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Thermochemical pretreatment and anaerobic digestion of dairy cow manure: Experimental and economic evaluation

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HIGHLIGHTS

- Acid and alkali pretreatment were technically and economically evaluated.
- A S/I ratio of 0.25 g g^{-1} showed the best results in terms of degradation kinetic.
- The methane potential increased 23.6% with a dose of 10% of NaOH at 100 °C for 5 min.
- The methane potential increased 20.6% with a dose of 2% of HCl at 37 °C for 12 h.
- Economically, anaerobic digestion without pretreatment outperforms the other options.

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ABSTRACT

The aim of this study was to assess technically and economically the application thermochemical pretreatment in the anaerobic digestion of dairy cow manure. After selecting the optimum substrate to inoculum (S/I) ratio in a preliminary BMP test, the following tests compared 20 different pretreatment conditions varying temperature (100 and 37 °C), exposure time (5 and 30 min and 12 and 24 h) and chemical doses (0.5, 2, 6 and 10% of HCl or NaOH). The highest value of maximum production rate was achieved at an S/I ratio of 0.25 g VS_s g VS_i^{-1}. The major improvements of the methane potential were 23.6% with 10% of NaOH at 100 °C for 5 min and 20.6% with 2% of HCl at 37 °C. The technical-economic analysis showed that the implementation of neither thermal alkali nor thermal-acid pretreatment would be feasible and the conventional one-step anaerobic digestion outperforms both alternatives.

1. Introduction

Anaerobic digestion (AD) represents one of the most sustainable ways of treating waste and wastewater due to the production of biogas, which can be harnessed as electricity and/or heat replacing the use of fossil fuels. Furthermore, the nutrient-rich digestate can be used for soil amendment. Currently, AD is widely used in Europe where the technology is considered consolidated. In Chile, around 50 MW of electricity are generated from biogas; however there are plenty of other AD plants where the biogas is wasted and not well energetically utilized.

Dairy cow manure (DCM) is the most used substrate for AD, particularly in the south of Chile, where this type of livestock is farmed. Therefore, it is crucial to count with a better understanding of the anaerobic biodegradability of this substrate and the economic and energetic viability of the technology application. In this context, the biochemical methane potential (BMP) test is the most used and accepted procedure to evaluate both the methane maximum production, as well as the hydrolysis rate when this step is the limiting reaction in the AD process. The initial condition of a BMP test, i.e. the ratio between substrate and inoculum (S/I ratio), is the only variable that can be manipulated and it has been proven that exerts a significant influence upon the results of BMP test. Concerning the AD of cow manure, previous research obtained methane yields between 200 and 340 $mlCH_4$ g VS^{-1} depending on the applied S/I ratio (Kafle and Chen, 2016; Moset et al., 2015). However, the majority of the studies have focused on the co-digestion of cow manure with other substrates (Zheng et al., 2015).

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Since the hydrolysis step is limiting the AD of particulate and complex substrates, such as DCM, pretreatment methods may be applied for solubilizing organic matter and, consequently, increasing AD rate and extent. In fact, plenty of research have reported improvements on the AD of several solid and semi-solid substrates by employing pretreatment techniques (Carrere et al., 2015). Nonetheless, for cow manure, few results have been carried out so far, although from those all of them aimed at breaking down the fiber present in the biomass. For instance, Jin et al. (2009) used microwave and chemical pretreatments for evaluating the biodegradability of dairy manure. In this case, acids and bases yield the best results. Alkali along with mechanical pretreatment were assessed by Angelidaki and Ahring (2000). The results obtained showed that an improvement on the methane potential was achieved depending on the size of the pretreated fibers. Moreover, an important aspect besides the pretreatment effectiveness, regards the economic feasibility of its implementation. For chemical pretreatment, the few studies that can be found are carried out to evaluate waste activated sludge pretreatment (Cho et al., 2014; Ruffino et al., 2016). Results obtained indicated that the economic benefit is highly dependent on the chemical doses.

The aim of this study was to compare acid and alkaline thermochemical pretreatments prior to the anaerobic digestion of DCM in BMP tests. For this, the first step consisted in optimising the S/I ratio by investigating different amounts of DCM and digested sewage sludge. After selecting the optimum S/I ratio, several temperatures, exposure times and chemical doses were varied for studying the pretreatment effectiveness on the susbtrate anaerobic biodegradability. Afterwards, the pretreated and raw DCM were used as substrate for BMP test and the results were analyzed by using the Gompertz equation. Finally, a preliminary techno-economic assessment of full-scale application was carried out for the best pretreatment conditions as well as the model parameters drawn from the BMP test.

