Process Biochemistry 45 (2010) 431–440

Contents lists available at ScienceDirect

Process Biochemistry

journal homepage: www.elsevier.com/locate/procbio

Review

Alternative methods for determining anaerobic biodegradability: A review

M. Lesteur [a,*], V. Bellon-Maurel [b], C. Gonzalez [c], E. Latrille [a], J.M. Roger [b], G. Junqua [c], J.P. Steyer [a]

[a] INRA, UR050, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, Narbonne F-11100, France
[b] Cemagref, UMR ITAP – Information and Technologies for AgroProcesses, BP 5095, 34033 Montpellier Cedex 1, France
[c] Laboratoire Génie de L'Environnement Industriel, Ecole des Mines d'Alès, 6 avenue de Clavières, 30319 Alès Cedex, France

ARTICLE INFO

Article history:
Received 24 August 2009
Received in revised form 18 November 2009
Accepted 28 November 2009

Keywords:
Waste characterization
Biodegradability
Methane production
Spectroscopy
Near-infrared spectroscopy
Oxidation

ABSTRACT

The characterization of solid wastes is a necessary step before they can be used in anaerobic digestion. The quantities of different compounds (carbohydrates, proteins, lipids and fibers) and anaerobic biodegradability (capacity to produce methane) are important information required to characterize waste. The Biochemical Methane Potential (BMP) test is one of the most relevant tests for assessing the biodegradability of waste materials. The BMP test is run under anaerobic conditions, using bacteria populations, which makes it very time consuming, i.e., about 30 days. This paper presents alternative methods for determining the anaerobic biodegradability of solid waste. First, we describe the already existing tests for characterizing organic matter. Then we correlate an aerobic test with an anaerobic test in order to estimate anaerobic biodegradability and biogas production. This shortens the analysis time to 5 days. Models using physico-chemical characteristics as input data (total carbohydrate, total nitrogen, fiber, etc.) can predict the amount of methane produced by correlation. Pyrolysis is a very fast analytical test that can be used to characterize solid waste. Lastly, spectroscopy techniques seem to be useful for determining biodegradability, in particular by taking into account the interaction between different molecules in the organic matter.

Contents

* Corresponding author. Tel.: +33 04 68 42 51 78; fax: +33 04 68 42 51 60.
E-mail address: lesteur@supagro.inra.fr (M. Lesteur).

1359-5113/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.procbio.2009.11.018

1. Introduction

Anaerobic digestion of solid waste materials is increasingly used by local authorities, agro-industrial companies and farms to produce methane. In 2007, about 4000 digesters were used in Germany by farmers. In Europe, about 4 million tons per year of Municipal Solid Waste (MSW) are processed by about 120 full-scale plants [1]. A wide range of waste can be used as substrate for anaerobic digestion [2–7]. Before starting a digestion process, the substrate must be characterized. This involves determining the amounts of major component families (carbohydrates, lipids, proteins and fibers, such as cellulose, hemicellulose and lignin), and also estimating the biodegradability or quantity of methane that can potentially be produced under anaerobic conditions. Until now, organic matter has been characterized using either a chemical or biological method. Conventional chemical and colorimetric approaches, using reactants for chemical analyses, i.e., Anthrone or Lowry methods, can be expensive, very time consuming and may use hazardous substances. Anaerobic biodegradability is typically evaluated using a biological test, the Biochemical Methane Potential (BMP) test [8], which produces two values: the BMP value, which is the ultimate amount of methane produced under anaerobic conditions, and the production kinetics. These data are currently used to design and operate full-scale anaerobic digesters. They enable the loading rate and Hydraulic Retention Time (HRT) to be defined. Unfortunately, since this test is only based on microbial processes, is very time consuming – about 30 days, or more – and therefore unusable for resetting biodigesters. However, there is a relationship between the quantity of methane produced and the organic matter used: not only the biodegradable fraction but also the non-biodegradable fraction (lignin, hemicellulose). Some studies have successfully found this relationship by building mathematical regression models that compare the quantity and/or quality of the organic matter and the amount of methane produced [9,10]. However, the direct correlation between the kinetics and the organic matter is difficult to determine, because the microorganism population plays a significant role that needs to be taken into account. Moreover, characterizing the organic matter using standard (i.e. chemical) methods is very time consuming. It is of prime interest to find faster ways to characterize the organic matter, and consequently to determine the biodegradability. Faster and easier analytical methods for characterizing organic matter are already being used.

The objective of this paper is to present and evaluate the various strategies and analytical methods, in order to predict the potential methane production and digestion kinetics while reducing the time needed for this analysis as compared with the standard BMP test.

After presenting the standard way of measuring BMP, the following strategies are described:

- quick respirometric tests, with the objective of accelerating the biological response;
- analyzing the chemical composition of the waste and calibrating the BMP versus these chemical parameters;
- spectroscopic techniques, in order to find faster ways for this chemical analysis;
- adding a new dimension by "chemically modifying" the sample and analyzing the resulting product.

In the conclusion, these various methods are compared and critically analyzed, and innovative techniques for faster and more relevant BMP assessment are proposed.

2. The BMP test

2.1. An anaerobic respirometric test

The BMP value can be used as an index of the anaerobic biodegradation potential. The BMP is the experimental value of the maximum quantity of methane produced per gram of volatile solid (VS). The BMP is measured with the BMP test, which consists in a respirometric test, i.e., measuring the methane or biogas produced by a known quantity of waste in a batch in anaerobic conditions [8]. The digestion kinetic, also obtained with the BMP test, is sometimes used for designing and operating anaerobic digesters [10]. They can also help to identify microbial inhibition, overloading, and adaptation [8]. The biogas pressure (or the cumulated volume) should be measured almost every day, and the biogas composition has to be determined using gas chromatography.

