COD (Phase II), which were obtained by dilution of slurry with clean water to ratios of 0.5:1.5 (Phase I) and 1:1 (Phase II). Biogas flows from the UASB reactor were measured with a device described by Veiga et al. (1990). Slurry samples of input and output from the UASB system were taken daily to determine their odor and physicochemical characteristics. The details of the UASB system are described in Figure 1.

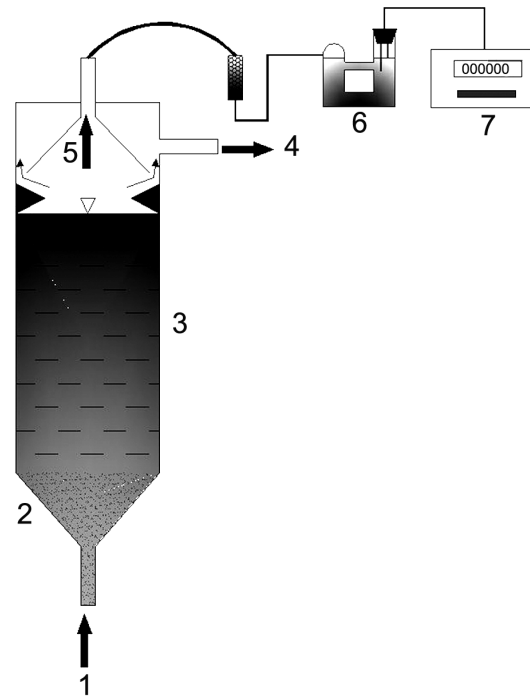


Figure 1 – Upflow Anaerobic Sludge Blanket (UASB) reactor scheme. (1) Wastewater input, (2) granule biomass, (3) reactor, (4) wastewater output, (5) biogas output, (6) glass columns with saline solution, (7) biogas counter.

### Odor detection and recognition threshold

Odor measurements were performed in the batch systems and the UASB reactor, which were obtained via dilution to threshold by olfactometry (D-T). This sensory technique uses olfactometer equipment, which dynamically dilutes odorous air with ambient air (filtered by activated carbon filters). The odor is measured as a dilution factor (D-T), or the value representing how many times the odorous air had to be diluted until it could just be detected or recognized by one or more individuals (panelists):

$$D - T = DT^{-1} \quad (1)$$

in which D-T denotes the dilution ratio, D is the carbon-filtered pure air volume and T is the odorous air volume. The odor recognition threshold requires less carbon-filtered air than the odor detection threshold. Therefore, the odor detection threshold is always higher than the odor recognition threshold. The detection and recognition threshold of odor definition is described by ASTM standard E679-04 (2004a).

Odors were measured with a portable Nasal Ranger. Prior investigations show that Nasal Ranger equipment is efficient in the measurement of odors resulting from livestock production (Newby, 2004). Thus, it has less variability and correlation ( $R^2 = 0.49$  to  $0.51$ ) with the information provided by dynamic olfactometry in the laboratory (Dynamic, Triangular Olfactometry Forced Choice), also that the variability of panelists' responses is low with both devices. Potential measurement errors using the Nasal Ranger field olfactometers are largely due to the range of available dilutions and incremental differences in dilutions between readings or sub-sample events.

In this investigation, odor measurements from the Nasal Ranger required three steps. In the first part, four panelists were chosen (two men and two women), whose ages ranged from 25 to 35 years, in accordance with ASTM standard E1432 (2004b). Panelists were exposed to an olfactory sensitivity test called "Single Test Administered to  $\eta$ -butanol odor pen from the pen kit" described by Hummel et al. (1997). In the second part, the Nasal Ranger was calibrated to detect/recognize odor from swine slurries according to the range available to the device (dilution factors or D-T from 60 to 2). Finally, the standardized panelists and the calibrated Nasal Ranger were used to obtain odor measurements in batch systems and the UASB reactor.

The Nasal Ranger calibration procedure used dilutions of 50, 25, 12.5 and 6.25 % swine slurry. Dilutions were made in volumetric flasks (class A) with distilled water. Measurements were performed immediately in an isolated room. The odor evolution was evaluated daily over a 10-day period with direct measurements on swine slurries. Results of each dilution are described in Figure 2. The dilution range suitable to establish detection/recognition threshold of odor of swine slurries was

between 25 and 6.25 % because at 50 % dilution, the detection threshold exceeded the range established by the device ( $> 60$ ).

Measurements in the batch systems and the UASB reactor were made with the range established by calibration and using the same procedure. Batch samples were taken daily for 10 days. Meanwhile, reactor samples were taken at the input and output of the UASB system considering the residence time. Finally, all D-T values were reported as the geometric mean between boundaries from dilution ranges measured with the Nasal Ranger ( $> 60$ , 60-30, 30-15, 15-7, 7-4, 4-2,  $< 2$ ).