2. Material and methods

2.1. Substrate, inoculum and S/I ratio assay

The DCM used as substrate in this study was obtained from two small scale dairies located in the cities of Melipilla and Casablanca (Chile), for S/I ratio and thermochemical pretreatment/BMP test, respectively. The anaerobic inoculum was obtained from a continuous mesophilic lab-scale stirred tank reactor, fed with primary sludge and waste activated sludge at an organic load rate (OLR) of 0.8 g VS L^{-1} d^{-1}, and had a concentration of 5 g VS L^{-1}. The reactor was made of plexiglass with a total volume of 5 L, placed in a thermo-regulated chamber and mechanically stirred. The mixed sewage sludge was taken from the wastewater treatment plant of Santiago, Chile.

The S/I ratio influence was assessed at five different conditions, namely: 0.25, 0.50, 0.75, 1.0 and 2.0 in terms of volatile solids (g VS_S g VS_I^{-1}). This first step was used to obtain an optimum S/I ratio, which was subsequently applied for thermochemical pretreatment in BMP tests.

2.2. Thermochemical pretreatments

Thermochemical pretreatment was studied at twenty (20) different conditions for acid (HCl) and alkaline (NaOH) chemicals, as detailed in Table 1. Four temperature and time pair conditions: 100 °C for 5 min, 100 °C for 30 min, 37 °C for 12 h and 37 °C for 24 h, were combined with four chemical doses: 0.5, 2.0, 6.0 and 10.0% in VS basis. For substrate heating, a Soxhlet equipment with thermo-regulation at 100 °C and a water bath at 37 °C were used.

Table 1
Anaerobic digestion of dairy cow manure under different thermochemical pretreatment conditions.

Trial	Temperature (°C)	Exposure time	Chemical dose (mL/100 g VS)
Acid (HCl)/Alkali pretreatment			
C	–	–	–
$P_{1.0}$	100	5 min	–
$P_{1.1}$	100	5 min	0.5
$P_{1.2}$	100	5 min	2.0
$P_{1.3}$	100	5 min	6.0
$P_{1.4}$	100	5 min	10.0
$P_{2.0}$	100	30 min	–
$P_{2.1}$	100	30 min	0.5
$P_{2.2}$	100	30 min	2.0
$P_{2.3}$	100	30 min	6.0
$P_{2.4}$	100	30 min	10.0
$P_{3.0}$	37	12 h	–
$P_{3.1}$	37	12 h	0.5
$P_{3.2}$	37	12 h	2.0
$P_{3.3}$	37	12 h	6.0
$P_{3.4}$	37	12 h	10.0
$P_{4.0}$	37	24 h	–
$P_{4.1}$	37	24 h	0.5
$P_{4.2}$	37	24 h	2.0
$P_{4.3}$	37	24 h	6.0
$P_{4.4}$	37	24 h	10.0

Pretreatments were prepared in solutions and subsequently added to BMP tests in a solid to liquid ratio of 0.05 g VS mL^{-1} in order to maintain the S/I ratio of 0.25.

For comparing the effect of only the temperature, a thermal pretreatment without chemical addition was evaluated for the four temperature-time pair conditions. Furthermore, a control trial with raw DCM without any pretreatment was also assessed. The pH of each test was measured right after the chemical addition at the beginning and at the end of the thermal pretreatment.

2.3. Biochemical methane potential tests

BMP tests were carried out according to the guidelines proposed by Angelidaki et al. (2009). To this aim, glass bottles of 120 mL with 100 mL of working volume were added with DCM as organic substrate and digested sewage sludge as inoculum at different proportions for the first part of this study and at an optimum S/I ratio for the second part. Sodium bicarbonate was added in a concentration of 1 g $NaHCO_3$ g VS^{-1} of inoculum. After the addition of chemical (HCl or NaOH), pH was adjusted to neutral values of 7.1 (±0.1). Blank trials with only inoculum were used to quantify the amount of methane produced by endogenous respiration. Each BMP was performed in triplicate. The temperature of the assay was set at mesophilic temperature (37 °C) and was controlled by a thermoregulated chamber.

The methane production was measured by liquid displacement using NaOH solution (40 g L^{-1}), which absorbs CO_2. Results were expressed in methane yield, which was calculated by dividing the accumulated volume of methane produced by the VS content in each bottle (mlCH_4 g VS^{-1}). The net value of methane yield was obtained by subtracting the endogenous production of the blank bottle and converted to normal conditions of temperature (0 °C) and pressure (1 atm).

2.4. Parameter estimation

Experimental data from BMP tests were modeled using the modified Gompertz equation, as described below (Eq. (1)), where B is the methane yield at a time t (mlCH_4 g VS^{-1}), P is the maximum methane production (mlCH_4 g VS^{-1}), R_m is the maximum