2.2. Sensitivity of the BMP test

BMP test values are sensitive to several parameters. Some of them depend on the operating conditions, such as temperature, pH, and agitation intensity. Temperature and pH have a direct effect on the microorganisms present. Temperature is generally maintained at 35 °C. Thermophilic conditions (55 °C) lead to faster breakdown due to higher methanogenic activity [11]. The pH has an effect on the microorganism enzymes, it can change their configurations and influence the kinetics of the reactions [12–14]. A low pH can bring about an accumulation in Volatile Fatty Acid (VFA), which inhibits digestion, while a high pH leads to an increase in free ammonia, which is also toxic for the methanogenic populations. That is why a buffer has to be used in the BMP test. The size of the particles influences the kinetics, due to variations in the substrate's available specific surface area for microorganisms. The hydrolysis rate is lower for particulate matter than for dissolved polymers: the smaller the particles, the larger the specific surface available to the enzymes and the better the production [13]. In some cases, decreasing the size of poorly digestible substrates containing a large quantity of fiber improves gas production (especially when it affects the structure of the solid in a way that some zones are made accessible to the enzymatic attack) and reduces digestion time [15]. The solubilisation potential also influences the BMP test. The more soluble the organic matter is (simple carbohydrates, amino acids, simple lipids, and VFA), the faster the degradation. Complex and high molecular mass molecules, such as proteins and fibers, need to be hydrolyzed in order to be accessible. It is mainly carried out by external enzymes. Theoretically, the inoculum/substrate ratio has an effect only on the kinetics, and not on the ultimate methane yield, which only depends on the organic matter content [16,17]. This ratio also seems to have an effect on the lag phase, which is shorter for higher ratios [12]. A small amount of inoculum is preferred because of the endogenous biogas production, which can biases the results [13]. Ratios between 1 and 3 are often chosen. Each substrate has its best ratio, taking into account the potential amount of VFA produced and its capacity to buffer the medium due to the ammonium produced by the hydrolysis of protein. A compromise must thus be found between the inoculum's own production of biogas, the tolerated lag time, and the buffer capacity.

Various publications have reported on the anaerobic digestion of different waste materials to determine their BMP value. Table 1 presents some of them with the associated methane yields. As observed in these studies, methane production levels vary greatly among the different wastes, which is mainly due to differences between their organic matter compositions. Fig. 1 shows examples of results obtained using the BMP test.

Table 1
Comparison of waste types with the ultimate methane yields obtained by anaerobic digestion.

Waste	BMP (SD) ($ml\,CH_4\,g^{-1}\,VS$)	References	Waste	BMP (SD) ($ml\,CH_4\,g^{-1}\,VS$)	References
Apple-pulp	306[a]	[83]	*Macrocystis*	390–410	[84]
Apple-slurry	279[a]	[83]	Mango peels	454 (13)	[85]
Apple waste	317	[10]	Mixed food waste	472	[86]
Asparagus peels	219[a]	[83]	Napier grass	357 (13)	[85]
Banana peels	289 (16)	[10]	Onion peels	400 (14)	[85]
Barley	20	[5]	Orange peels	297 (26)	[10]
Carrot peels	388 (35)	[10]	Pig manure	356 (28)	[3]
Carrot waste	418[a]	[83]	Pineapple	356 (9)	[85]
Cattle manure	148 (41)	[3]	Potato peels	390 (25)	[10]
Cellulose	419 (19)	[85]	Salad (lettuce)	294 (30)	[10]
Citrus	473 (11)	[85]	Saw manure	275 (36)	[3]
Coffee waste	255	[5]	Sorghum	404 (36)	[85]
French bean waste	343[a]	[83]	Source-sorted OFMSW	275–410	[30]
Garden beet	231 (8)	[85]	Spinach waste	314[a]	[83]
Garden pea	390 (13)	[85]	Straw	195 (5.9)	[3]
Grape	231 (15)	[85]	Strawberry	262[a]	[83]
Harvested grass	388 (35)	[10]	Tomato	297 (12)	[85]
Laminaria sp.	260–280	[84]	Woods	260 (5)[a]	[6]

[a] Values calculated from reference data.

2.3. BMP, anaerobic biodegradability, and digestibility assessment

BMP, anaerobic biodegradability, and digestibility are similar. They all deal with the degradation of organic matter (waste or forage) by microorganisms in anaerobic conditions. Degradation of organic matter in anaerobic digestion leads to the production of biogas (methane and carbon dioxide). At high gas production, less organic matter remains after fermentation, which indicates a higher biodegradability.

The relationship between anaerobic biodegradability (BD) and BMP is expressed by Eq. (1) [10].

$$BD = \frac{BMP\,(ml\,CH_{4,STP}\,g^{-1}\,VS)}{350 \times COD_{waste}\,(g\,COD\,g^{-1}\,VS)} \tag{1}$$

where COD is the Chemical Oxygen Demand and BMP the Biochemical Methane Potential value expressed in the Standard Temperature and Pressure (STP), respectively 273.15 K (0 °C) and 100 kPa (1 atm).

It is admitted that 1 g l^{-1} of COD produces about 350 ml of CH_4 [13]. This biodegradability value is not accurate, since bacterial growth uses part of the organic matter that is consumed during methane production [13].

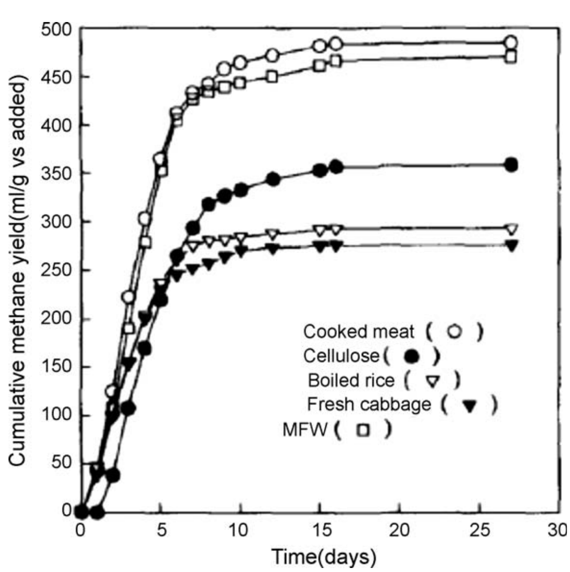


Fig. 1. Cumulative methane production of various samples [86]. MFW: Mixed Food Waste.

2.4. Conclusion

The BMP test has the advantage of being applicable to all kinds of waste. The conditions of use do not change too much with the waste. Since the BMP experiment takes 25 days, it is difficult to decide to add a new waste material into an industrial bio-reactor without the risk of reducing the microbial population thereby decreasing the methane yield. It is thus necessary to find other methods for assessing the BMP value in less time. The first and most straightforward way is to reduce the length of the respirometric tests.

