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A new model for including the effect of fly ash on biochemical methane potential

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ABSTRACT

The modelling of the effect of trace elements on anaerobic digestion, and specifically the effect of fly ash, has been scarcely studied. Thus, the present work was aimed at the development of a new function that allows accumulated methane models to predict the effect of FA on the volume of methane accumulation. For this, purpose five fly ash concentrations (10, 25, 50, 250 and 500 mg/L) using raw and pre-treated sewage sludge were used to calibrate the new function, while three fly ash concentrations were used (40, 150 and 350 mg/L) for validation. Three models for accumulated methane volume (the modified Gompertz equation, the logistic function, and the transfer function) were evaluated. The results showed that methane production increased in the presence of FA when the sewage sludge was not pre-treated, while with pretreated sludge there is inhibition of methane production at FA concentrations higher than 50 mg/L. In the calibration of the proposed function, it fits well with the experimental data under all the conditions, including the inhibition and stimulating zones, with the values of the parameters of the methane production models falling in the range of those reported in the literature. For validation experiments, the model succeeded in representing the behavior of new experiments in both the stimulating and inhibiting zones, with NRMSE and R^2 ranging from 0.3577 to 0.03714 and 0.2209 to 0.9911, respectively. Thus, the proposed model is robust and valid for the studied conditions.

1. Introduction

Currently, sewage sludge produced in waste water treatment has become a worldwide problem (Zhao et al., 2010). Particularly in Chile, since 2009 there is a new regulation for its treatment, disposal, and reuse. One of the technologies proposed for treating and valorizing this waste is anaerobic digestion, which can reduce the organic load of sewage sludge, generating biogas as well as slurry that can be used as fertilizer (Ennouri et al., 2016). However, the process still has some problems related to its long hydraulic retention time (HRT), a situation that affects the volume of biodigestors, due mainly to its low biological breakdown rate (Braguglia et al., 2015). One way to improve the breakdown rate is the use of trace elements in the process, which are know to be insufficient for anaerobic microorganisms when solid waste is used alone as feedstock for anaerobic digestion (Moestedt et al., 2016). Recently, several researchers have emphasized the importance of supplementing with trace elements to improve methanogenic activity (Choong et al., 2016; Romero-Guiza et al., 2016; Thanh et al., 2016). Unfortunately, their use in the process is limited mainly by the high cost of the trace element salts. Therefore, the use of a cheaper source of trace elements could help control this parameter without additional expenses (Huilinir et al., 2015). A source of trace metals is fly ash (FA), which has been applied to the anaerobic digestion of municipal solid waste (Lo et al., 2010; Romero-Guiza et al., 2016), to sewage sludge coming from the pulp and paper industry (Huilinir et al., 2015), and recently to sewage sludge coming from a municipal wastewater treatment plant (Huiliñir et al., 2017). The inclusion of fly ash in all cases increases methane production and reduces the concentration of volatile solids (VS), as long as the fly ash concentrations are within ranges that stimulate the process. Therefore, the use of FA as a source of trace elements in anaerobic digestion has been shown to be a good way to recover this waste.

Although the use of FA has been explored experimentally, few studies have dealt with modelling the effect of FA on the process. The construction of a model that can predict the effect of FA on the process can help to decide the concentration that should be

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used in the process to improve the anaerobic digestion. The modelling of biogas production was presented by Lo et al. (2010), who studied the effect of FA and bottom ash on the co-digestion of municipal solid waste, stating that the modified Gompertz model could be used, with its parameters influenced positively by the FA. A similar situation was found by Huilinir et al. (2015), who also proposed the Gompertz model for modelling biogas production coming from paper and pulp sewage sludge, with a good fit of the experimental data. However, none of these studies have presented an independent function that can include the effect of the FA regardless of the model used to represent the accumulated methane volume. Thus, the objective of the present work was to develop a new function that would allow accumulated methane models to predict the effect of FA on methane volume accumulation in the case of stimulation or inhibition. As far as we can tell, this is the first time that a function with these characteristics is proposed.

2. Methodology

2.1. Experimental setup

Experimental data for the model's calibration and validation were obtained from four 280-mL anaerobic mini-digesters with effective operating volumes of 250 mL each, measuring methane by liquid displacement according to Huilinir et al. (2015). These mini-digesters were operated in discontinuous mode for 43 days until the gas accumulation remained constant. The digesters were stirred manually once or twice per day before reading the volume displaced by methane according to Huilinir et al. (2015).

For the aerobic pretreatment of sewage sludge, a 1 L glass reactor operating with an effective volume of 900 mL was used, according to Montalvo et al. (2016). In each pretreatment air was injected continuously into the bioreactors by mini-compressors (0–10 Lpm) and distributed by small diffusers (Montalvo et al., 2016). The conditions used for pretreatment were 0.35 vvm for 48 h at 35 °C. After aerobic pretreatment, the pretreated sludge was fed to a mini-anaerobic digester with a total volume of 280 mL.