The Variation Rate of Odor (VRO) from batch reactors was determined as the odor slope (detection/recognition threshold) at each interval. Negative VRO values show that odor decreased over time. Equation 2 details the determination of the VRO:

$$VRO = [(D - T_i) - (D - T_{i+1})] (t_i - t_{i+1})^{-1} \quad (2)$$

in which VRO is the Variation Rate of Odor  $D-T$   $d^{-1}$ ,  $D-T_i$ ,  $D-T_{i+1}$  corresponding to thresholds for detection/recognition start and end at each interval as  $D-T$ ,  $t_i$  and  $t_{i+1}$  are odor threshold start and end at each interval as days.

Removal efficiency of odor threshold, organic matter and transfer to the gaseous phase of part of ammonium from UASB reactor, were determined according to Equation 3, as follows:

$$Ef = 100 [(C_{initial} - C_{end}) C_{initial}^{-1}] \quad (3)$$

in which Ef is the removal efficiency (%),  $C_{initial}$  is input loading (influent) and  $C_{end}$  is output loading (effluent). The difference between  $C_{initial}$  and  $C_{end}$  corresponding to loading removed ( $C_{removed}$ ).  $C_i$  values are expressed in mg or  $D-T$   $d^{-1}$ .

### Analytical methods

Swine slurry samples were physicochemically characterized from measurements of Chemical Oxygen Demand (COD), Biological Oxygen Demand ( $BOD_5$ ), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS) and Ammonium ( $NH_4^+$ ), using methods described by APHA (2005). Total Nitrogen (TN) (2,6-dimethylphenol method) and Total Phosphorus (TP) (Phosphor-molybdenum blue method) were evaluated by spectroquant NOVA-60 specific kits. Total and Partial Alkalinities (TA and PA) were determined by the method described by Ripley et al. (1986). The Intermediate Alkalinity (IA) was obtained from the difference between TA and PA. Finally, pH, Redox Potential (Eh), Electric Conductivity (EC) and temperature were assessed with an Oakton PC650 portable meter.

It is important to specify that the  $IA/TA^{-1}$  ratio was assessed in order to indirectly establish VFA accumulation. Values above 0.4 usually involve VFA accumulation

