Fast prediction of organic wastes methane potentials by Near Infrared Reflectance Spectroscopy (NIRS): a successful tool for agricultural biogas plant monitoring.

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Introduction

The European Union has set the objective of achieving 20% share of renewable energy in its overall energy consumption for 2020 (Directive 2009/28/CE, 2009). Among renewable energies carriers, anaerobic digestion (AD) process has gained interest this last decades as a robust process permitting to treat a large range of organic waste as sludges, agricultural residues, OFMSW, algae… (Carrere et al., 2016). Due to the increasing number of anaerobic digester in Europe, the monitoring of several operational and performances parameters on these biogas plants appears essential to ensure an optimal operation and optimize the overall energetic balance. One of the key elements to drive and optimize a biogas plant is the determination of the methane potential (expressed in NL CH_4 kg^{-1} VS), which allow the design of the biogas plant, the control of the raw materials quality and the potential carbon losses during their storage. Today, the Biochemical Methane Potential (BMP) test is widely applied to determine the anaerobic biodegradability of wastes. It is based on a fermentation process, which is time consuming, about 30-50 days according the biodegradability of the feedstocks (Lesteur et al., 2011; Doublet et al., 2013).

Several techniques have already been developed to predict the BMP value faster than with the biochemical way (Lesteur et al., 2011; Monlau et al., 2012). These techniques were based on BMP prediction through the chemical composition of substrates (Monlau et al., 2012) or by accelerating the biodegradation process with enzymes (Rodriguez et al., 2005). Even if relatively good estimations of the BMP could be obtained in shorter time using these methods, time consuming laboratory experiments remain necessary (Doublet et al., 2013). As a consequence, alternative methods such as Near Infrared Reflectance Spectroscopy (NIRS) have been investigated for methane potential determination (Lesteur et al., 2011). In this case, the prediction of the BMP value is based only on spectral data without any chemical or biological analysis requirement (Doublet et al., 2013). Recently, Ward (2016) reviewed seven studies about the use of the Near Infrared Reflectance Spectroscopy (NIRS) for BMP prediction showing that these research topic is still in its infancy and need further investigation. Furthermore, databases and existing models can hardly be adapted from a laboratory to another due to various parameters like: 1) sample preparation, 2) difference in protocol of the BMP reference method, and 3) sample categories used for the calibration of the predictive model. Indeed, the main NIRS models described in the literature are limited to few types of substrates and agricultural wastes (manure, slurries, crops residues, silages…) used in farm biogas plants are generally under-represented. For this purpose, the main objective of the following study was to develop a global predictive model "BMP-NIRS" using NIRS technology and calibrated mainly with agricultural residues.

Materials and methods:

For the "BMP-NIRS" model development, various feedstocks commonly used in anaerobic digestion plant were considered (**Table 1**) with mainly agriculture residues (53%) and animal breeding wastes (23%). Among the 182 samples investigated, 113 were used for the prediction model, 46 for the validation model and 23 for an independent validation model. TS (Total Solids) and VS (Volatile Solids) of the samples were determined according the protocol of APHA (2005).

The BMP (Biochemical Methane Potential) test was carried out in duplicate for each sample in mesophilic conditions (35°C). The concentration applied was 6 g VS substrate/L of inoculum. The remaining volume to obtain 600 mL is done with tap water. Hydrochloric acid was used to fix the mixture to a pH around 7. The accumulated gas production (*i.e* H_2, N_2, CO_2, CH_4, N_2, H_2S) was analyzed using a micro gas chromatography Varian CP4900. The inoculum was an agricultural digestate produced in our laboratory. The BMP test method is described in detail in Angelidaki et al. (2009).

Table 1. List of samples by families and data samples sets: calibration, validation, independent validation.