3. Shorter respirometric tests: the aerobic test

The aerobic respirometric test involves carrying out the test under aerobic conditions and measuring O_2 consumption and/or the amount of CO_2 released [18]. It is used to estimate the biodegradability of the waste or determine the maturity and stability of compost [19]. The kinetics and biodegradability of biodegradable materials have been tested using similar tests [20]. These aerobic respirometric tests generally take about 30 days. However, some aerobic tests can be performed in a few days, hours, or even minutes. Two kinds of measurements can be carried out under aerobic conditions, either "closed-bottle," where no aeration takes place, or "dynamic", where oxygen is allowed to flow during the test. Each method provides its own index [21,22]. For example, the OD_{20} test (Oxygen Demand in a 20 h respirometric test) or the BOD_5 test (Biochemical Oxygen Demand, in 5 days) [23,24]. Biodegradability is sometimes also expressed as BOD/COD [25,26]. Even though these methods are carried out under aerobic conditions, they are currently used to assess the methane production obtained under anaerobic conditions [27]. A good correlation (r^2 = 0.80 and 0.94) has been found between the Respiration Index (RI_4, cumulative oxygen consumption in 4 days) and the biogas production index (GS_{21} Generation Gas Sum measured after 21 days of incubation) [26,28].

These short aerobic methods offer the advantage of being less time consuming than the BMP method, and can be implemented with all kinds of waste. However, this can also be a disadvantage, because only the readily available and easily degraded organic matter is broken down. Complex organic matter, such as cellulose, is not taken into account in the measurement. Moreover, it still uses bacterial populations, and is therefore dependent on the quality of the inoculum. Other methods should be considered, which indirectly predict BMP, based on analysis of the chemical composition.

4. BMP prediction based on chemical composition analysis

Whereas the methods described above are designed to mimic, but at the same time accelerate, the breakdown process, the following approaches use a different strategy: they look for relationships between the BMP and the chemical composition of the sample. Two approaches are used: in the first the sample is analyzed in function of its component elements, while in the second the composition of the sample is expressed in terms of major families, such as carbohydrates, lipids, and proteins.

4.1. Elemental composition analysis (C, O, H, and N)

In 1933, Simons and Buswell developed the Buswell Formula (2) for calculating the theoretical potential quantity of methane ($B_{o,th}$) produced using a stoichiometric equation based on the chemical composition of the waste material with regard to the elements C, O, H and N.

$$C_nH_aO_bN_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right)CO_2 + cNH_3$$

$$B_{o,th} = \frac{22.4(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8})}{12n + a + 16b + 14c}\ \mathrm{l\,CH_{4,STP}\,g^{-1}\,VS} \quad (2)$$

This value is the ultimate quantity of methane that a given waste product can produce if all the matter it contained were biodegradable and converted into methane.

Measuring the elemental composition is very fast, taking only a few hours with the exception of oxygen. But the value obtained takes into account all organic matter. There is no way of differentiating between biodegradable and non-biodegradable matter. In addition, part of the biodegradable organic matter, used by the bacteria to grow, does not contribute to the BMP value [29]. The elemental composition value therefore overestimates the BMP value ($B_{o,th}$ > BMP) [30].

One way to differentiate between the biodegradable and non-biodegradable fractions is to measure the component composition (carbohydrates, proteins, and fibers).

4.2. Component composition analysis (carbohydrate, protein, and fiber content)

Organic matter can be fractionated into easily biodegradable compounds (carbohydrates, lipids, and proteins) and poorly biodegradable compounds (fibers, humic and fulvic acids) [31].

Biodegradable organic matter can be divided into different substrate categories. Simple carbohydrates, such as glucose, sucrose or lactose, amino acids or VFAs, do not need any hydrolysis phase to be broken down, so they are easily biodegradable. Complex carbohydrates, such as cellulose, proteins, and Long Chain Fatty Acids (LCFAs), have to be hydrolyzed into degradable monomers before anaerobic digestion. From Bushwell's formula, we can see that the breakdown of carbohydrates gives the least amount of methane per gram of VS (415 l CH_4 kg^{-1} VS), while the breakdown of lipids leads to the largest amount of methane (1014 l CH_4 kg^{-1} VS). However, this relationship is valid only for low concentrations of lipids. High lipid content, especially of LCFAs, could have an inhibiting effect on the biological process [32,33]. LCFAs damage the bacterial membrane, decreasing the efficiency of the metabolism. Lipids and LCFAs could also affect bioavailability, building up a

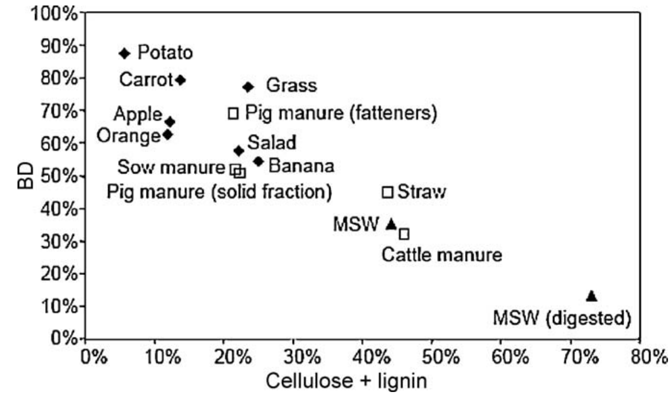


Fig. 2. Inverse relationship between lignin + cellulose content and biodegradability [10] (MSW: Municipal Solid Wastes).

physical barrier around the other components [34]. Protein digestion is slightly more productive than carbohydrates (496 l CH_4 kg^{-1} VS), but could lead to increased levels of ammonia, which is toxic at certain concentrations and interferes with the biological process by increasing the pH [35]. Determining the amount of protein before starting the methanization process could help to estimate ammonia production and thus reduce the toxic effect.

