Lab-scale Anaerobic Digester Follow-up by Near Infra-Red Spectroscopy

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Abstract
Near Infra-Red Spectroscopy (NIRS) as an alternative tool to monitor anaerobic digestion of organic substrates was investigated. More than 250 samples from one- and two-phases anaerobic digesters were used to provide absorbance spectra and were correlated to their reference value for parameters such as total and volatile solids, COD, TVFA (Total Volatile Fatty Acids) and acetate concentration. NIRS predictions were satisfactory for total solids (RMSEC = 4.73 $g.L^{-1}$ on a 24 to 56 $g.L^{-1}$ range; $R^2 = 0.72$), and acetate concentration (RMSEC = 1.87 $g.L^{-1}$ on a 0 to 14 $g.L^{-1}$ range; $R^2 = 0.72$). Representative high variability datasets are required to develop accurate models.

Keywords
Near Infra-Red Spectroscopy; PLS; VFA; Anaerobic Digestion

INTRODUCTION

Several parameters, such as substrate characterisation, volatile fatty acids analysis, pH monitoring, nitrogen concentration measurement, etc., are used to control and enhance the efficiency of anaerobic digesters. NIR spectroscopy is an alternative to classic lab approaches for fast quantitative and qualitative characterisation of organic matter content. One single spectrum, according to available models, could be used to determine the value of key parameters useful for anaerobic digestion operational monitoring. NIRS suitability has been demonstrated for monitoring anaerobic digestion process (Jacobi *et al.*, 2009; Lomborg *et al.*, 2009), characterising the incoming feedstock (Jacobi *et al.*, 2011) and predicting BMP of MSW (Lesteur *et al.*, 2011), meadow grasses (Raju *et al.*, 2011) or varied organic substrates (Doublet *et al.*, 2011). The aim of our work is to develop NIRS models for the prediction of classic parameters used in AD in a codigestion context. Parameters such as total solids (TS), volatile solids (VS), chemical oxygen demand (COD), total volatile fatty acids (TVFA) and acetate concentrations were selected because of their capacity to characterise the anaerobic digestion state.

MATERIALS & METHODS

Samples

More than 250 samples were collected from 16 lab-scale digesters (5 and 10 liters) fed with a mixture of substrates representative of co-digestion scenario (municipal and industrial sludge, agricultural waste, agro-industrial waste…). The lab-scale digesters were operated at different operational parameters (hydraulic retention time, organic loading rate, temperature, pH and phase separation) to generate variability on the collected samples.

Reference values

TS and VS contents were determined according to French standards NFEN12880 and NFEN12879.

COD was determined using Hach Lange kits.

TVFA and acetate concentrations were determined thanks to a GC-FID (Agilent) equipped with a HP-FFAP column.

Spectra acquisition
Spectra were taken with a Thermo Scientific Antaris II, a Fourier-transform NIR spectrophotometer with wavenumbers ranging from 10.000 to 4.000 cm^{-1} with a step of 8 cm^{-1}. For each sample, two different spectra were recorded on a rotating cup spinner (each spectra is the average of 68 scans) and both absorbance spectra were averaged.

PLS model and Chimiometric methods
Samples were split into a calibration data set and a validation data set (2:1). Calibration was performed by Partial Least Square (PLS) regression on transformed absorbance spectra.

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 datapoints on both sides.

The spectral information of the entire data sample set was studied using Principal Component Analysis (PCA).

The quality of models was evaluated by the coefficient of determination (R^2) and the Root Mean Square Error (RMSE) and the bias for predicted values (Reed et *al.*, 2011).

$$R^2 = \frac{\sum(\hat{y}_i - \bar{y})^2}{\sum(y_i - \bar{y})^2} \qquad RMSE = \sqrt{\sum_{i=1}^{n} \frac{(\hat{y}_i - y)^2}{n}}$$

With $\hat{y}_i$, the predicted value of the sample i in the data sample set, $\bar{y}$, the average of the measured values of the data sample set, y_i, the measured value of the sample i in the data sample set and n, the number of samples in the data sample set