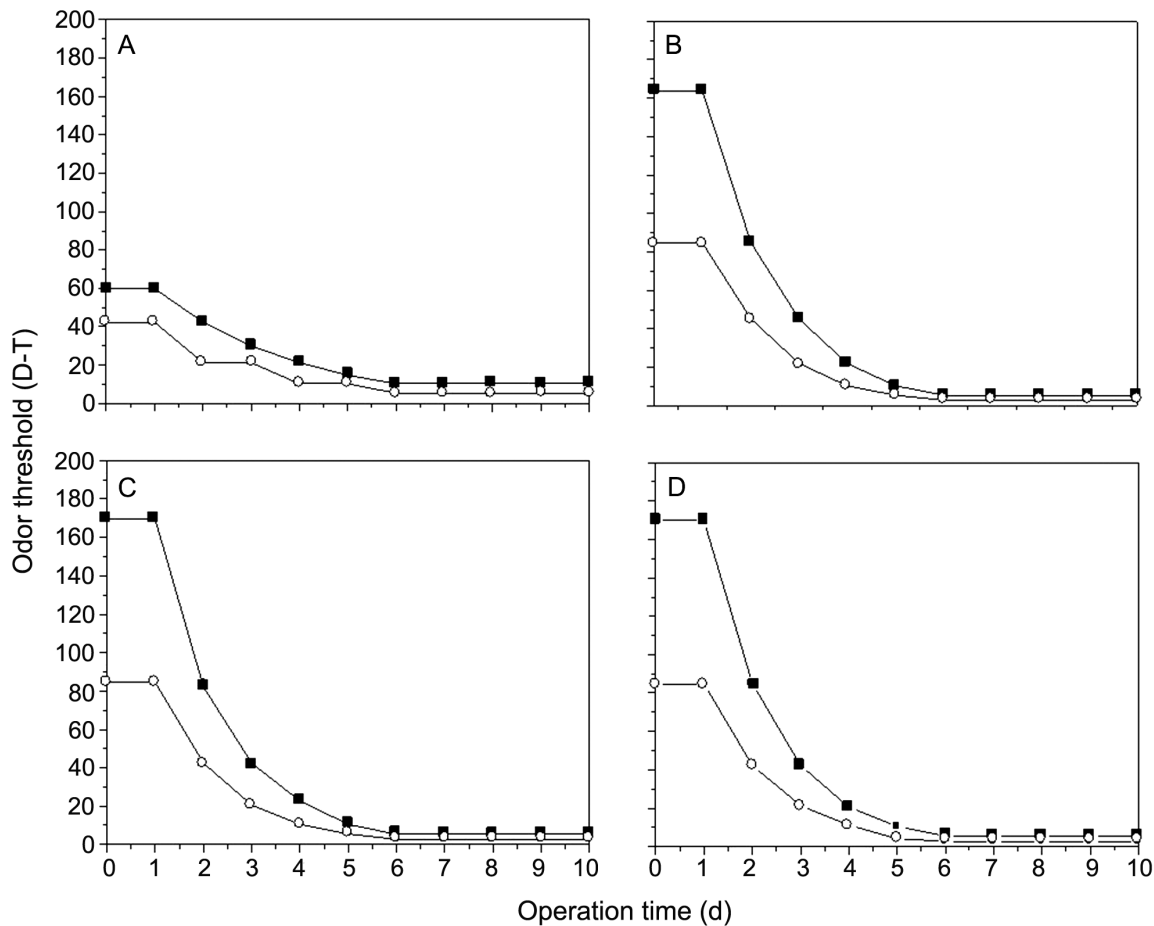


Figure 2 – Nasal Ranger calibration for odors from swine slurries at 50, 25, 12.5 and 6.25 % dilution. A) 50 %, B) 25 %, C) 12.5 %, D) 6.25 %. (○) Odor detection threshold, (■) Odor recognition threshold.

in the system (Ripley et al., 1986). On the other hand, the free ammonia evolution was theoretically estimated by equation (4) described according to Hansen et al. (1998):

$$[\text{NH}_3][\text{NH}_4^+]^{-1} = (1 + 10^{\text{pKa} - \text{pH}})^{-1} \quad (4)$$

in which  $[\text{NH}_3]$  corresponds to free ammonia concentration in  $\text{mg L}^{-1}$ ,  $[\text{NH}_4^+]$  to total ammonia or ammonium content in  $\text{mg L}^{-1}$ ,  $\text{pKa}$  to the logarithm of the acid dissociation constant, given by  $(0.09018 + 2729.92/T)$ , and  $T$  to temperature in K.

#### Statistical analysis

Data from batch experimental units and the UASB reactor were evaluated by variance analysis. The statistical analysis considered two factors (pH, temperature) in the batch units and one factor (organic loading rate) in the UASB reactor. In the experimental batch units the variables subjected to statistical analysis were the odor detection/recognition threshold, free ammonia and  $\text{IA}/\text{TA}^{-1}$  ratio. Meanwhile, in the UASB reactor the variables analyzed were odor threshold reduction, organic load-

ing removed and free ammonia/biogas. Normality and variance homogeneity were previously verified by the Levene and Shapiro Wilks tests, respectively. Nonparametric analysis (Kruskal Wallis test) was used when distributional assumptions (homogeneity and normality) were not met. The significance level tested was 0.05. The statistical software was Infostat 2009.

## Results and Discussion

### Influence of pH and temperature on odor generation: Batch experiments

The first interval (0 to 1 day) was not reported in Figure 3 due to the fact that it did not exhibit changes in the odor detection/recognition threshold. The general trend in all tested pHs was an initial increase (1<sup>st</sup> or 2<sup>nd</sup> day) in odor generation (increased detection/recognition threshold) as temperature increased. Specifically, thermophilic conditions ( $T_3 = 55^\circ\text{C}$ ) in this study registered the highest increased odor thresholds, which were between 36 ( $\text{pH}_1 = 6.0$ ) and 17 (rest of pHs) times higher than previously characterized swine slurry values. From