Hemicellulose and lignin are not easily degraded under anaerobic conditions [4,36]. For example, only 20 ml CH_4 g^{-1} VS was obtained from barley waste, apparently due to its high carbohydrates fiber content (about 69%) [37]. It has been reported that there is an inverse relationship between lignin content and the efficiency of enzymatic hydrolysis [3,10,31,38]. The relationship between "lignin + cellulose" content and biodegradability is shown in Fig. 2 [9]. Mathematical regression models based on component composition successfully predicted the ultimate methane yields of solid fruit and vegetable wastes [9]. However, neither simple (carbohydrates) nor two-variable (carbohydrates/fiber) regression models were successful. Only multiple linear regression models gave good results. The best models were those that included total carbohydrate (C), lignin, lignin/Acid Detergent Fiber (ADF), C/ADF, total Kjeldahl nitrogen and ash content. The model for BMP prediction gave r^2 = 0.90. Restricting the kinds of waste to only sorghum and Napier grass provided models where r^2 = 0.99. If lipids are present in the waste, their amount should be added to the input data to improve the regression. According to these results, one surprising point is that the BMP values are explained using only the carbohydrate content (total carbohydrates and cellulose) as biodegradable matter, but not the proteins. Total N is always a negative factor in these models, which could be due to the toxic effect of ammonia.

Therefore, models based on biodegradable and non-biodegradable organic matter compositions can predict the ultimate methane yield. However, the chemical composition is obtained using chemical methods, which are very time consuming. Although it is shorter than the BMP test, such chemical analysis could require several hours to several days.

Other models have been developed using the same method to predict the Anaerobic Biogasification Potential (ABP) of ingestates and digestates of a full-scale biogas plant [24]. Multiple stepwise linear regression models predicted the ABP with r^2 = 0.92. Volatile solids (VS), total organic carbon (TOC), organic matter soluble by the Van Soest method [39], and the specific oxygen uptake rate (oxygen demand during the 20-h test, OD_{20}) were used as input data. Other regressions presented negative regression factors with some components, such as Total Kjeldahl Nitrogen (TKN), ammonia (NH_3), Acid Detergent Lignin (ADL), Acid Detergent Fibers (ADFs) and P_2O_5. These negative regression slopes indicate

Table 2
Theoretical and experimental methane potential for several waste samples [30].

Samples	Theoretical methane potential[a] (ml CH_4 g^{-1} VS)	Theoretical methane potential[b] (ml CH_4 g^{-1} VS)	Experimental methane potential (ml CH_4 g^{-1} VS)
1	623	532	489
2	594	498	298
3	635	503	500
4	658	495	515
5	612	534	404
6	583	525	464
7	629	539	573
8	734	543	388
9	697	544	566
10	605	545	380
11	658	530	454
12	591	537	495
13	703	548	445
14	651	653	472
15	620	519	556

[a] Theoretical methane potential based on elemental composition (C, H, O, and N).
[b] Theoretical methane potential based on component composition (fat, protein and carbohydrate).

that a high amount of these compounds can interfere with or reduce the methane yield under anaerobic conditions. Measuring the amounts of these different compounds may be necessary for estimating the inhibition potential of the waste.

The effect of the lignin content on biodegradability has been modeled by Chandler et al. [40]. Several kinds of substrate, such as manure, newspaper, straw, leaves and other agricultural materials, were used to develop the model, predicting the effect of lignin content on biodegradability. Chandler's predictive model is as follows:

$$B = 0.83 - (0.028) \times X_1 \quad (3)$$

where B is the biodegradable fraction of VS ($0 < B < 1$) and X_1 ($0 < X_1 < 20\%$) the initial lignin content (as % VS). The correlation coefficient of Eq. (3) is 0.94. One percent of lignin decreases the digestion of volatile solids by about 3%. The equation also shows that a maximum of 83% of volatile solids could be broken down. The remaining (17%) is used for the growth of bacterial cells and metabolic products.

Two theoretical Methane Potential Models (TMPs) were compared against experimental methane potential data for the source-sorted organic fraction of municipal solid waste [30]. One TMP was predicted using the elemental composition (C, H, N, and O) and the other using the component composition (fat, protein, and carbohydrate). The TMP based on component composition was closer to reality than the element-based model, which was always higher than the experimental one (Table 2).

4.3. Conclusion

There is a clear link between the quantity and quality of organic matter and the methane yield in anaerobic digestion. In order to speed up BMP assessment, faster analytical methods must be found for analyzing the chemical composition of the waste. As they generally require little or no preparation, non-destructive methods such as spectroscopic methods are good candidates for the fast characterization of the BMP value of complex samples.

5. BMP prediction based on non-destructive analytical methods: spectroscopy

Spectroscopy is the science that studies the interaction between photon energy and matter. Various spectral ranges (UV–vis, NIR, and MIR) are used to study the organic matter in waste in order to predict its chemical composition or directly measure its biodegradability.

Table 3
Wavelengths of interest and their ratios [44].

Wavelengths (nm)	Interest of this range
260–280	Lignin and quinone moieties, material at the beginning of the transformation
460–480	Reflects the organic material at the beginning of humidification
600–670	Indicative of the humidified material

Ratios used: $Q_{2/6}$ = 280/664; $Q_{4/6}$ = 472/664; $Q_{2/4}$ = 280/472.

5.1. UV–vis: ultra-violet–visible spectrometry

UV–vis light ranges from 200 to 800 nm, with the UV–vis separation at 400 nm, which is the range of valence electron transition. UV–vis is useful for studying unsaturated molecules, such as aromatics (fibers like lignin), unsaturated lipids, and proteins with aromatic amino acids. UV spectrometry is generally used with dissolved organic matter. Solid waste must therefore be dissolved before they can be studied using UV spectroscopy, with the exception of thin layers analyzed using transmittance (e.g. plastics).

UV–vis spectroscopy has been used to characterize Olive Mill Wastewater (OMW) before and after aerobic biodegradation [41]. The shoulder at 290 nm was attributed to the aromatic compounds generated by lignin digestion. UV spectroscopy has proven to be a useful method for monitoring composting processes, because aromatic groups, which are characteristics of the humidification process absorb wavelengths in the 250–300 nm range [42]. In [42], several ratios of UV absorbance bands were computed. The changes in these ratios mainly indicated the humidification and aromatic condensation that occurred during the composting process. Table 3 gives some ratios and examples of relevant UV wavelengths. Ratio methods have also been developed to assess the maturity of olive mill waste compost [43], and sewage sludge composts [44].

