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Predicting the biochemical methane potential of wide range of organic substrates by near infrared spectroscopy

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HIGHLIGHTS

- ▶ The use of near infrared spectroscopy (NIRS) to predict the biochemical methane potential (BMP) was investigated.
- ▶ The NIRS appears as a suitable method for the fast prediction of BMP.
- ▶ The integration of the entire diversity of waste remains nevertheless difficult.
- ▶ The NIR model for non-stabilised substrates could be practically used.

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ABSTRACT

The use of near infrared spectroscopy (NIRS) as an alternative method to predict the biochemical methane potential (BMP) of a broad range of organic substrates was investigated. A total of 296 samples including most of the substrates treated by anaerobic co-digestion were used for NIRS calibration and validation. The NIRS predictions of the BMP values were satisfactory (Root Mean Square Error = 40 ml CH_4 g^{-1} VS_{fed}; $r^2 = 0.85$). The integration of the entire substrate diversity in the model remained nevertheless difficult due to the specific organic matter properties of stabilised substrates and the high level of uncertainty of the BMP values. The elaboration of a model restricted to "fresh" substrates allows the practical use of the NIR technique to design and operate anaerobic co-digestion plants. The addition of more samples in the dataset in order to perform local calibrations would probably make the elaboration of a global NIR-model possible.

1. Introduction

The Biochemical methane potential (BMP) evaluates the ultimate amount of methane produced by any given waste or biomass under anaerobic conditions. The information provided by the BMP value is important when evaluating potential substrates and for optimising the design and functioning of an anaerobic digester (Raposo et al., 2011a).

Anaerobic co-digestion of organic solid substrates, defined as the anaerobic treatment of a mixture of at least two types of substrates, is increasingly popular in Europe (Alvarez et al., 2010). It indeed offers several advantages in terms of biogas yield as well as the diversity of substrates treated. The feasibility of adding new co-substrates in an already established process have been tested for many kind of substrates such as meat waste (Buendia et al., 2009), fat, oil and grease waste (Long et al., 2011), municipal solid waste (Hartman and Ahring, 2005), fruits and vegetables (Callaghan et al., 2002), household waste, sludge and manure (Angelidaki and Ahring, 1997), etc.

Because of the wide range of BMP values of the different substrates considered in anaerobic co-digestion projects, the knowledge of the BMP value of a new substrate is crucial before its addition in an existing process or for the design of the industrial plant for its treatment.

However, the BMP test is time consuming (30–50 days) and expensive, making the current protocol non-adapted for industrial plant management and optimisation. New technologies providing fast determination of BMP become thus necessary. Several biochemical models have already been developed to predict faster the BMP value (reviewed in Lesteur et al., 2010). Although a relatively good estimation of the BMP value is obtained in a shorter time with these models, time consuming laboratory experiments remain necessary.

Alternative methods have been studied. It has been demonstrated that near infrared spectroscopy (NIRS) is a suitable method for fast prediction of a wide range of organic parameters for plant

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biomass, waste, or soil. It is a spectroscopic method using the infrared region of the electromagnetic spectrum (800–2500 nm). The prediction of the reference value is based only on spectral data without any chemical or biological analysis requirement. Moreover, a huge advantage of the NIRS is that many parameters, either complex or composition dependant, can be successfully predicted by one simple NIR spectrum acquisition. Its suitability has been demonstrated for the monitoring of anaerobic digestion process (Jacobi et al., 2009; Lomborg et al., 2009; Reed et al., 2011; Ward et al., 2011), the control of the incoming feedstock (Jacobi et al., 2011) and finally for the prediction of BMP of municipal solid waste (MSW) (Lesteur et al., 2011) and meadow grasses (Raju et al., 2011).

The use of NIRS to predict the BMP value is a promising alternative. However, the current published NIR methods for BMP estimation are limited to few types of substrate. For that reason, they are not suitable for the diversity of substrates than can be treated in a co-digestion context. The build-up of NIRS models taking into account this variability remains thus necessary.

The aim of our study is to develop a NIRS calibration model for the prediction of the BMP values in a co-digestion context, that is, for a broad range of organic substrates (MSW, agro-industrial waste, meat waste, vegetables, fruits, crops…).

2. Methods

2.1. Data sample set

The data sample set included 296 organic samples: 57 agro-industrial waste (AGRO), 1 macro algae (ALG), 20 biowaste (BIO), 4 energy crops (ECROP), 11 fatty waste (FAT), 14 meat waste (MEAT), 2 co-digestion mix (MIX), 66 municipal solid waste (MSW), 42 plants and vegetables (PLANT), 18 agro-industrial sludge (SL_{agro}), 30 sewage sludge from wastewater treatment plants (SL_{wwtp}) and 31 stabilised municipal solid waste (STAB).

