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Thermophilic anaerobic digestion of pre-treated orange peel: Modelling of methane production

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ABSTRACT

The valorisation of waste generated during orange juice manufacturing (OPW) by anaerobic digestion is gaining attention due to the several economic, social and environmental advantages of the process. Given that anaerobic digestion is a process that requires rigorous control to improve the biodegradability of the waste and methane production, this paper highlights the importance of modelling for adequate process monitoring. Specifically, this study fitted three sigmoidal models (Logistic, Gompertz, and Sigmoid models) to methane production from OPW. At laboratory scale, two thermophilic continuously stirred-tank reactors working in semi-continuous mode was used. D-limonene removal of 70% was previously reached by applying a pre-treatment on OPW. The results showed a biodegradability of the pre-treated waste of up to 96.7% in COD. The Logistic, Gompertz and Sigmoid models fitted adequately to cumulative methane production (R^2 was 0.9691; 0.9492 and 0.9511, respectively). However, the Logistic model showed the best fit to the experimental data even under critical conditions. Specifically, the Logistic model predicted the maximum methane production rate within loads of 2.5–5.0 g COD/L. Therefore, this model might be very useful in predicting the maximum methane production rate and the maximum load that could be added without the inhibition of anaerobic digestion at real scale.

1. Introduction

From an environmental standpoint, organic wastes are currently one of the major problems of agriculture, making the use of this biomass for generating energy of vital importance (Domínguez-Bocanegra et al., 2016). As regards orange peel waste (OPW), world orange production for 2013–2014 increased by 5 percent over the previous year to 51.8 million metric tons with an orange juice production of 2.0 million metric tons. Citrus by-products resulting from citrus processing account for about 50% of the weight of the raw material (Allaf et al., 2013). Citrus waste has been used to produce several products of high economic value such as flavonoids (Inoue et al., 2010), pectin (Kim et al., 2004), fibre (Lessa et al., 2017), essential oils (Boukroufa et al., 2015) and also animal feed. Despite these applications, large amounts of citrus waste are still generated annually that are not being valorised.

As a result, alternative valorisation processes are being promoted in order to convert this biomass into useful energy. This conversion can be carried out through chemical processes such as pyrolysis, which allows obtaining bio-oil that could replace fuel (Aboagye et al., 2017) or biological processes such as composting or anaerobic digestion that allow stable organic matter (fertiliser) production or biogas generation, respectively. Although the fertiliser obtained through the composting process (compost) has several agricultural advantages (Altieri et al., 2014; Bernal-Vicente et al., 2012; Raviv, 2018; Atiyeh et al., 2002), citrus waste is not generally accepted for composting by non-hazardous waste management plants due to its low pH, the presence of inhibitory essential oils and the fast biodegradation of this waste, which can cause anaerobiosis problems in compost piles (Ruiz and Flotats, 2014). However, citrus waste composting is successful by adjusting its C/N ratio, pH, and

Abbreviations: Alk, alkalinity (mg CaCO3/L); *b*, model parameter of Logistic Gompertz and Sigmoid models; C_2, acetic acid with two carbon atoms; COD, chemical oxygen demand (mg O_2/g, g COD/L, g COD/g VSS d, g COD); CSTR, continuously stirred-tank reactor; G, methane production (mL$_{STP}$ CH_4); Gmax, maximum methane production (mL$_{STP}$ CH_4); GAL, synthetic solution composed of glucose sodium acetate and lactic acid; FS, fixed solids (%); N-kjeldahl, total kjeldahl nitrogen (mg/g); N-NH_4^+, ammoniacal nitrogen (mg/g); OPW, orange peel waste; STP, standard conditions of temperature and pressure (0 °C 1 atm); TS, total solids (%); VA, volatile acidity (mg acetic acid/L); VOC, volatile organic compounds; VS, volatile solids (%, g/L); VSS, volatile suspended solids (%, g/L); X_0, model parameter of Logistic Gompertz and Sigmoid models; *y*, volume of methane accumulated (mL, at 1 atm, 0 °C).

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moisture content and piling the modified substrate under shelter (Van Heerden et al., 2002).

In the case of anaerobic digestion, this biological process prevents landfilling of biodegradable organic materials (e.g. food and agroindustrial waste) as well as the composting process. In addition, anaerobic digestion allows producing biogas rich in methane, which is a renewable source of energy (Calabrò et al., 2016), and reducing methane emissions from landfills. Although most landfills in developed areas have biogas collector systems that generate waste materials that are not completely stabilised, this waste should undergo a previous aerobic digestion process in order to stabilise the material and hence prevent fires. During aerobic digestion, most of the organic matter susceptible of being transformed into methane is eliminated into the atmosphere in the form of CO_2 and VOCs. Moreover, agricultural waste is often disposed of in an uncontrolled manner near production sites, potentially leading to several problems, such as VOC emissions (Gallego et al., 2014), methane and ammonia emissions (Pagans et al., 2006), odours and fresh and groundwater pollution (Littarru, 2007).

