Hyperspectral imaging techniques applied to the monitoring of the anaerobic digestion process of bio-waste

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Introduction

The Anaerobic Digestion (AD) process was historically used for stabilisation of sludge in wastewater treatment plants. In the last few years, improved waste production, in particularly organic waste, and the corresponding increase in energy consumption, has led the scientific community to study the possible AD process and technology improvements with the aim to apply it for the stabilisation and energy valorisation of organic wastes.

The anaerobic digestion process operates in the absence of oxygen to transform organic materials to gases such as methane and carbon dioxide. A reduction of the quantity of solids and pathogenic organisms, and the production of an optimal fertiliser is also achieved. It occurs in several steps, starting with the fermentation process (hydrolysis and acidogenesis) of all complex substances (e.g., fats, proteins, carbohydrates) present in organic matter that are converted into monomers and then into volatile fatty acids (VFAs). In acetocenesis, the transformation of VFA and alcohol into acetic acid, hydrogen and carbon dioxide by acetogenic bacteria occurs. Finally, in methanogenesis, methane is produced by transforming acetic acid (acetoclastic methanogens) and hydrogen and carbon dioxide (hydrogenophilic methanogens).

The anaerobic digestion process is sensitive to total solids (TS), volatile solids (VS), volatile fat acids (VFA), pH, carbon and nitrogen content of the organic mixture. Currently, correct process characterisation[1] thus requires periodical sampling of the organic mixture in the reactor[2,3] and analysis of the samples by traditional physico-chemical methods.[4,5] Whether the digestion is "wet" (e.g. solid fraction in the digester below 10% in weight) or "dry" (e.g. semi-solid fraction in the digester over 20-25% in weight) different sampling strategies have to be applied: liquid sampling, in the first case, or sampling of the "mud" in the second case. Both approaches are discontinuous, time-consuming, expensive and do not allow a continuous monitoring of the solid fractions in terms of either composition or homogeneity. The possibilities offered by a new analytical approach based on near infrared (NIR) hyperspectral imaging (HSI) were investigated and critically evaluated in this study.

Materials and Methods

Anaerobic digestion

A galvanized-steel cylindrical anaerobic bioreactor of 200 l nominal and 150 l working volume with instruments for continuous pH, temperature and biogas monitoring was used (Figure 1).[6] Cow manure and bio-waste from wine production were added to the digestion system in varying ratios. Tests were carried out utilising white grape marc (WGM) and red grape marc (RGM) as organic substrates and cow manure (CM) as the inoculum (Table 1). Two batch digestion trials were completed; in Test 1, 30.24 kg of WGM and 10 kg of CM were mixed together while in Test 2, 40.86 kg of RGM and 10 kg of CM were mixed together. The humidity of the digestate was approximately 90% in both tests. The same quantity of inoculum and the same mesophilic conditions (35°C ± 2°C) were utilised. Tests were carried out using the same reactor at two different times and each test was conducted for 14 days. Samples for NIR HSI and traditional solid fraction analyses were collected from the digester every two days: 14 samples were collected in total.

Samples analyses and NIR HSI spectra acquisition

TS, moisture, VS, ash contents and COD analyses were carried out to characterise WGM, RGM, and CM (Table 1) together with the digestate samples collected during the anaerobic reaction (Table 2). TS, moisture, VS and ash weight values were determined according to ANPA standard methods; the COD concentration values in liquid organic matter was measured according to analytical methods illustrated by ISRA-CNR[13] and according to the Italian directive D.M. 13/09/1999 for the COD concentration values in solid organic matter. Nitrates were measured by ion chromatography utilizing a Shimazu CDD-10AVP™.

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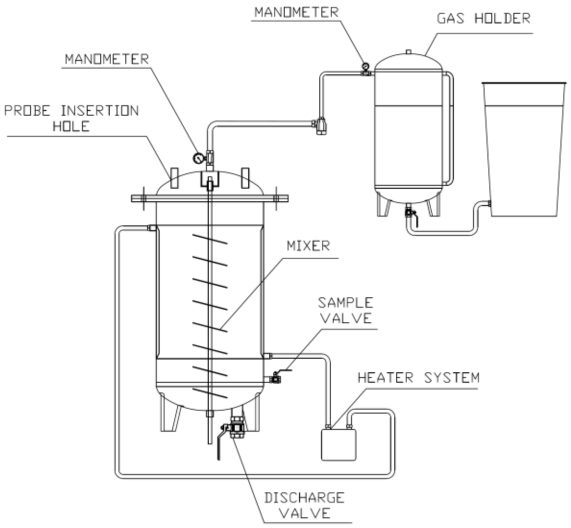

Figure 1. Scheme of the pilot anaerobic digestion system.