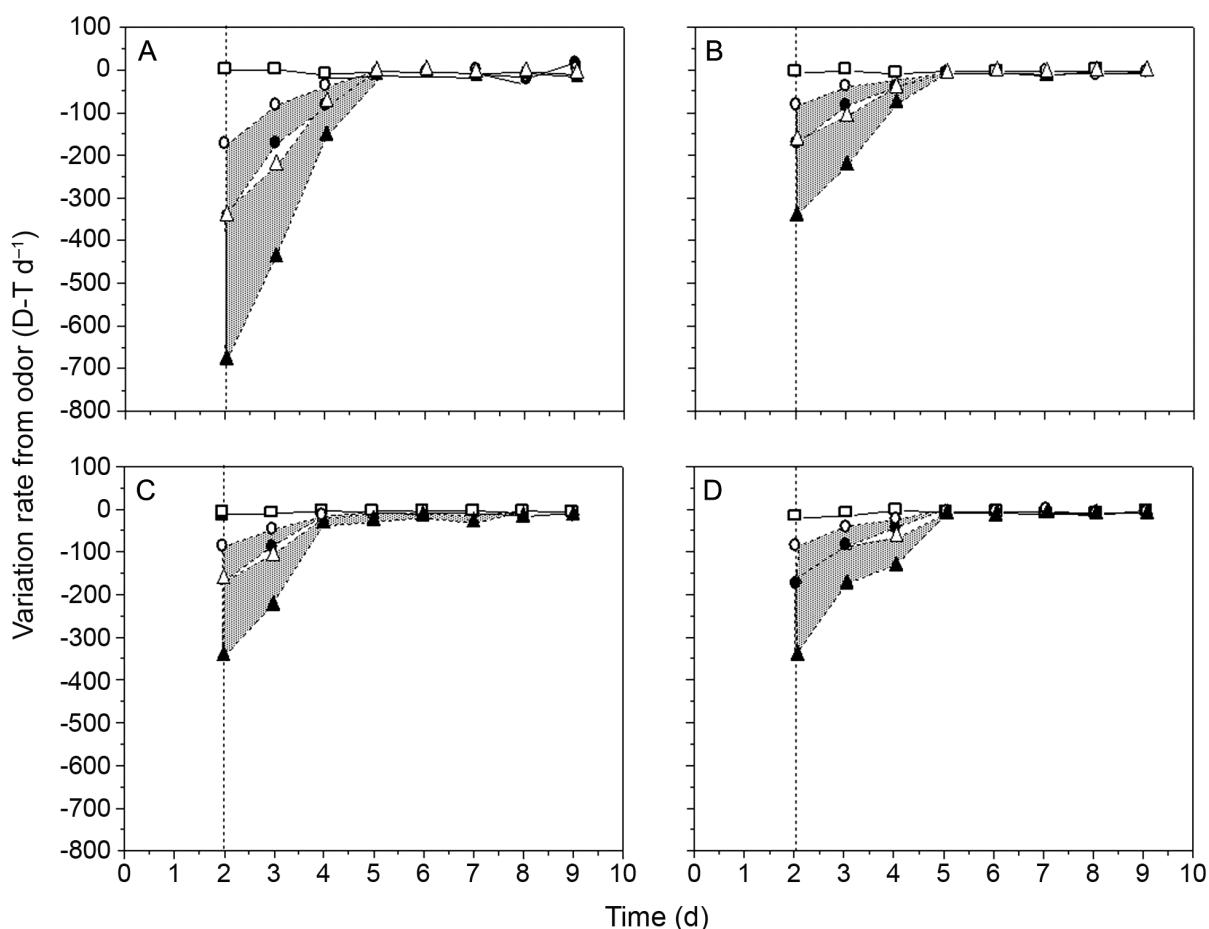


Figure 3 – Variation rate of odor at each pH and temperature. A) 6. B) 6.5. C) 7. D) 8. Odor detection threshold (▲) 55, (●) 35, (■) 20 and Odor recognition threshold (△), 55 (○) 35, (□) 55.

then on, all batch units decreased the odor detection/recognition threshold by up to 65 % during the first five days of storage. Thus, under acid conditions ( $\text{pH}_1 = 6.0$ ) the maximum VRO values were recorded, which ranged from -79 ( $T_1 = 20 \text{ }^\circ\text{C}$ ) to -678 ( $T_3 = 55 \text{ }^\circ\text{C}$ ) D-T d<sup>-1</sup>. Therefore, the temperature functioned as a determining factor in odor generation, while pH conditioned odor generation time.

Thermophilic temperatures (55 °C) increase anaerobic hydrolysis rates, favoring VFA formation with respect to mesophilic conditions (35 °C) (Labatut et al., 2013). In addition, increased temperature has a direct and exponential influence on increased free ammonia (Rajagopal et al., 2013). Therefore, under thermophilic conditions, VFA and free ammonia increased. However, Horiuchi et al. (2002) suggest that increasing proton H<sup>+</sup> favor butyrate production (> 60 % volatile organic acids) with respect to acetate and propionate. Butyrate has a detection threshold 1,000 times lower than acetate and propionate (Mackie et al., 1998). Therefore, this suggests the reasons that the highest odor threshold and VRO were recorded in  $\text{pH}_1 T_3$ .

The specific temperature effects on odor generation have been reported in the bibliography. Pan and De-Bruyn (2007) found an increase in the odor threshold of swine facilities of about 10 D-T between 20 and 30 °C. Furthermore, during the composting of swine slurry, it has been observed that increasing the temperature from 30 to 70 °C produces an increase in odor concentration (30 OU m<sup>-3</sup> d<sup>-1</sup>) (Hanajima et al., 2010).

Figure 4 shows the relationship between the detection/recognition threshold of odor (a), IA TA<sup>-1</sup> (B) and free ammonia (C) at each pH and temperature. The detection/recognition threshold range (Figure 4A) (4 to 1,358.0 D-T), alkalinity ratio (Figure 4B) (0.2 to 0.9) and free ammonia (Figure 4C) (1.4 to 1,347.0 mg L<sup>-1</sup>) increased with an increase in temperature from 20 to 55 °C. Therefore,  $T_3 \text{pH}_1$  (55 °C, 6.0) presented higher values of odor threshold (2 and 17 times) and alkalinity ratio (1.3 to 1.9 time) than the rest of the experimental units. Meanwhile,  $T_3 \text{pH}_4$  (55 °C, 8.0) evidenced the highest values of free ammonia (6 and 200 times). Regarding pH, the detection/recognition threshold of odor range was lower ( $p < 0.05$ ) at 20 °C; while IA TA<sup>-1</sup> and

free ammonia increased ( $p < 0.05$ ) with an increase in temperature. In relation to temperature, odor threshold ranges showed no difference ( $p > 0.05$ ) to different pHs; however, alkalinity decreased ( $p < 0.05$ ) and free ammonia increased ( $p < 0.05$ ) with increased pH.

