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The hydrolytic stage in high solids temperature phased anaerobic digestion improves the downstream methane production rate

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ABSTRACT

The role of the hydrolytic stage in high solids temperature phased anaerobic digestion was investigated with a mixture of cattle slurry and maize silage with variable ratios (100, 70 and 30% volatile solids coming from cattle slurry). It was incubated for 48 h at 37, 55, 65 and 72 °C. Soluble chemical oxygen demand and biochemical methane potential were measured at 0, 24 and 48 h. Higher temperatures improved the amount of solubilized COD, which confirmed previously reported results. Nevertheless, solubilization mostly took place during the first 24 h. The rate of methane production in post-hydrolysis BMPs increased after 48 h hydrolysis time, but not after 24 h. The first order kinetic constant rose by 40% on average. No correlation was observed between soluble COD and downstream methane production rate, indicating a possible modification of the physical structure of the particulate solids during the hydrolytic stage.

1. Introduction

The anaerobic digestion of agricultural wastes and especially animal dejections is of interest, since it provides an answer to the waste management issue, while providing a local energy source as heat and electricity. Temperature phased anaerobic digesters (TPAD) have received a growing attention over the past 10 years (Lv et al., 2010). They are generally operated as two stage systems, with a combination of a high temperature stage (for instance thermophilic) followed by a low temperature stage (for instance mesophilic). The high temperature stage is supposed to favor the solubilization rate of complex substrates, while the low temperature stage offers a stable operation for methane production (Sung and Santha, 2003). The first (hydrolytic) stage is thus dedicated to hydrolysis and solubilization at temperatures ranging from 55 °C to 65 °C or even 70 °C (Ge et al., 2010). In the second (methanogenic) stage, acetogenesis and methanogenesis can occur in smoother conditions. The interest of phasing anaerobic digestion in two or more stages are mostly: to increase the methanogenic activity, to enable lower retention times, and to get a better stability towards acidification (Verrier et al., 1987; Roberts et al., 1999; Shen et al., 2013). In addition, temperature phasing provides a higher VS removal (Han et al., 1997).

This role of the hydrolytic stage is the most critical in terms of performance, since the hydrolysis is the limiting step of the global anaerobic digestion process of complex substrates (Appels et al., 2008). Temperature and hydraulic retention times (HRT) are the main operating parameters. An elevated temperature is known to enhance the hydrolysis rate. Operating this stage at a higher temperature is thus interesting. In addition, some authors report that a high-temperature hydrolysis can reduce the amount of pathogens (Han et al., 1997; Huyard et al., 2000; Skiadas et al., 2005).

The literature review shows that many investigations focused on the effect of thermal pretreatment before anaerobic digestion. In this case, the effect of temperature on organic matter is a thermal disintegration (especially above 80 °C). On the opposite, the effect of temperature on biological hydrolysis (below 70 °C) has received less attention. Wang et al. (1997) did first examine the effect of lower temperature pretreatments on the digestion of secondary sludge. They operated at 60, 80, 100 and 120 °C (from 5 to 60 min pretreatments). They observed a considerable release of soluble compounds for all tested conditions. In continuous mode, a 30 min pretreatments led to 30–50% increase of the methane produced when compared to the control sludge, the maximum being obtained at 60 °C (+52%).

Veeken and Hamelers (1999) have measured the hydrolysis constant by performing biochemical methane potential tests on several solid biowaste. They assumed that hydrolysis was the limiting step for methane production. Using a mesophilic inoculum, they observed an increase of the kinetic constant between 20 and 40 °C according to the Arrhenius law. On the opposite, Donoso-Bravo et al. (2009) found that the hydrolysis rate of starch between 12 and 45 °C reached a maximum at 35 °C. In both cases, the hydrolytic step was investigated in batch

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mode with a mesophilic inoculum, which may be a limiting aspect since inoculum adaptation to temperature is an important issue. Nges and Liu (2009) investigated the temperature range from 25° to 70° for anaerobic pretreatments and obtained the best results (BMP) with 50° pretreatments and 2 days. Orozco et al. (2013) have investigated the effect of thermophilic hydrolysis (55 °C) in continuous mode at various HRT on the biochemical methane potential (BMP) of grass silage. The BMP after 20 days increased from 282 L_{STP}/gVS (without hydrolysis) to 368 L_{STP}/gVS (obtained at 4 days HRT). Longer HRT in the hydrolytic stage did not improve the BMP, probably because some methanogenic activity can occur under these conditions.

Gavala et al. (2003) investigated the effect of a 70 °C pretreatment of primary and secondary sludge (from 0 to 7 days) on the methane production during batch mesophilic and thermophilic digestion. The pretreatment was effective for almost all tested conditions, with an important increase of the methane potential (+80%) and of the average methane production (+64–77%) after the pretreatments. In the same research group, Skiadas et al. (2005) compared in continuous mode a 2-days HRT hydrolytic stage (at 70 °C) followed by a 13 days HRT thermophilic digester (TPAD system), to a single stage 15 days HRT thermophilic control. The TPAD system reached 11% more methane than the control, and a much higher extent of VS removal (55% vs. 43%). In addition, 60% of the VS reduction took place in the hydrolytic stage.