The anaerobic digestion of citrus waste produces a fuel in the form of methane, while eliminating or mitigating disposal issues. The main disadvantage of orange peel anaerobic digestion is the D-limonene content of this waste. Several studies have shown that an organic loading rate of 2.0–3.5 g VS/day of citrus peel may inhibit microbial activity (Ruiz and Flotats, 2014; Forgács et al., 2011; Martín et al., 2010a; Martín et al., 2013; Mizuki et al., 1990; Lane, 1980). Nevertheless, microbial activity can be also inhibited at higher loading rates during the anaerobic digestion of different energy crops.

The application of kinetic models to anaerobic digestion processes is important in order to evaluate the efficiency as well as different variables of monitoring processes. Borja et al. (2003) determined the maximum specific growth rate of microorganisms and the kinetic constants in the mesophilic anaerobic digestion of thermally pre-treated two-phase olive pomace (TPOP) using the Chen-Hashimoto methane production model. Several authors have applied modelling for hydrolysis (Batstone et al., 2002; Vavilin et al., 2008) and volatile fatty acid degradation kinetics to gain more knowledge about anaerobic digestion, which is a complex process and regulated by many factors (Mani et al., 2016; Vavilin et al., 2004; Vasiliev et al., 1993; Fukuzaki et al., 1990). Other authors have used sigmoidal growth functions to model methane production kinetics (Yalcinkaya and Malina, 2015; Serrano et al., 2017) due to the presence of a lag phase during the first loads. Ware and Power (Ware and Power, 2017) evaluated the methane production kinetics of complex poultry slaughterhouse wastes using sigmoidal growth functions (Richards, Logistic and Gompertz models). Siles et al. (2011) used the Logistic model to evaluate methane production during the anaerobic digestion of coagulated-flocculated wastewater from biodiesel manufacturing.

However, the literature on modelling anaerobic digestion is highly complex and often contradictory, making it impossible to draw reliable conclusions. The major reason for these variations is the complexity of the anaerobic digestion process where mechanisms such as antagonism, synergism, acclimatisation and formation of complexes could significantly affect the phenomenon of inhibition (Chen et al., 2008). This can also be attributed to the differences in substrates and inocula concentrations, environmental conditions such as temperature and pH, and acclimatisation periods (Angelidaki and Ahring, 1994).

For this reason, kinetic studies are helpful for reproducing the empirical behaviour of the process and understanding the inhibitory mechanisms of biodegradation, while saving time and money (Galí et al., 2009). Nevertheless, the development of an up-to-date model of organic matter anaerobic digestion is fraught with considerable difficulties due to the numerous variables involved in an anaerobic system. Anaerobic digestion models have basically focussed on sewage sludge, pig waste or crops, although modelling the treatment of other residues like wastewater and agro-wastes have recently drawn much attention (Martín et al., 2010b).

Due to the numerous advantages of applying models to different parameters of anaerobic digestion, this research study fits three different models to the production of methane generated during the anaerobic digestion of pre-treated orange peel (after removing D-limonene). Three sigmoidal models were evaluated: (1) the Logistic model, (2) the Gompertz model and (3) the Sigmoid model. The aim was twofold: (1) to determine the model that best explains the variation in methane production and (2) to evaluate which model allows predicting maximum methane production, as this is the most interesting variable to be simulated in anaerobic digestion as a valorisation process.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up used at laboratory scale for the anaerobic digestion of orange peel waste derived from orange juice manufacturing consisted of two 3.5-L continuous stirred-tank reactors (CSTR) with four connections to load feedstock, ventilate the biogas, inject inert gas (nitrogen) to maintain the anaerobic conditions and remove effluent. The reactor content was stirred using a stirring blade connected to a motor. Temperature was maintained by means of a thermostatic jacket containing glycerol at $52 \pm 2\,^{\circ}C$ for thermophilic assays. All of the experiments were carried out in batch mode. The volume of methane produced during the process was measured using 2-L

Boyle–Mariotte reservoirs connected to each reactor. To remove the CO_2 produced during the process, tightly closed bubblers containing a NaOH solution (6 N) were connected between the two elements. NaOH was replaced every three days to avoid saturation. The methane volume displaced an equal measurable volume of water from the reservoir. This volume was corrected in order to remove the effect of the vapour pressure of water. The methane volume was then expressed at standard temperature and pressure ($0\,^{\circ}C$ and 1 atm, respectively). The anaerobic digestion was simultaneously evaluated in two parallel reactors.

The reactors were inoculated with termophilic active granular biomass obtained from a full-scale anaerobic reactor used to treat vegetable and agricultural wastes from Colsen International b.v. (Hulst, The Netherlands).

2.2. Characterisation of the inoculum

The thermophilic experiments were carried out by inoculating biomass from a full-scale thermophilic anaerobic reactor used to treat vegetable and agricultural wastes from Colsen International b.v. (Hulst, The Netherlands). The sludge was selected on the basis of its high methanogenic activity (Fannin, 1987; Field et al., 1988) and showed values ranging from 0.98 to 1.09 g COD/g VSS d for thermophilic microorganisms. It is important to note that the high initial alkalinity (8500 mg $CaCO_3$/L) of the inoculum is due to its origin from an industrial digester that treats agricultural waste.

2.3. Orange peel substrate

The organic waste used in this research study was orange peel derived from orange juice manufacturing processes carried out at the Cítricos del Andévalo Company (Huelva, Spain). Anaerobic digestion might be an interesting alternative for the Cítricos del