III Symposium on Agricultural and Agroindustrial Waste Management
March 12-14, 2013-Sao Pedro, SP, Brazil

SHORT-CHAIN FATTY ACIDS GENERATION IN SWINE MANURE PITS STORED AT LOW TEMPERATURE

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ABSTRACT: Currently, there are many alternatives to treat the swine manure with high efficiency. In this context, the storage time is an important step in the treatment of this effluent. The hydrolysis and acidogenesis are steps of anaerobic digestion responsible for the short-chain fatty acids (SCFA) generation, and usually occur even when the swine wastewater is stored before the treatment. Because the SCFA are an important substrate to wastewater treatment, the hydrolysis and acidogenesis have a significant contribution on the treatment efficiency. In this work, we studied the behavior of SCFA generation in swine manure storage at 10 °C. We observed that the SCFA formation in the first 8 days followed a linear progression. Acetic, propionic and butyric acids were the most representative SCFAs. Those result showed that hydrolysis and acidogenesis occurs before the wastewater treatment begin even at low temperature.

KEYWORDS: hydrolysis, acidogenesis, swine manure storage.

INTRODUCTION

The wastewater from confined animal feeding operations (CAFOs) has a high environmental impact potential. CAFOs effluent management and treatment are important to avoid contaminant input, e.g. nutrients and organic matter, in soil, air and surface water and groundwater (Zhu, 2000; Kunz et al., 2009a; Techio, et al., 2011).

There are many alternatives to minimize the swine manure environmental impacts (Kunz et al., 2009b). Two main ways, based on heterotrophic biological steps treatment are usually used. One of them is nutrients removal, mainly nitrogen by nitrification-denitrification and other is anaerobic digestion to energy recovery by the biogas (Burton and Turner, 2003). In both treatments, organic carbon is necessary and its bioavailability will determine the process efficiency. In this way, organic matter hydrolysis and acidogenesis generate organic carbon species highly biodegradable, that can increase the assimilation by anaerobic (biodigestion) and anoxic (denitrificaction) microorganisms.

Hydrolysis is the process in which hydrolytic bacteria, using extracellular enzymes, cleave complex organic compounds as starch, pectin, cellulose, hemicellulose, lipids and proteins, to simpler compounds as amino acids and volatile fatty acids (Evans and Furlong, 2011).

Acidogenesis is the process that sugars, amino acids, peptides, long-chain fatty acids, and other low-molecular weight molecules are metabolized to short-chain fatty acids (SCFA), CO_2, H_2, NH_3, SO_4^{-2} and alcohols by the acidogenic bacteria. SCFA produced during acidogenesis include formic acid (CH_2O_2), acetic acid ($C_2H_4O_2$), propionic acid ($C_3H_6O_2$), butyric and iso-butyric acid ($C_4H_8O_2$), iso-valeric and valeric acid ($C_5H_{10}O_2$), caproic and iso-caproic acid ($C_6H_{12}O_2$) and heptanoic acid ($C_7H_{14}O_2$) (Metcalf & Eddy, 2003).

Swine manure hydrolysis and acidogenesis are important steps in the organic matter degradation and interfere directly in the treatment efficiency due to degradation and solubilization of complex macromolecules that are present in manure liquid and solid

fractions and are considered rate-limiting steps in anaerobic degradation (Eastman and Ferguson, 1981; Elefsiniotis and Wareham, 2007).

Temperature is also important during manure storage and can affect the generation of SCFA. During winter the temperature in swine manure storage lagoons are close to psychrophilic condition (Vivan et al., 2010), hydrolysis and acidogenesis reactions are strongly regulated by temperature. Yuan et al. (2011) observed 62% decrease in the SCFA generation when the temperature decreased from 24.6 °C to 14 °C in waste activated sludge anaerobic degradation.

The aim of this work was to evaluate the SCFA generation in swine manure simulating storage conditions at low temperature to simulate storage in winter season and determine SCFAs composition at different storage times.