In summary, the results exhibited similar behavior between the detection/recognition threshold of odor and alkalinity ratio. Free ammonia had an independent behavior. In this regard, reactors fed with swine slurry have reported increased free ammonia ( $0.8 - 1.6 \text{ g L}^{-1}$  of  $\text{NH}_3$ ) and VFA ( $4.8 - 11.5 \text{ g L}^{-1}$  of  $\text{CH}_3\text{OOH}$ ) by increasing the temperature from 37 to 55 °C (Hansen et al., 1998). This confirms that temperature enhances the gen-

eration of these compounds. Meanwhile, pH favors the dominance of free ammonia (pH = 8.0) and VFA (pH = 6.0). Therefore, the higher odor generation of acid pH observed in this work is related to the fact that acetic acid (VFA) has a lower odor detection threshold ( $1,000 \mu\text{g L}^{-1}$ ) than free ammonia ( $4,700 \mu\text{g L}^{-1}$ ) (Mackie et al., 1998). With regard to this fact, some authors mention the relationship between odor and the  $\text{IA}/\text{TA}^{-1}$  ratio, also noting synergism with odor from various acids (Zahn et al., 2001).

### Relationship between odor generation and biogas production: UASB reactor

During Phase I ( $0.4 \text{ g L}^{-1} \text{ d}^{-1}$  of COD), organic matter removal efficiency and transfer to the gaseous phase of part of ammonium were up 72 % and 26 %, respectively (Table 3). During Phase II ( $1.1 \text{ g L}^{-1} \text{ d}^{-1}$  of COD), organic matter removal efficiency and transfer to the gaseous phase of part of ammonium were, on average, 70 % and 25 %, respectively. Sánchez et al. (2005) and Rodríguez et al. (2011) have reported that a UASB fed with swine slurry and a loading operation lower than  $1.0 \text{ g L}^{-1} \text{ d}^{-1}$  of COD removes 80 % of organic matter on average. Anaerobic reactors with loadings of around  $1.0 \text{ g L}^{-1} \text{ d}^{-1}$  of COD often report transfer to the gaseous phase of part of ammonium close to 29 % (Belmonte et al., 2011).

During Phases I and II, the alkalinity ratio decreased from 0.5 to 0.3 and pH increased from 7.1 to 8.1. This is also related to partial alkalinity increasing from 2 to 5 times in the effluent. An increase in the  $\text{HCO}_3^-$  ion from anaerobic processes at output is often associated with the presence and reaction of  $\text{CO}_2$  and  $\text{NH}_3$  from nitrogen breakdown compounds, whereas alkalinity ratios exceeding 0.4 at output correspond to VFA accumulating in the system (Ripley et al., 1986). In this regard, UASB systems with loadings above  $2.0 \text{ g L}^{-1} \text{ d}^{-1}$  of COD have shown an alkalinity ratio over 0.4 and VFA accumulation with average values of  $800 \text{ mg L}^{-1}$  (Sánchez et al., 2005). Meanwhile, results obtained in this study showed that in loadings of  $1.1 \text{ g L}^{-1} \text{ d}^{-1}$  of COD, there is no VFA accumulation in the system ( $0.1 < \text{IA}/\text{TA}^{-1} < 0.4$ ).

Odor detection thresholds were reported at  $0.4 \text{ g L}^{-1} \text{ d}^{-1}$  of COD (Phase I) and at  $1.1 \text{ g L}^{-1} \text{ d}^{-1}$  of COD (Phase II) with corresponding values from 21.2 to 42.4 and from 42.4 to 84.9 D-T, respectively. Meanwhile, odor recognition thresholds varied from 10.3 to 21.2 (Phase I) and from 20.5 to 42.4 (Phase II). UASB system phases were able to reduce the detection/recognition of odor to minimum detectable values (2.0 - 2.8) corresponding to an average removal efficiency of 95 %.

In Phase I, the odor threshold decreased to rates between 1.0 and 7.3 D-T  $\text{d}^{-1}$ , organic loading was reduced to  $0.3 \text{ g L}^{-1} \text{ d}^{-1}$  of COD and biogas and free ammonia were  $0.4 \text{ L g}^{-1} \text{ COD}_{\text{removed}}$  of biogas and  $31.2 \text{ mg L}^{-1}$  of  $\text{NH}_3$ , respectively (Figure 5). In Phase II, the odor threshold decreased to rates between 1.5 and 11.1 D-T  $\text{d}^{-1}$ , organic loading was decreased to  $0.7 \text{ g L}^{-1} \text{ d}^{-1}$  of COD, and biogas and free ammonia were  $0.6 \text{ L g}^{-1} \text{ COD}$