Table 1. Characteristics of the substrates utilised to perform the tests.

Parameter	**WGM**[a]	**RGM**[b]	**CM**[c]
Moisture (% weight)	58.94	62.53	84.74
Total Solids (%)	41.06	37.47	15.26
Volatile Solids (%)	94.70	92.54	79.17
Ash (%)	5.30	7.46	20.83
COD (mg $O_2.g_{GM}^{-1}$ and mg $O_2.l_{IN}^{-1}$)	172.37	120.66	-

[a]WGM: white grape marc. [b]RGM: red grape marc. [c]CM: cow manure

analytical unit. Each sample was previously centrifuged (5 min at 3500 rpm) and the supernatant filtered through 0.45 µm cellulose filters. Details of the analytical procedure adopted can be found in Alvarez et al.[12]. The pH values were measured by a pH collecting device (J DIGITAL™ pH) installed in the anaerobic reactor.

A NIR hyperspectral imaging system constituted by a Specim ImSpector™ N17E (Oulu, Finland) and a temperature-stabilised InGaAs camera was utilised. Sample spectra acquisition was carried out on 21 ml of liquid sample placed in a glass container. Fourteen hyperspectral images were acquired from 14 different samples extracted following the sampling strategy previously outlined. Reflectance spectra in the 1000–1700 nm wavelength range were acquired (Figure 2) at a spectral resolution of 7 nm; a total of 121 wavelengths were thus measured. The spectrometer was coupled to a 50 mm lens. A diffuse light cylinder architecture with aluminum internal coating and five halogen lamps was used as an energising source.

NIR data pre-treatment and analysis

All the HSI processing was completed using the PLS Toolbox™ (Eigenvector Research Inc. Wenatchee, WA, USA) inside Matlab™ environment (Mathworks Inc., Natick, Massachusetts, USA). The spectral data range was reduced to 1000–1600 nm followed by a baseline correction. Then an absolute value correction was applied to shift negative values obtained after the baseline correction to positive values (Figure 2).

Table 2. Digestate sample characteristics.

	WGM[a] **Experiment**			**RGM**[b] **Experiment**		
	Mean	**Min**	**Max**	**Mean**	**Min**	**Max**
Total Solids (%)	2.1	1.59	3.69	6.32	1.64	5.06
Volatile Solids (%)	64.1	56.00	78.35	57.56	51.23	63.55
pH	5.41	4.82	6.14	5.45	4.85	6.13
COD (mg $O_2.l^{-1}$)	37 607	32 500	58 750	18 579	10 613	29 817
Nitrate (mg.l^{-1})	19.38	9.47	40.14	41.98	9.5	63.23

[a]WGM: white grape marc. [b]RGM: red grape marc.

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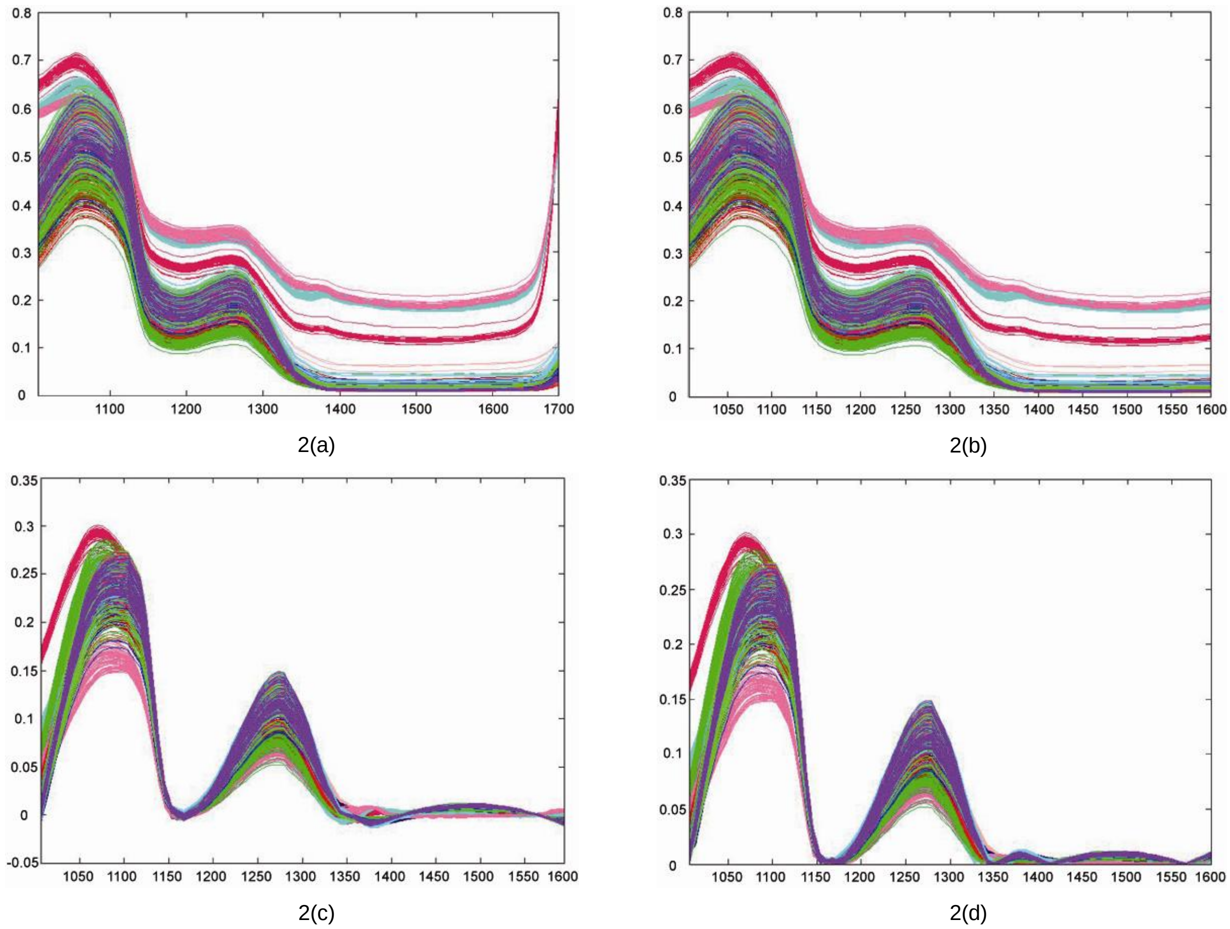