Deconvolution of the UV spectra with reference spectra of humic acid, fulvic acid and a non-humidified fraction of compost provided an index for evaluating the maturity of compost [42].

As explained in Part 2, BOD/COD can be used as an index of biodegradability. UV spectrometry has already been used to determine these two values separately. The COD of wastewater has been determined using UV–vis spectroscopy and turbidity values as input into an Artificial Neural Network (ANN) [45]. A turbidity range of 0–150 NTU (Nephelometric Turbidity Unit) seems to be the limit of the method. The BOD_5 of slurry and effluents can be estimated by UV spectrometry at 280 nm [46].

With some molecules, the absorption of photons in the UV range leads to fluorescence (photon emission). Classical UV fluorescence is mainly carried out on dissolved organic matter, but solid materials can be analyzed by front-face fluorescence [47,48]. Only molecules that have an aromatic cycle or conjugated double bands, such as some proteins, humic acid and lignin, fluoresce at specific wavelengths. Carbohydrates, lipids and VFAs cannot be detected directly using this technique. A linear relationship has been found between the BOD_5 of wastewater and fluorescence at 340 nm (excitation at 280 nm) [49]. Fluorescent spectroscopy techniques have also been used to study the evolution of domestic and industrial biowaste composts [50].

5.2. Mid-infrared (MIR) spectrometry

MIR spectrometry corresponds to the 2500 nm to 25,000 nm spectral range (400–4000 cm^{-1}), i.e., to the energies of molecular bond vibrations and rotations.

MIR measurement is generally carried out by reflectance, using an ATR cell, or transmission, after mixing the waste with KBr and packing it into a pellet. The samples must be dried beforehand by lyophilization or heating in an oven (48 h at 60 °C). Aside from this preparation time, MIR measurements are very fast (a few minutes).

Infrared spectrometry has been used to characterize the organic matter in waste and monitor the decomposition of compost. Aromatic C/aliphatic C (1650/2930 cm^{-1}) absorbance band ratios have been computed in order to create an index for describing municipal solid waste composting processes and monitoring the decrease in easily biodegradable aliphatic substances, and consequently the increase in concentration of aromatic substances such as lignin [51]. The disappearance of certain bands is indicative of compost stabilization [52,53]. For example, the band at 2925 cm^{-1}, attributed to aliphatic methylene groups, and the band at 1240 cm^{-1}, attributed to C–O stretch vibrations of amide II, decrease or disappear when the compost is mature. In compost, MIR spectrometry also enables accurate prediction of humic acid content (r^2 = 86; Standard Error of Prediction (SEP) = 2.8% Organic Dry Matter) and respiration activity (r^2 = 92; SEP = 3.5 mg g^{-1} Dry Matter) [54].

5.3. Near-infrared (NIR) spectrometry

Near-infrared spectroscopy (NIRS) covers the 1000–2500 nm spectral range, which is the region of harmonics and combinations of vibration absorption bands [55]. NIR is typically used in a wide variety of applications to classify or predict the characteristics of complex media, including solid bulk material. It is a non-destructive, low-cost and rapid method. Measurement can be carried out directly in the batch by reflectance using fiber probes, and therefore no sampling is needed [55,56]. In waste treatment processes, several characteristics linked to BMP have been predicted using NIR spectroscopy.

The first way to use NIR spectrometry for BMP assessment is to determine the component composition of the input material and then deduce the BMP value by regression, as described in Section 2.2. The concentration of components relevant to biodegradation processes can be predicted using NIRS in various media. Green cereal crop, ash, crude protein (CP), crude fiber (CF), neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) have all been successfully quantified [57,58]. Several kinds of materials have already been successfully used to make up calibration datasets, such as wet and dry grape skins, de-oiled grape pips, coffee cake, coca shells, olive pulp and rice hulls [59]. The technique gave much better predictions with regard to fibrous components (hemicellulose, cellulose, lignin and NDS) than those made using chemical parameters (Ash, C and total N). Other relevant analyses for BMP include: fat, fiber, crude proteins, and pH prediction in animal feeds [60], and fiber content and chemical parameters in undried grass silage [61]. A number of studies have shown that several forage digestibility parameters can be obtained by NIR spectrometry [61–64].

Table 4
Prediction of gas production parameters using chemical data and NIRS [69].

Y	X variables		R^2	SEP
GP24	Chemical data	NDF, ash, ADL	0.789	6.757
	NIRS	NIR (p = 3)	0.889	3.877
GP96	Chemical data	Ash, ADL, LIG, CP	0.767	3.910
	NIRS	NIR (p = 6)	0.827	2.416
A	Chemical data	Ash, ADL, LIG, CP	0.819	3.716
	NIRS	NIR (p = 5)	0.801	2.711
C	Chemical data	NDF	0.906	0.0043
	NIRS	NIR (p = 4)	0.941	0.0038
L	Chemical data	–	–	–
	NIRS	NIR (p = 3)	0.597	0.288

The second way of obtaining biodegradability parameters is directly predicting them from the spectra through a dedicated calibration. For instance, the decomposition process of waste has been monitored using NIR spectroscopy by studying the variations in absorption peaks on the original and second derivative spectra [65]. Other predictions have been made using NIR spectrometry, such as the decomposability of litter, digestibility, and gas production from forage.

Litter decomposability, and more specifically Litter Mass Losses (LMLs) and the kinetic parameter k of Decomposition Equation (4) have been successfully calibrated by NIRS as can be seen in Fig. 3 [66].

$$\mathrm{LML} = e^{-kt} \tag{4}$$

where t is time.

The *in vivo* digestibility of whole-crop wheat has been predicted using various variables, such as *in vitro* digestibility, chemical composition and NIR spectra parameters [62]. The best prediction was obtained with NIRS: r^2 = 0.87, Standard Error of Calibration (SEC) = 13.0 g kg^{-1} for a 558–708 g kg^{-1} range.