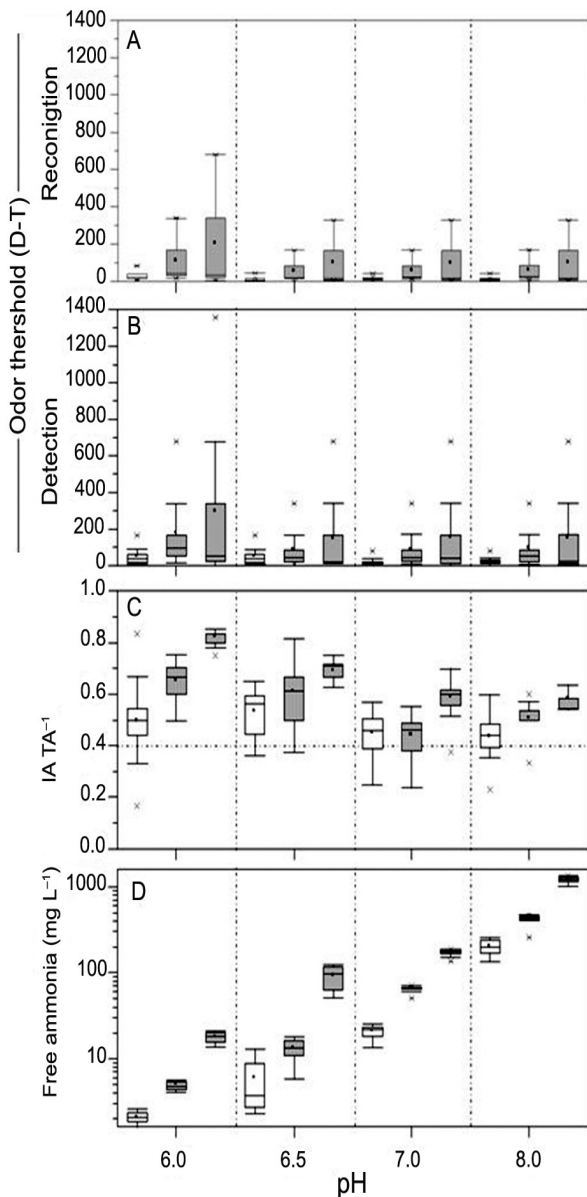


Figure 4 – A) Odor recognition threshold, B) Odor detection threshold, C)  $\text{IA}/\text{TA}^{-1}$  and D) Free ammonia per pH A) (□) 20, B) (▨) 35, (■) 55.

Table 3 – Operating parameters of the Upflow Anaerobic Sludge Blanket (UASB) reactor during study period.

Parameter	Unit	Phase			
		I		II	
		Influent	Effluent	Influent	Effluent
Operation time	d	48		93	
Flow	L d <sup>-1</sup>	0.3 (0.2 to 0.5)		0.3 (0.2 to 0.4)	
HRT	d	9 (8 to 11)		10 (7 to 13)	
pH		7.1 (6.8 to 7.3)	8.0 (7.8 to 8.2)	7.1 (6.8 to 7.3)	8.1 (7.8 to 8.5)
OLR	g L <sup>-1</sup> d <sup>-1</sup> COD	0.4 (0.2 to 0.6)	0.1 (0.1 to 0.2)	1.1 (0.7 to 1.6)	0.3 (0.1 to 0.5)
NLR	g L <sup>-1</sup> d <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	0.06 (0.04 to 0.09)	0.05 (0.03 to 0.07)	0.15 (0.08 to 0.25)	0.10 (0.06 to 0.16)
IA TA <sup>-1</sup>		0.5 (0.5 to 0.6)	0.2 (0.1 to 0.3)	0.5 (0.4 to 0.6)	0.3 (0.1 to 0.4)
Odor detection threshold	D-T	38.6 (21.2 to 42.4)	2.8	74.5 (42.4 to 84.9)	2.4 (2.0 to 2.8)
Odor recognition threshold	D-T	19.2 (10.3 to 21.2)	2.0	37.1 (20.5 to 42.4)	2.0

( ) = range, HRT = Hydraulic Rate Time, OLR = Organic Loading Rate, NRL = Nitrogen Loading Rate, IA/TA-1 = alkalinity ratio.