MATERIAL AND METHODS

The study was conducted at Embrapa Swine and Poultry, Concordia, Santa Catarina, Brazil. The fresh swine manure used in this study was collected at the experimental swine facilities at Embrapa Swine and Poultry.

Samples of fresh manure were collected directly inside finishing houses; feces and urine were collected separated (to conserve the manure properties and make it possible to start the experiment in control conditions). At the laboratory, feces and urine were mixed in three different batches (333.2 ± 0.3 g of feces and 376 ± 0.0 g of urine adjusted at 2 L with tap water). The flasks were maintained in thermostatic bath at 10.0 ± 0.6 °C. Samples (8 mL) were collected daily for 15 days and submitted to gas chromatographic (GC) analyses (acetic, propionic, isobutyric, butyric, isovaleric and valeric acids). GC samples were prepared in a 2 mL Eppendorf tube adding 100 µl of H_3PO_4 10% (v/v), 750 µL of 200 mg L^{-1} octanoic acid ethanolic solution (as internal standard (IS)), and 750 µL of collected sample. The resultant suspension was mixed for 3 s and centrifuged for 11 min at 13.000 ***g*****.** Supernatant was filtered 0.22 µm-pore PVDF membrane and clear 1 µL of this solution was directly injected into the GC (Varian CP-3800 with a flame ionization detector (FID). Samples were injected in the split mode at ratio of 1:5. Separations were carried out using a Rtx-Wax silica capillary column of 30 m x 0.25 mm I.D. coated with 0.25 µm film thickness. The oven temperature was operated at gradient conditions 80 °C for 1 min, raised to 180 °C at 8 °C min^{-1}, then increased to 200 °C at 20 °C min^{-1}, and finally held at 200 °C for 2 min. Nitrogen was used as the carrier gas. Injector temperature: 250 °C. FID temperature: 280 °C.

RESULTS AND DISCUSSION

According Figure 1, in first period (8 days) the SCFA generation was linear. This indicates that hydrolysis and acidogenesis were going on without any kinetic limitation or SCFA consumption reaching. Total SCFA concentration achieved 1532.7 mg L^{-1} on linear phase. The SCFA maximum generation rate in the linear period was 141.1 mg L^{-1} d^{-1} that is greater than the results obtained by Yuan et al. (2011) that achieved 35.7 mg L^{-1} d^{-1} in waste activated sludge anaerobic digestion, the difference in this results can be explain by highest swine manure biodegradability. For all storage period (15 days), the SCFA concentrations were modeled using a quadratic regression fit with a high correlation (R^2 = 0.9674) (Figure 1).

After the linear period, the SCFA concentration increasing stopped. Between 8 and 12 days, SCFA concentration was 1556.2 ± 24.1 mg L^{-1} under a very constant period. After 12 days SCFA started to decrease reaching 1258.1 mg L^{-1} at day 15. In the same way, Popovic and Jensen (2012) observed SCFA generation increased until 15 days of storage in different temperature conditions after that they observed SCFA concentration decreased.

One of the possibilities to explain this SCFA concentration decrease during the experiment is that methanogenesis activity was higher than SCFA generation after 12 days and not hydrolysis or acidogenesis inhibition. However, some authors observed the methanogenesis activity was higher than SCFA generation after 2.5 days of waste activated sludge storage. It should be noted, there are big differences in effluents biodegradability when compared waste activated sludge with swine manure and different hydrolysis and acidogenesis generation rates (Eastman and Ferguson, 1981; Ucisik and Henze, 2008; King et al., 2011).