The prediction of cumulative volumes of gas produced (GP) *in vitro* using Kikuyu grass as substrate after 6, 12, 24, 36 and 48 h was first attempted in 1996, based on NIR spectrometry [67]. The prediction was improved by using spectrally structured sample populations, i.e., after selecting representative samples of the whole sample population [68]. But only the asymptote value (A), i.e., the cumulative volume of gas in Kinetic Equation (5) was

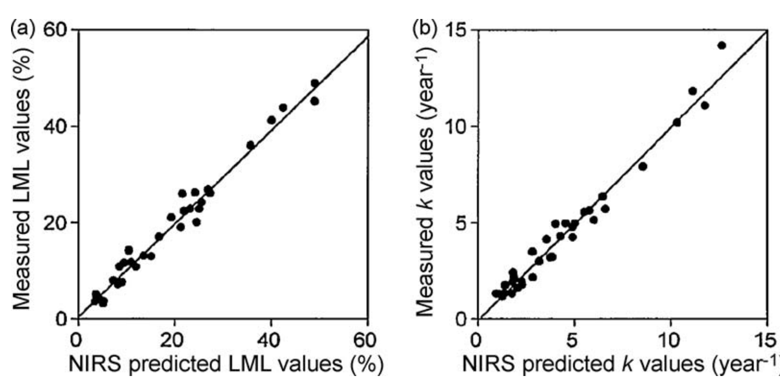


Fig. 3. Relationship between values predicted using NIRS and values measured in the calibration dataset for (a) Litter Mass Loss (LML) after 1 week of incubation and (b) the rate constant k of the single-exponential decay model [66].

correctly calibrated. The other parameters, c and L, were not correctly predicted. The authors explained that this was due to the poor fit between the NIRS and the exponential models.

$$GP = A[1 - e^{-c(t-L)}] \quad (5)$$

Another study showed the possibility of predicting the c parameter with a good degree of accuracy [69]. Better predictions were obtained with NIR spectra parameters as variables than with chemical composition parameters, due to their better representation of interactions between organic matter and physical properties, which influence the results (Table 4). Unfortunately, the latency, i.e., the L parameter, seems to be unpredictable using NIRS, since it is influenced not only by the waste but also by the bacterial population. This is also the reason why it cannot be predicted using chemical composition parameters. In addition, a wide range of GP values and high number of samples seem to be required in order to successfully predict the equation parameters.

As stated above, COD and BOD_5 are relevant parameters for biodegradability assessment. These parameters can be quantified using NIRS. The COD of a domestic wastewater treatment plants has been predicted by NIR reflectance [70]. Coefficient correlation as high as 0.96 and SEP of 19 mg O_2 l^{-1} were obtained. The same methodology, but using transmittance through 0–140 μm filters instead of reflectance, has also been successfully used to obtain BOD_5 values for wastewater (SEP = 27.6 mg l^{-1}).

5.3.1. Conclusion

Spectroscopic optical techniques have been used on solid and liquid samples to predict both the elemental composition and component composition, together with biogas production and biodegradability parameters, which are close to the BMP index.

6. Destructive techniques with fast analytical techniques

Another approach is to add a new dimension through the destruction/modification of the molecules in the waste then analyzing the resulting molecules. Two destructive methods have been used: pyrolysis and the Advanced Oxidation Process.

The various methods described hereafter provide data which are used either to predict the chemical composition of the organic matter, which is subsequently used to predict the BMP, or to predict the BMP directly by regression.

6.1. Pyrolysis combined with GC–MS

Pyrolysis is a high temperature process where biomass is rapidly heated in the absence of oxygen [71]. Pyrolysis produces a liquid, which is analyzed using Gas Chromatography/Mass Spectrometry (GC/MS). This combination is often called Py–GC/MS. Using Py–GC/MS to characterize the liquid produced can provide information about the organic matter initially contained in waste.

Pyrolysis/GC–MS has been used to characterize wastewater sludges and their neutral detergent fractions [72,73]. Pyrolysis products can reveal differences in chemical compositions between the studied sludges. Relative quantification of the insoluble organic fraction of sewage sludge has been tested. Three families of compounds (lipid-derived compounds, lignin-derived compounds and nitrogen-derived compounds) were quantified using this method [72]. Pyrolysis can also establish the relationship between organic matter content and the carbon mineralization/humidification level of the sludge ($r = -0.96$) [73]. In wood samples, a good correlation was found between the lignin content measured using chemical means (the sulfuric acid method) and the pyrolysis–GC/MS method [74]. In chemical pulps, the pyrolysis–GC/MS method can determine the relative carbohydrate composition (such as glucan, mannan, xylan, and arabinan) [75]. Plant, humus, and soil samples or extracts have also been studied using pyrolysis and the relative quantity and

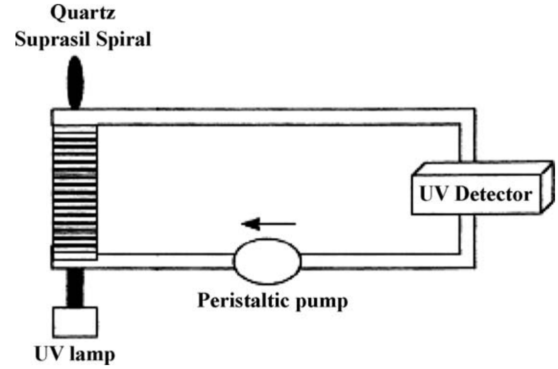
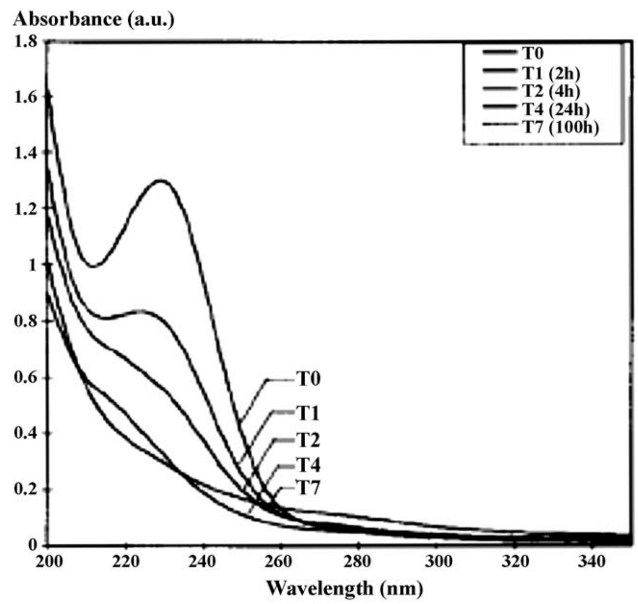


Fig. 4. Schematic diagram of a photo-oxidation reactor, with UV detection [81].