Figure 2. Different steps of spectra pre-treatment. 2(a) raw spectra (as acquired), 2(b) cut spectra, 2(c) baseline corrections, and 2(d) absolute value correction. X axis: wavelength (nm) – y axis: reflectance (%).

The partial least squares (PLS) method was used to calculate a model able to predict pH, COD, VS and nitrate concentration in the mixtures. A dataset of 1400 spectra was used to calculate and validate the PLS model; a cross-validation procedure (e.g. k-fold validation) was used for validation.

Results and Discussion

The digestate characteristics of the WGM and RGM anaerobic digestion trials are reported in Table 2. The spectra obtained by NIR HSI showed a marked decrease in the wavelength region between 1300 and 1700 nm (Figure 2) due to sample water content variation caused by the progression of the digestion process.[8,9]

The results, related to the adopted prediction models[10,11] utilised for the characterisation of the chemical and physical parameters of the digestate, are shown in Figure 3 and Table 3. The calibration model for COD was very good (r^2 = 0.90 and RMSEC = 5222.89 mg O_2/l) and a good validation was obtained (RMSECV = 5495.16 mg O_2/l. Good values were also obtained for the VS and pH calibration models, with r^2 values of 0.76 and 0.71, respectively. The errors for calibration (RMSEC) and validation (RMSECV) were also acceptable for both parameters (RMSEC = 5.09% TS and RMSECV = 5.29% TS for VS model; RMSEC = 0.17 and RMSECV = 0.18 for pH model)**.** Such results are positively evaluated if referred to those usually obtained following the classical sampling-analytical approach but requiring complex sampling procedures and longer analytical times. Furthermore, the r^2 values obtained for COD, VS, pH and TS are useful for the industrial process. Less satisfactory results have been obtained for nitrate predictions: the model shows a r^2 of 0.68 and RMSEC and RMSECV values equal to 12.32 mg.l^{-1} and 12.83 mg.l^{-1}, respectively. Preliminary results obtained in this study show the NIR HSI approach is a feasible technique to rapidly and accurately quantify several parameters in anaerobic digestion processes (COD, pH, VS and Nitrate) without performing any classical analysis at chemical laboratory scale (e.g. reduction of costs). Further tests will be carried out to improve and validate the results.

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Conclusions

The application of the proposed technique was to identify and demonstrate the correlation existing, in terms of quality and reliability of the results, between the classical physico-chemical analytical approach and the NIR HSI based one.