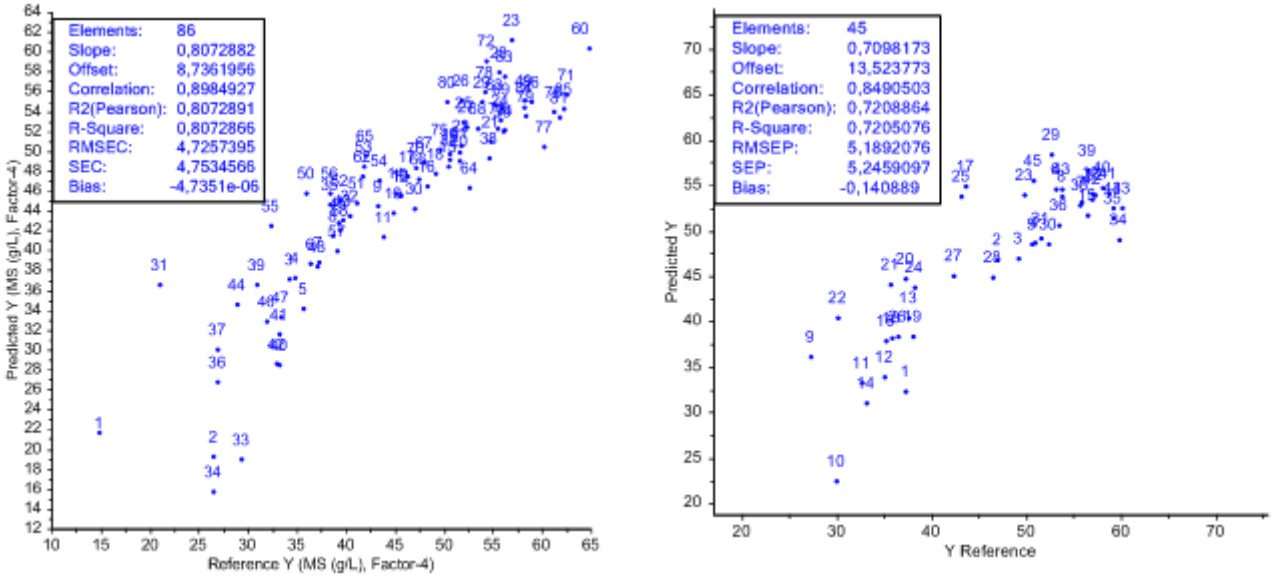
All transformations and calibrations were performed with The Unscrambler 10.2 software (CAMO Software AS, Norway).

RESULTS & DISCUSSION
Most of the parameters (total solid, volatile solid, COD) observed a normal distribution. TVFA and acetate observed an exponential distribution.

PCA were performed on raw samples to identify atypical samples. Two groups were identified as outliers. The first one was characterized by strong VFA and COD concentration (samples obtained in the hydrolytic phase of a two-phase system) with the lower baseline on raw spectra plot. The second group included all the samples from a single phase anaerobic digester with an atypical comportment.

Focus on Total Solids model
Total solid prediction was facilitated by the strong absorbance of water in the infrared region. The variations of spectra were therefore well correlated to the variations of total solids contents of the samples. The results of the calibration and the prediction models were respectively RMSEC = 4.73 $g.L^{-1}$ on a 15 to 61 $g.L^{-1}$ range; R^2 = 0.81 and RMSEP = 5.18 $g.L^{-1}$ on a 24 to 56 $g.L^{-1}$ range; R^2 = 0.72 (Figure 1). The loss in performance between calibration and validation sets might be due to size of the prediction set, allowing more weight to limit value as sample n°10 (Figure 1b)

The model was used to predict the total solid value of a reactor excluded from the calibration set and the model appeared to be performing well for this follow-up. The prediction of total solids by the NIRS could therefore replace the determination by oven drying and weighting.