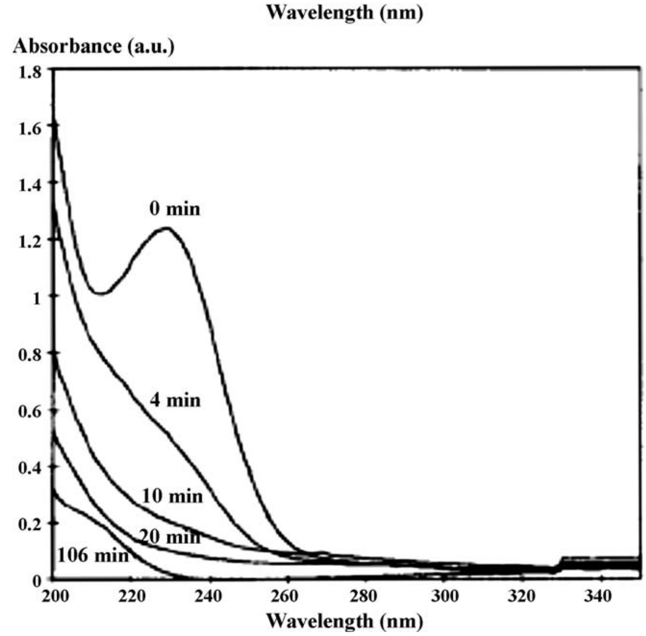


Fig. 5. Comparison of UV spectra acquired during biodegradation (top) and photodegradation (bottom) [81].

Table 5
Summary of the different kinds of tests.

Test	Measurement time	Information and practical uses
BMP	$t > 20$ days	Potential toxicity detectable, no component composition available. Biodegradability of any kind of waste available [2–6].
Aerobic test	hours $> t >$ days	Potential toxicity detectable, no component composition available. Used to estimate the maturity of compost [19]. Used to estimate biodegradability (BOD_5/COD) [25,26,28].
Elemental composition analysis	$t < 1$ h	No distinction of biodegradable vs non-biodegradable matter, overestimation of methane potential. Comparison between the prediction of BMP using Bushwell's formula and component composition analysis [29].
Component composition analysis	$t \approx 4$ days	Precisely characterizes the organic matter (soluble or insoluble): carbohydrates, proteins, lipids, fibers, total nitrogen, total carbon, etc. Predicts the biodegradability using a regression model. Prediction of BMP: fruit and vegetable waste [9]; ingestates and digestates of full-scale biogas plant [24]; municipal solid waste [30].
Pyrolysis/GC–MS	$t < 1$ h	First stage of molecular cracking by pyrolysis followed by GC–MS. Characterizes the quality and quantity of carbohydrates, lignin, nitrogen compounds and lipids. Prediction of: the biodegradability of plant, humus, and soil [76]; the decomposition stages of biowaste [77]; the biodegradability of poly(butylene succinate-co-butylene adipate) [78].
UV/UV method	$t \approx 2$ h	Monitoring of compost process, using band ratios and presence or disappearance of bands [42,44]. Able to assess reaction kinetics, and determine degradability using UV spectra [81,82].
NIR	$t < 1$ h	Prediction of chemical composition (carbohydrate, lipid, fiber, etc.) [57,58]. Prediction of litter mass decomposability [66]. Prediction of gas production kinetic parameters for forage [69].

type of lignin, polysaccharides and nitrogen compounds have been obtained [76]. Pyrolysis–GC/MS enables the different phases in a composting process to be monitored and characterized [77]. The biodegradability of polymer film (butylene succinate-*co*-butylene adipate) has also been assessed using this method. Good correlations were found between the relative amounts of the fatty acid esters quantified by pyrolysis/GC–MS and weight loss during a soil burial degradation test [78].

Based on these previous experiments, which show that pyrolysis–GC/MS is a good method for classifying organic matter into families or assessing the biodegradability of polymer films, we can assume that it would certainly provide appropriate data for assessing the BMP of organic matter.

6.2. Advanced Oxidation Process

The UV/UV method (Fig. 4) is a good example of an Advanced Oxidation Process (AOP). The UV/UV method deals with the UV oxidation of the material, with or without adding an oxidant agent, and with the UV spectroscopy detection of the compounds formed. This is relevant for estimating not only product composition, but also directly establishing biodegradation indexes. For instance, global sugar concentration can be quantified through the oxidation of sugars in carbonyl, which are detected by absorption at 268 nm [79]. Using the same method, total nitrogen in wastewater has been measured versus Kjeldahl nitrogen with correlation coefficients as high as 0.99 [80].