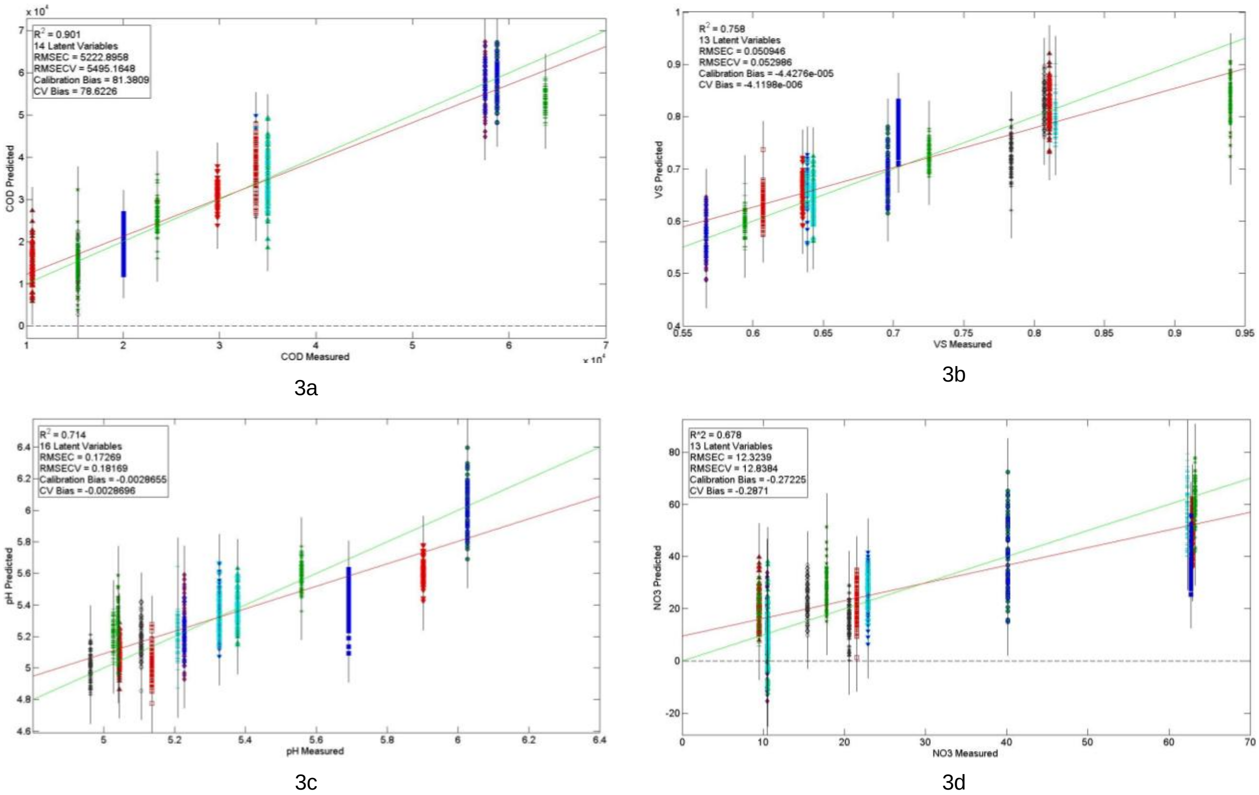

Figure 3. Predicted versus measured plots for: 3a chemical oxygen demand, 3b volatile solids, 3c pH and 3d nitrate.

Table 3. Digestate samples characteristics related to WGM and RGM as resulting from prediction models.

	Raw data				Pretreated data			
	LVs[a]	**r^2**[b]	**RMSEC**[c]	**RMSECV**[d]	**LVs**[a]	**r^2**[b]	**RMSEC**[c]	**RMSECV**[d]
Volatile Solids [%TS]	11	0.68	5.85	6.07	13	0.76	5.09	5.29
pH	11	0.67	0.19	0.19	16	0.71	0.17	0.18
COD [$mgO_2.l^{-1}$]	15	0.77	7 879	8 321	14	0.90	5 223	5 495
Nitrate [$mg.l^{-1}$]	12	0.57	14.19	14.81	13	0.68	12.32	12.83

[a]LVs: Latent Values – [b]r^2: Correlation factor
[c]RMSEC: Root-Mean-Square Error of Calibration – [d]RMSECV: Root-Mean-Square Error of Cross-Validation

More specifically, with reference to anaerobic digestion processes and the phenomena occurring in the solid fraction inside bioreactors, the proposed approach, capable of being implemented on-line (e.g. digestion liquid continuous recirculation inside a measuring cell hyperspectral probe equipped) could be profitably applied not only to perform a full control of the process but also: i) to carry out a real-time (e.g. no physical collection of the digestion liquid is required) identification of possible reductions in biogas production due to some inhibitory events in the anaerobic reaction, ii) to develop optimised biomasses recipes for biogas production according to the different available natural wastes and iii) to set up innovative control strategies to perform a full continuous control of the process.

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