Family samples	Total	Calibration	Validation	Independent validation
Manure	36	14	13	9
Animal slurries	4	3	1	-
Stercoric materials	2	2	-	-
Urbans and agro-industrial sludges	5	5	-	-
Urbans and agro-industrial effluents	1	-	-	1
Bio-waste, fruits and vegetables	16	13	-	3
Vegetable cutlery, fresh grasses	28	14	11	3
Issus et Résidus céréaliers, Céréales	17	11	5	1
Agricultural Sillage	19	14	3	2
Lignocellulosic wastes	29	19	7	3
Grape marcs	4	2	2	-
Algae	3	2	1	-
Organical Municipal Wastes	2	2	-	-
Lipid wastes	1	1	-	-
Anaerobic digestates	3	1	2	-
Mix of agricultural feedstocks	6	5	-	1
Other wastes	6	5	1	-
Total	182	113	46	23

Prior to spectral acquisition, samples were oven-dried at 60°C up to constant weight and then milled using a centrifugal milling "Retsch ZM 200" with a mesh of size 1mm. Solid wastes samples were scanned in reflectance over 4000–400 cm-1, with a resolution of 8 cm-1, using a spectrophotometer "BUCHI NIRFlex N-500" fitted with the Petri dish accessory. Each sample was divided in three, each part being scanned independently in order to get spectral triplicate per sample. Data analysis and spectrum processing were performed using the "Buchy NIR Cal" tool. Similarly, models were build using this tool according to the PLS (Partial Least Square) regression method.The following pre-treatments were applied for each spectrum: Standard Normal Variate (SNV) (Barnes et al., 1989), first derivative, using the Savitsky–Golay algorithm (Savitsky and Golay, 1964) in order to reduce the scattering effect and delete the base line. In order to judge the reliability and robustness of this model, several indicators are relevant, but the most used ones are the determination coefficient (R^2), the Root Mean Squares Error of Prediction (RMSEP, equation 1) and the Ratio of Performance to Deviation (RPD, equation 2).

$$RMSEP = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2} \quad (1) \qquad RPD = \frac{SD_y}{RMSEP} \quad (2)$$

with : n the number of samples, y_i the mean reference value of the i-th sample, $\hat{y}_i$ its predicted BMP value, and SDy the Standard Deviation of the whole 182 samples set.

Results and discussions:

The VS content (expressed in % of TS) of the entire data sample set varied between 52.8 % (pig manure) to 99.1 % (wastewater sludge treating food wastes effluents). The BMP values varied from 90 to 776 NL CH_4 kg^{-1} VS and from 104 to 621 NL CH_4 kg^{-1} VS for the calibration and validation set respectively (**Table 2**). The average of the BMP for the calibration and validation set were similar (305 and 276 NL CH_4 kg^{-1} VS, respectively). Such values of BMP are similar to previous model developed using NIRS technology as Doublet et al. (2013) used samples sets with BMP average of 291 and 305 NL CH_4 kg^{-1} VS for calibration and validation data set respectively.

Then, to estimate the quality and the accuracy of the “BMP-NIRS” model developed, several coefficient and factors ((R^2, RMSEP, RPD, previously described) were estimated (**Table 2**).

Table 2. Comparison of prediction results between samples sets

Set of samples		Calibration	Validation	Independent validation
Number of samples		113	46	23
BMP-Ref	**Minimum***	90	104	167
	Maximum*	776	621	403
	Mean*	305	276	282
	SDr*	15,6	11,2	11,7
BMP-NIR	***RMSEP****	22,0	21,1	32,1
	R²	0.96	0.95	0.83
	RPD	4.94	4.24	2.19

* in NL CH_4 kg^{-1} VS, knowing that mean is around 290 in this study.

In **Fig. 1A**, the predicted BMP values vs measured BMP are screened for the calibration data set. The R^2 of both calibration and validation sets are high and similar to the best ones in the literature (for sets Cal. / Val.: Doublet et al. (2013): 0.92 / 0.85, Lesteur et al. (2011): 0.79 / 0.76). The RMSEP values determined for the calibration and validation data sets are close to those of literature (in NL CH_4 kg^{-1} VS for sets Cal. / Val.: Doublet et al. (2013): 36 / 40, Lesteur et al. (2011): 31 / 28). Finally, high values of the RPD of 4.94 and 4.24 were estimated for the calibration and validation set respectively.