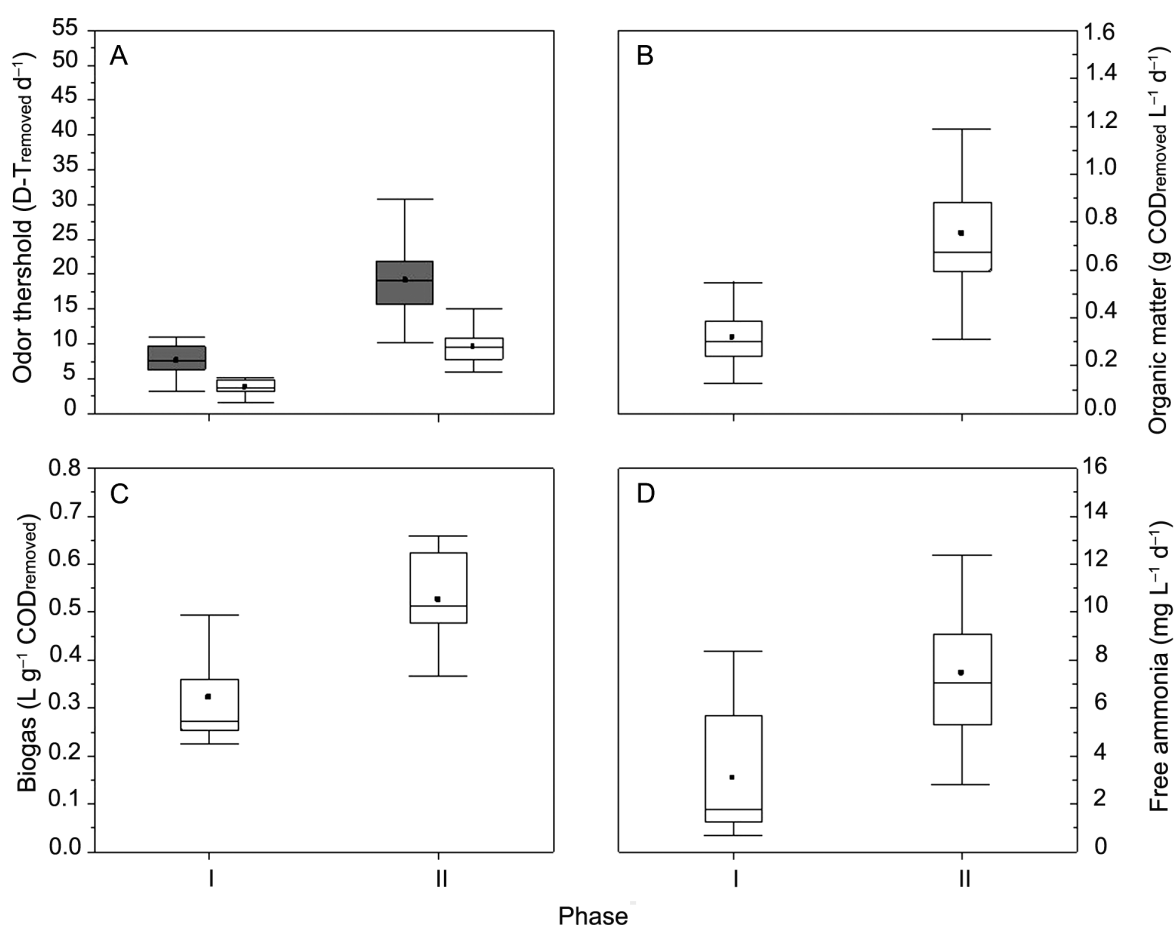


Figure 5 – Odor threshold reduced relationship with ORL, biogas and free ammonia from UASB reactor. A) (■) Odor detection threshold (□) Odor recognition threshold. B) Organic matter C) Biogas. D) Free ammonia.

of biogas and 62.1 mg L<sup>-1</sup> of NH<sub>3</sub>, respectively. Findings of the total UASB system operation show that the increased OLR (0.4 to 1.1 g L<sup>-1</sup> d<sup>-1</sup> of COD) decreases odors (1.7 times), but increases the biogas production (1.6 times) and free ammonia (2.2 times). Therefore, the odor decrease depends on the organic matter removal by biogas production.

## Conclusions

During the incomplete anaerobic digestion of stored swine slurry, the pH (favors bacterial growth) allows the intermediate compounds production from the anaerobic process (volatile fatty acids, free ammonia). Meanwhile, the temperature (catalyzes the biochemical

reactions) intensifies the odoriferous compounds formed by other reactions under a given pH. Thus, stored swine slurry generates more odors by acidification (volatile acids fatty production) than by free ammonia production, process that is favored at acidic pH6 and intensified at thermophilic temperatures (55 °C).

Anaerobic treatment of swine slurry reduced odors, because it transforms volatile fatty acids (main cause of odors) into biogas. Therefore, anaerobic operation in optimal organic loading is an effective strategy in mitigating odors from the slurries.

### Acknowledgements

This study was supported by CONICYT/PBCT (Grant TPI-01), Innova Bio-Bio (Grant 07-PC S1-198), Red Doctoral REDOC.CTA, MINEDUC project UCO 1202 at University of Concepción and CONICYT/FONDAP/15130015. Authors thank Mr. C. Contreras from Sucesion Yanine for use of their facilities in the realization of this study and Ms. María José Ortega with Ms. Rocío Baeza for collaboration in the laboratory.