The agro-industrial waste samples included solid food processing waste and non-conformed end products whereas the agro-industrial sludge samples only included sludge produced during the wastewater treatment on the agro-industrial plants. The municipal solid waste samples included fresh MSW collected on different mechanical–biological treatment plants and at different points of the sorting process. The biowaste category contained household organic waste originating from source separated collection and catering waste. The meat waste category is mainly composed of slaughterhouse waste or stale meat. The fatty waste was collected from industrial sludge digesters that use such kind of substrate to increase methane production yield. The sewage sludge samples were collected on different wastewater treatment plants and at different steps of the process (primary, secondary and mixed sludge, thermally and mechanically pre-treated sludge and anaerobically digested sludge). The plants and vegetables category included agricultural waste (residues from wheat, barley…) and vegetables (potatoes, tomatoes…). Four samples of energy crops (maize, switch grass) one sample of macro algae and two industrial co-digestion mixtures were also included in the data sample set. Finally, the stabilised MSW samples were collected during landfill drillings. The stabilised MSW samples cannot be considered as viable co-substrates for biogas plants due to their generally low BMP values. However, this latter characteristic makes them useful to increase the validity range of the calibration of the NIR model for the low BMP values.

2.2. Sample characterisation

In order to conduct the NIRS measurement, all samples were oven-dried at 40 °C during 2 days or freeze-dried and then ground at 1 mm. No differences were detected on the spectra depending upon the drying method.

The Total Solid (TS) and Volatile Solid (VS) contents were determined according the French standards NF EN 12880 and NF EN 12879.

For all samples, except the wastewater sludge, the BMP was determined on freeze or oven dried and ground samples. In the case of municipal sludge, the BMP tests were performed on fresh samples. All tests were performed in 0.5 L serums bottles, under mesophilic conditions and with a substrate/inoculum ratio ranging from 0.2 and 0.5 g of $VS_{substrate}$ per gram of $VS_{inoculum}$. The cumulated biogas production was measured until the end of the production (from 30 to 90 days) and analysed by micro-gas chromatography. The tests were carried out in duplicate. More details about the method are available in Angelidaki et al., (2009) and Hansen et al., (2004). All BMP values are expressed in ml CH_4 g^{-1} Volatile Solid fed (VS_{fed}). The Standard Deviation of repeatability (SDr) for the BMP assays was computed as:

$$SDr = \sqrt{\frac{1}{n}\sum Variance(duplicate\ of\ each\ sample)}$$

With n the number of duplicated samples.

2.3. NIR analysis

The NIR spectra were recorded on a Fourier-transform NIR spectrophotometer (Antaris II, Thermo electron, USA) in the range of wavenumber from 10000 to 4000 cm^{-1} (equivalent to wavelength ranged from 1000 to 2500 nm) with a step of 8 cm^{-1}. For each sample, two different spectra were recorded on a rotary cup spinner (68 scans) and both absorbance spectra were averaged.

2.4. Data processing

In order to reduce the baseline variation and to enhance spectral features, the following pre-treatments have been tested: Standard Normal Variate, SNV (Barnes et al., 1989), Detrend, Dt (Barnes et al., 1989), and first and second derivative using the Savistsky–Golay algorithm (Savistsky and Golay, 1964) with smoothing calculated over 7 data points on both sides.

The spectral information of the entire data sample set was studied using Principal Component Analysis (PCA). Two hundred and forty-three samples were selected for calibration and 53 samples were used as a prediction set (Table 1). The prediction samples were chosen after ordering the BMP values in the range of 150–600 ml CH_4 g^{-1} VS_{fed} and by selecting 1 over 5 samples. Calibration

Table 1
Distribution of samples in the calibration and the prediction data sets. AGRO: agro-industrial waste; ALG: macro algae; BIO: biowaste; ECROP: energy crop; FAT: fatty waste; MEAT: meat waste; MIX: co-digestion mix; MSW: Municipal solid waste; PLANT: plant and vegetable; SL_{agro}; agro-industrial sludge; SL_{wwtp}: wastewater sludge; STAB: stabilised municipal solid waste.

	Calibration data set	Prediction data set
All	243	53
AGRO	46	11
ALG	0	1
BIO	18	2
ECROP	3	1
FAT	9	2
MEAT	10	4
MIX	2	0
MSW	51	15
PLANT	33	9
SL_{agro}	16	2
SL_{wwtp}	28	2
STAB	27	4