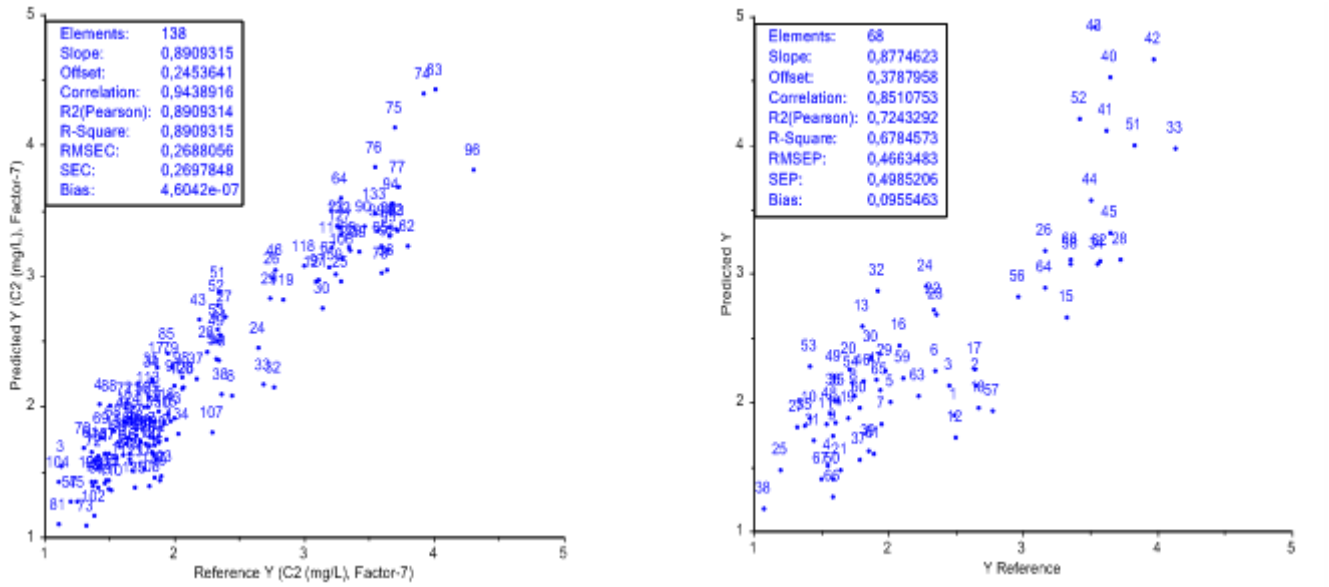
A) B)

Figure 1.Predicted versus measured values for the total solid model calibrated on SNV transformed spectra for the calibration set (A) and the validation set (B).

Focus on Acetate model

According to the exponential distribution of the reference values for acetate, the logarithm has been applied to bring back the reference values to a normal distribution. To optimize the model, a powder of sodium acetate was used to determine the regions of the spectra correlated to the atomics bonds of the acetate. The selected regions minus the characteristic regions for OH bound were used in the PLS regression as the only variables. The result of the calibration and validation models (Figure 2) were respectively RMSEC = 1.87 $g.L^{-1}$ on a 0 to 14 $g.L^{-1}$ range; R^2 = 0.89 and RMSEP = 2.95 $g.L^{-1}$ on a 0 to 14 $g.L^{-1}$ range; R^2 = 0.72. The loss in performance might be due to the difference in datasets size.

The acetate model can be improved with a lower range but this new range is not suitable for anaerobic digestion optimization. After calculations of the lab repeatability, this model is as good as the VFA-chromatograph used for the acquisition of reference values. Without enhancing this lab measurement, the acetate model cannot be improved for this range of data.



A) B)

Figure 2. Predicted versus measured values for the acetate model calibrated on SNV transformed spectra and wavelengths selection and log-transformed reference values for the calibration set (a) and the validation set (b).

CONCLUSION

Both presented models, for total solids (RMSEC = 4.73 $g.L^{-1}$) and acetate (RMSEC = 1.87 $g.L^{-1}$), show that NIRS is a suitable technique for anaerobic digesters follow-up also in a codigestion context. The number of available parameters-based models can be increased with the enhancement of the variability of the databases.

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