### References

- American Public Health Association [APHA]. 2005. Standard Methods for Examination of Water and Wastewater. 21ed. APHA/AWWA/WPCF, Washington, DC, USA.
- American Society for Testing and Materials [ASTM]. 2004a. E679 - Standard Practice for Determination of Odor and Taste Thresholds by a Forced-Choice Ascending Concentration Series Method of Limits. ASTM, Philadelphia, PA, USA.
- American Society for Testing and Materials [ASTM]. 2004b. E1432 - Standard Practice for Defining and Calculating Individual and group Sensory Thresholds from Forced-Choice Data Sets of Intermediate Size. ASTM, Philadelphia, PA, USA.
- Blanes-Vidal, V.; Hansen, M.N.; Adamsen, A.P.S.; Feilberg, A.; Petersen, S.O.; Jensen B.B. 2009. Characterization of odor released during handling of swine slurry. Part II. Effect of production type, storage and physicochemical characteristics of the slurry. *Atmospheric Environment* 43: 3006-3014.
- Chae, K.J.; Jang, A.; Yim, S.K.; Kim, I.S. 2008. The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure. *Bioresource Technology* 99: 1-6.
- Donham, K.J.; Wing, S.; Osterberg, D.; Flora, J.L.; Hodne, C.; Thu, K.M.; Thorne, P.S. 2007. Community health and socioeconomic issues surrounding concentrated animal feeding operations. *Environmental Health Perspectives* 115: 317-320.
- El-Mashad, H.M.; Zeeman, G.; Loon, W.K.P. van; Bot, G.P.A.; Lettinga, G. 2004. Effect of temperature and temperature fluctuation on thermophilic anaerobic digestion of cattle manure. *Bioresource Technology* 95: 191-201.
- Espinoza-Escalante, M.; Pelayo-Ortíz, C.; Gutierrez, H.; Gonzalez, Y. 2009. Anaerobic digestion of the vinasses from the fermentation of *Agave tequilana* Weber to tequila: The effect of pH, temperature and hydraulic retention time on the production of hydrogen and methane. *Biomass & Bioenergy* 33: 14-20.
- Hanajima, D.; Kuroda, K.; Morishita, K.; Fujita, J.; Maeda, K.; Morioka, R. 2010. Key odor components responsible for the impact on olfactory sense during swine feces composting. *Bioresource Technology* 101: 2306-2310.
- Hansen, H.H.; Angelidaki, I.; Ahring, B.K. 1998. Anaerobic digestion of swine manure: Inhibition by ammonia. *Water Research* 32: 5-12.
- Horiuchi, J.I.; Shimizu, T.; Tada, K.; Kanno, T.; Kobayashi, M. 2002. Selective production of organic acids in anaerobic acid reactor by pH control. *Bioresource Technology* 82: 209-213.
- Hummel, T.; Sekinger, B.; Wolf, S.R.; Pauli, E.; Kobal, G. 1997. 'Sniffin' sticks': olfactory performance assessed by the combined testing of odor identification, odor discrimination and olfactory threshold. *Chemical Senses* 22: 39-52.
- Kashyap, D.R.; Dadhich, K.S.; Sharma, S.K. 2003. Biomethanation under psychrophilic conditions: a review. *Bioresource Technology* 87: 147-153.
- Labatut, R.A.; Angenent, L.T.; Scott, N.R. 2013. Conventional mesophilic vs. thermophilic anaerobic digestion: A trade-off between performance and stability? *Water Research* 53: 249-258.
- Le, P.D.; Aarnink, A.J.A.; Ogink, N.W.M.; Becker, P.M.; Verstegen, M.W.A. 2005. Odour from animal production facilities: its relationship to diet. *Nutrition Research Reviews* 18: 3-30.
- Newby, B.D. 2004. Ambient and odour testing concentrated animal feeding operations using field and laboratory olfactometers. *Water Science and Technology* 50: 109-114.
- Pan, L.S.X.; DeBruyn, J. 2007. Factor analysis of downwind odours from livestock farms. *Biosystems Engineering* 96: 387-397.
- Rajagopal, R.; Massé, D.I.; Singh, G. 2013. A critical review on inhibition of anaerobic digestion process by excess ammonia. *Bioresource Technology* 143: 32-641.
- Ripley, L.E.; Boyle, W.; Converse J. 1986. Improved alkalimetric monitoring for anaerobic digestion of high strength wastes. *Journal of Water Pollution Control Federation* 58: 406-411.
- Rodríguez, D.C.; Belmonte, M.; Peñuelas, G.; Campos, J.L.; Vidal, G. 2011. Behavior of molecular weight distribution for the liquid fraction of pig slurry treated by anaerobic digestion. *Environmental Technology* 32: 419-425.
- Sánchez, E.; Borja, R.; Travieso, L.; Martín, A.; Colmenarejo, M.F. 2005. Effect of organic loading rate on the stability, operational parameters and performance of a secondary upflow anaerobic sludge bed reactor treating piggery waste. *Bioresource Technology* 96: 335-344.
- Veiga, M.C.; Soto, R.; Méndez, R.; Lema, J.M. 1990. A new device for measurement and control of gas production by bench scale anaerobic digesters. *Water Research* 24: 1551-1554.
- Zahn, J.A.; DiSpirito, A.A.; Do, Y.S.; Brooks, B.E.; Cooper, E.E.; Hatfield, J.L. 2001. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. *Journal of Environmental Quality* 30: 624-634.