Coelho et al. (2011) studied a thermophilic 2 days HRT followed by mesophilic or thermophilic methanogenic stage. The TPAD systems always performed better than the control single stage reactor, and most of the hydrolysis activity took place in the hydrolytic stage. The findings from Watts et al. (2006) were somewhat different. Indeed, the authors investigated the effect of temperature in the hydrolytic stage of a TPAD system (2 days HRT at 47/54/60 °C followed by a 13 days HRT mesophilic reactor) treating secondary sludge from a BNR plant. Only the operating period with a 60 °C hydrolytic stage offered significant advantages over the mesophilic single-stage control. Interestingly, they observed that the hydrolytic activity in the methanogenic stage was higher in TPAD mode, and proposed that some "partial hydrolysis" may have taken place in the hydrolytic stage. A later study from the same research group (Ge et al., 2010) revealed that for primary sludge, a higher extent of solubilization occurred in the hydrolytic thermophilic phase of the TPAD compared to that obtained in a hydrolytic mesophilic stage. ADM1 modeling analysis of the results was proposed in order to explain if the better performances were due to i) an increase of the extent of biodegradability of the sludge or ii) an increase of the hydrolysis rate during the hydrolytic stage. The results clearly showed an increase of the hydrolysis constant. A similar work was also published with waste activated sludge as substrate (Ge et al., 2011a), and the authors concluded that the mechanism responsible of the improved performance of the TPAD was the kinetics of hydrolysis in the hydrolytic tank. The same authors have developed a batch procedure for testing the hydrolytic stage with an adapted inoculum at various temperature, pH and retention times, together with BMP tests performed on the content of the hydrolytic batch tests (Ge et al., 2011b). Contrary to their previous work, their conclusion was that the temperature increase improved the extent of biodegradability of the biological sludge used, and accelerated the kinetics in the methanogenic (BMP) compartment, the kinetics of the hydrolytic stage being not influenced.

Several studies focused on the triggers of this first step of the anaerobic digestion process, studying the inhibiting conditions (Cazier et al., 2015), the most effective temperature (Donoso-Bravo et al., 2009; Orozco et al., 2013; Veeken and Hamelers, 1999) or the retention time (Demirel and Yenigün, 2004; Romero Aguilar et al., 2013). However, all these studies did look at the hydrolysis *via* the solubilized chemical oxygen demand (COD). This is obviously a good way to characterize hydrolysis, since any increase in COD found in the aqueous fraction of the samples comes from hydrolyzed particulate matter. However, this method does not account for the whole hydrolytic activity, because the reduction of the degree of complexity may produce fragments that are not soluble.

From this overview of research achievements, we can conclude that there are still contradictory results that may be attributed to several factors:

- Hydrolysis experiments performed in inoculated batch mode vs. continuous hydrolytic stages;
- The kinetics observed during BMP test depends on the experimental conditions, and more particularly on the BMP inoculum; in addition, using the same origin for the inoculum for different tests does not guarantee that the kinetics between the tests can be comparable.
- Nature and characteristics of the substrate (feedstock).

Moreover, the efficiency of the hydrolytic stage can be quantified by several factors:

- The hydrolysis/acidification yield, or the VS removal;
- The kinetics of the hydrolytic step;
- The kinetics of methane production in the methanogenic stage;
- The overall extent of methane produced.
- A model-based approach.

Much probably, partial hydrolysis may occur during the early stage of a TPAD. Accessing the reduction of the polymerization degree of macromolecules (carbohydrates or proteins) in such complex systems is a difficult task. This is the reason why the extent of solubilization is the most selected indicator for quantifying hydrolysis. It is worth noting that the reduction of the complexity of the tridimensional networks helps in improving the kinetics of an enzyme mediated reaction. With smaller molecules, enzymes can access more easily to the substrate, therefore increasing the reaction rate, as observed in other fields of research dealing with hydrolysis (Kong et al., 1992). Then, a lower complexity favors a faster production of methane in downstream sector, dedicated to methanogenesis.

The objective of the present work is to provide new elements for understanding the role of the hydrolytic stage in TPAD. We investigated different experimental conditions for the hydrolytic stage (retention time, temperature and feedstock composition). The substrate used was a mixture of cattle slurry and maize silage, without inoculum addition since cattle slurry was supposed to bring its own bacterial load. Since the hydrolytic stage was operated at a high total solid content, the amount of active hydrolytic biomass brought by cattle slurry was found sufficient. Moreover, since hydrolytic species are fast growing organisms. Finally, continuous TPAD experiments on a similar feedstock with very low HRT in the hydrolytic stage showed that there was no specific need for adaptation (Dooms et al., 2018).

The experiments were performed in continuously mixed high-solids batch mode. Hydrolyzed samples were characterized in terms of solubilization during the hydrolysis test, but also for BMP tests. These BMP tests were performed not only on the raw sample, but also on its separated aqueous and particulate fraction, thus providing valuable information when put together with the COD balance.

2. Materials and methods

2.1. Feedstock

The feedstock was composed of cattle slurry and maize silage. The characteristics are given on Table 1. Three different mixing ratio between the two products were used. The first (CS100) was only cattle slurry (CS), sampled in a farm growing cattle near Lyon (France). This input was used to see the impact of the hydrolysis step on a substrate that contains few readily fermentable compounds. The second one (CS70) was CS mixed with 30% maize silage (on volatile solids VS basis), taken from the same farm. This input represented a typical load for an agricultural plant, treating cattle wastes such as CS, and