2.2. Inoculum, substrate, and experimental design

The inoculum was obtained directly from the industrial reactor, filling three 5-litre jerrycans which were taken to the laboratory and kept in a refrigerator at 4 °C. The inoculum used for calibration tests had 0.59 ± 0.01 g VS/g of total solids (TS), 2.2 ± 0.42 g of soluble COD/L, and a pH of 7.23 ± 0.12. The inoculum used for validation had 0.67 ± 0.01 g VS/g of total solids (TS), 2.5 ± 0.33 g of soluble COD/L, and a pH of 7.1 ± 0.1. The substrate was mixed sewage sludge also from the municipal WWTP in Santiago, Chile. For the calibration experiments, this substrate had a ratio of 0.76 ± 0.01 g VS/g TS, 5.87 ± 0.87 g/L of soluble COD, and a pH of 5.69 ± 0.32 (Huiliñir et al., 2017). For the validation experiments, the substrate had a ratio of 0.84 ± 0.004 g VS/g TS, 5.91 ± 0.42 g/L of soluble COD, and a pH of 6.1 ± 0.2. Sewage sludge was refrigerated at 4 °C for no more than 3 days until its use.

The fly ash, with a particle diameter between 0.12 and 0.2 mm, was obtained from a thermoelectric power plant. The ash was taken from electrostatic precipitators used to collect particulate matter generated by the combustion of bituminous coal, placed before the gaseous effluents leave the plant. The main trace elements found in them were Fe (4.24 g/kg), Al (1.37 g/kg), Zn (5.8 mg/kg), Cr (3.93 mg/kg), Cu (2.32 mg/kg), Ni (3.85 mg/kg), Mn (37.7 mg/kg), V (26.4 mg/kg), Ba (64 mg/kg), Co (0.9 mg/kg), and B (25.4 mg/kg). Since the fly ash used in all the experiments came from the same sample obtained *in situ* from the thermoelectric power plant, the mass of trace elements used in all the experiments was proportional to the mass reported here.

In order to calibrate the model, data obtained from the work of Huiliñir et al. (2017) was used. The three assays were carried out as shown in Table 1, with fly ash concentrations varying between 10 and 500 mg/L. The first and second assays were carried out on pretreated sludge (P) and different FA concentrations. The third assay was performed only with raw sludge (mixed sludge) without pretreatment. The validation data were used in another separate assay (Table 1) in which different ash concentrations (40, 150, and 350 mg/L) were used to test the predictions made by the model. All the assays were carried out in duplicate.

In each anaerobic treatment the temperature was kept at 35 °C using three automatically controlled aquarium heaters, with a substrate/inoculum ratio (F/I) of 1.5 g VS substrate/g of VS inoculum according to Tomei et al. (2008). After the inoculum and substrate were put together in a mini-digester, the volume was completed with distilled water, stoppered with rubber stoppers, and sealed with white silicone to ensure anaerobiosis. They were also covered with aluminium foil to prevent the growth of photosynthetic organisms Huiliñir et al. (2014).

2.3. Chemical analyses

Methane production was measured by volumetric displacement, connecting an inverted falcon tube containing a 3% w/w NaOH solution in order to eliminate CO_2 and H_2S as main impurities from the biogas, displacing only the methane volume (Huiliñir et al., 2014). The resulting biogas travels through the flexible tubing to the Falcon tube, where it comes in contact with the NaOH solution, forming sodium carbonate and bubbling only methane. The methane collected in the Falcon tube is sucked with a syringe and released in a flame to detect its presence (Huiliñir et al., 2014).

In the liquid phase, the following parameters were determined only on the first and last (day 43) days of the experiments: total COD (t_{COD}), soluble COD (s_{COD}), and total and suspended solids. COD (total and soluble) was measured by a colorimetric method according to APHA (2012). Total and suspended solids were measured according to APHA (2012).

Table 1
Experimental conditions used in the anaerobic digestion assays.

Calibration assays			Validation assay
Assay 1	Assay 2	Assay 3	Assay 4
Pretreated, No FA (P—NFA1)	Pretreated, No FA (P-NFA2)	Not pretreated, No FA (NP-NFA)	Not pretreated, No FA (NP-NFA4)
–	Pretreated, 10 mg/L FA (P-10)	Not Pretreated, 10 mg/L FA (NP-10)	Pretreated, No FA (P-NFA4)
–	Pretreated, 25 mg/L FA (P-25)	Not Pretreated, 25 mg/L FA (NP-25)	Not Pretreated, 40 mg/L FA (NP-40)
–	Pretreated, 50 mg FA/L (P-50)	Not Pretreated, 50 mg/L FA (NP-50)	Not Pretreated, 150 mg/L FA (NP-150)
Pretreated, 250 mg/L FA (P-250)	–	Not Pretreated, 250 mg/L FA (NP-250)	Not Pretreated, 350 mg/L FA (NP-350)
Pretreated, 500 mg/L FA (P-500)	–	Not Pretreated, 500 mg/L FA (NP-500)	Pretreated, 40 mg/L FA (P-40)
–	–	–	Pretreated, 150 mg/L FA (P-150)
–	–	–	Pretreated, 350 mg/L FA (P-350)

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