The composition of different SCFAs during storage period had no significant changes (Figure 2). The acetic acid achieved the greatest concentration into the SCFA composition. Throughout the experiment, acetic acid was 56.7 ± 1.8% of total SCFA, propionic acid represents 19.7 ± 0.8% and butyric acid 11.8 ± 0.7%.Yuan, et al. (2009) found a significant difference between initial and final acetic acid concentration in sludge from activated sludge under anaerobic digestion and after 5 days, the acetic acid was 65% of total SCFA and drop to 49% after 10 days. In the same way, Xiong et al. (2012) also observed great difference in SCFA composition with high valeric acid generation in 24 hours of storage time.

CONCLUSIONS

After 8 days of storage the SCFA generation presented a linear progression reaching a generation rate of 141.1 mg L^{-1} d^{-1}. SCFA started to decrease after 1 week and the entire storage time were better described using a quadratic model with a high correlation coefficient (R^2 = 0.9674).

Acetic (56.7 ± 1.8%), propionic (19.7 ± 0.8%) and butyric (11.8 ± 0.7%) acids were the dominant SCFAs. Furthermore the SCFA composition did not change significant through the entire storage period.

ACKNOWLEDGEMENT

Brazilian National Council for Scientific and Technological Development (CNPQ)

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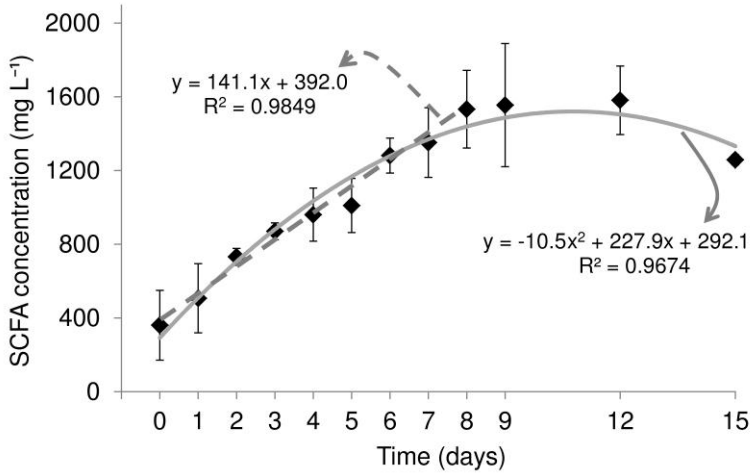

Figure 1: SCFA concentration in the storage time. The dashed line is the liner period of SCFA formation. The solid line is the fitting quadratic curving of SCFA formation.

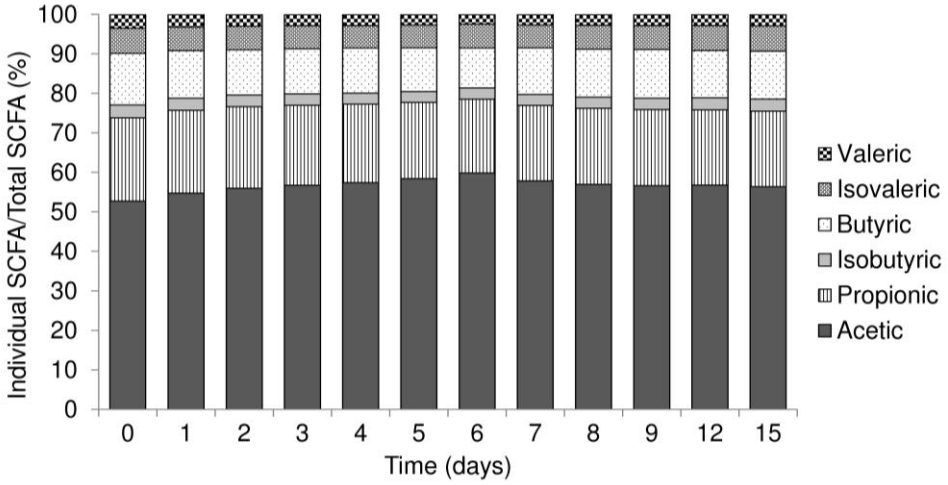

Figure 2: Percentage of individual SCFA related to total SCFA.