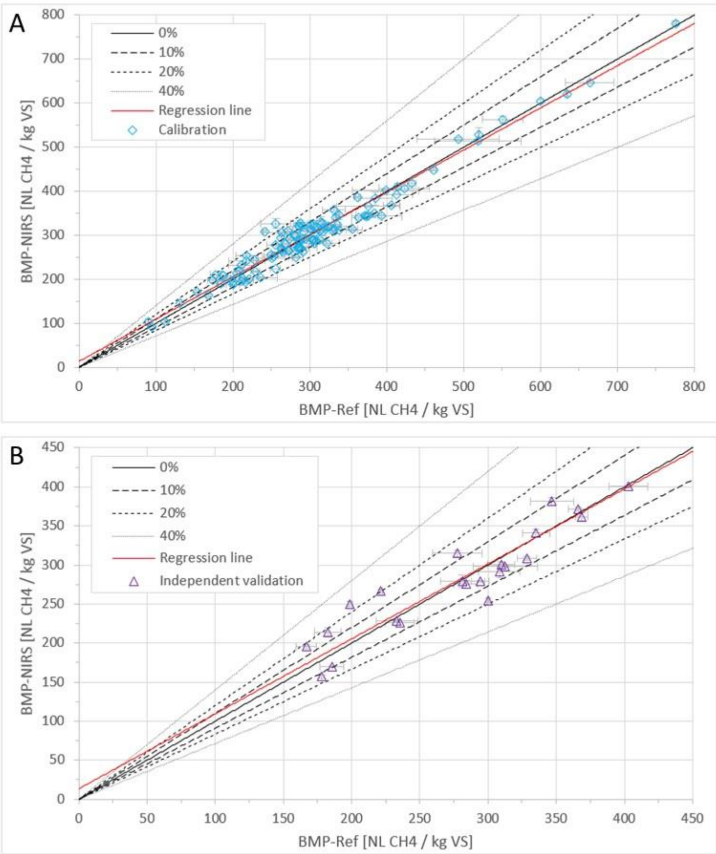

Fig. 1 Predicted versus measured BMP values for the calibration set (A) and independent validation set (B)

Finally, an independent validation has been carried out on independent samples (23 samples), different from the calibration and validation sets (different products, different origins, different scanning dates). The results of the predicted BMP values vs measured BMP for this independent set are represented in **Fig. 1B**. The independent validation set, mainly composed by agricultural and animal wastes, has a lower but still interesting value of R^2 (0.83) and RMSEP (32 NL CH_4 kg^{-1} VS). Interestingly, such values are higher than reported by Lesteur et al. (2011) on an independent validation set with R^2 (0.53) and RMSEP (78 NL CH_4 kg^{-1} VS). The higher values obtained in our study are mainly explained by the fact that our independent validation set is mainly composed of agricultural wastes (main samples used in calibration), whereas Lesteur et al. (2011) mainly used lignocellulosic wastes which were under-represented in their calibration data set and thus not well predicted by their model. Finally, a lower but satisfactory RPD values of 2.19 was obtained. The coefficient values (R^2, RMSEP, RPD) obtain for the independent validation data set are lower than previous reported for calibration and validation sets but still satisfactory, showing the accuracy of the BMP-NIRS model in predicting the BMP value of a range of organic substrates mainly composed of agricultural wastes.

Conclusions and perspectives:

To conclude, the predictive model “BMP-NIRS” developed by the APESA was found to be an efficient tool for fast determination of the Biochemical Methane Potential with a coefficient of determination (R^2) of 0.83 and a RMSEP value of 32.1 NL CH_4 kg^{-1} VS for the independent validation data set. In prospect, we intend to improve this model by adding more samples, but also to develop models dedicated to samples categories (agricultural biomass, animal wastes, etc.) and compare theirs performances with the “BMP-NIRS” model developed in this study.

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