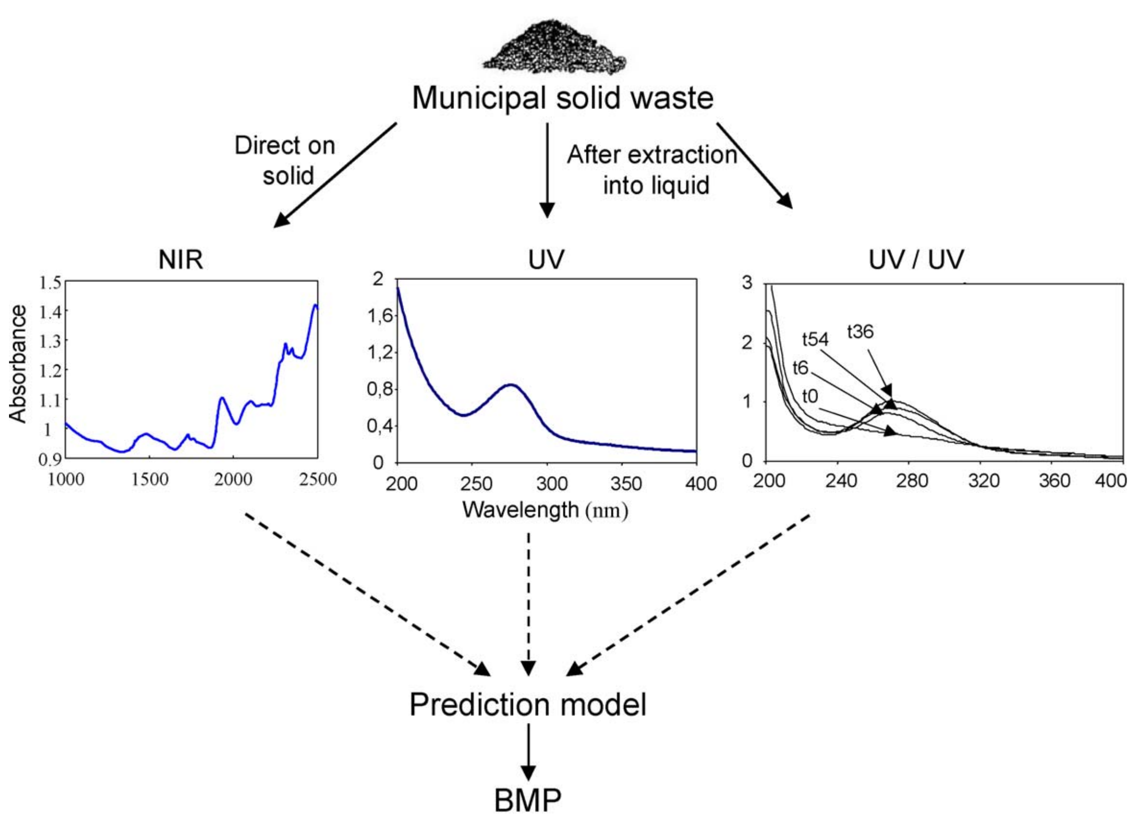


Fig. 6. BMP prediction based on spectroscopic and AOP approaches.

UV spectrophotometry applied to respirometric tests and the UV/UV method have been tested to estimate biodegradability in petrochemical wastewater [81]. The shape of UV spectra provides an index of the degree of treatability [82]. Fig. 5 compares UV spectra taken during respirometry and photodegradation tests of chemical and petrochemical wastewater. The modifications of the shapes of the spectra are the same in both the biological and photodegradation tests. The molecular transformation seems to be similar. The energy added by the UV photons accelerates the reaction, but does not change the reaction path. The UV/UV method seems to be helpful for the kinetic study of biological processes and could replace time-consuming biological tests.

7. Conclusion

In the future, anaerobic digestion will be one of the main solutions for the treatment and valorization of solid waste. It reduces quantities of waste and leads to the production of methane. One challenge will be to determine as soon as possible, when they enter the waste treatment plant, the methane production potential of the materials to be processed. Currently, biological and chemical tests are used to characterize the organic matter of solid waste. Biological tests, such as the BMP tests, are very time consuming and expensive.

The aim of this first study was to find or set up other analytical methods for predicting the ultimate methane yield and the kinetic production faster than the BMP test.

Other techniques have been developed to address this issue. They are summarized and compared in Table 5. Accelerated respirometric tests or BMP prediction based on elemental and chemical composition have been found to give relevant BMP parameters, in some cases. However, they are not totally satisfactory with regard to predicting performances or in terms of speed and cost requirements. Two other more innovative ways are therefore being explored.

The first one is to use fast measurement methods, i.e., spectrometry techniques, such as UV–Vis, NIR and MIR spectrometry. The most promising one is certainly NIR spectrometry, which, among other applications, has been successfully used to predict the gas production kinetic parameters of forage digestibility. NIR has the advantage of being very easy to perform and very fast. It can be used to directly predict the BMP value and, to some extent, certain kinetic parameters. NIR can also be used to characterize the organic matter in terms of component composition and inhibitory components (e.g., potential ammonia inhibition by estimating the quantity of protein). The drawback of NIRS is the calibration phase. Each kind of waste must have its own calibration model and a BMP test is still required to obtain the reference value. However, NIRS can be used without specific calibration to assess changes in any kind of waste by computing wavelength ratios.

The second way to speed up BMP prediction is to roughly simulate and accelerate the processes occurring in a biodegradation process, i.e., oxidation. Pyrolysis and UV oxidation show potential as methods for pre-analysis preparation. The UV/UV method is very promising: the reaction path seems to be the same as in biochemical processes, only the kinetics change. Therefore, biological degradation parameters can be expressed using photodegradation kinetic parameters.

Based on this analysis, we plan to develop an alternative method combining these two approaches, i.e., an oxidation process and fast analytical methods. We propose not only to use UV/UV oxidation and NIR spectrometry, as described in Fig. 6, but also to add "new dimensions" by simultaneously using several analytical techniques (as already tested in [79]). Both strategies should increase the sensitivity, selectivity, and speed of BMP kinetic parameter prediction.

Acknowledgments

Authors wish to acknowledge financial support for this work from EcoTech Languedoc Roussillon and ILEE (Institut Languedocien de recherche sur l'Eau et l'Environnement).

References

[1] De Baere L. Will anaerobic digestion of solid waste survive in the future? Water Sci Technol 2006;53:187–94.
[2] Nallathambi Gunaseelan V. Anaerobic digestion of biomass for methane production: a review. Biomass Bioenergy 1997;13:83–114.
[3] Moller HB, Sommer SG, Ahring BK. Methane productivity of manure, straw and solid fractions of manure. Biomass Bioenergy 2004;26:485–95.
[4] Lehtomäki A, Huttunen S, Lehtinen TM, Rintala JA. Anaerobic digestion of grass silage in batch leach bed processes for methane production. Bioresour Technol 2008;99:3267–78.
[5] Neves L, Oliveira R, Alves MM. Anaerobic co-digestion of coffee waste and sewage sludge. Waste Manage 2006;26:176–81.
[6] Turick CE, Peck MW, Chynoweth DP, Jerger DE, White EH, Zsuffa L, et al. Methane fermentation of woody biomass. Bioresour Technol 1991;37:141–7.
[7] Erguder TH, Guven E, Demirer GN. Anaerobic treatment of olive mill wastes in batch reactors. Process Biochem 2000;36:243–8.
[8] Hansen TL, Schmidt JE, Angelidaki I, Marca E, Jansen JlC, Mosbaek H, et al. Method for determination of methane potentials of solid organic waste. Waste Manage 2004;24:393–400.
[9] Nallathambi Gunaseelan V. Regression models of ultimate methane yields of fruits and vegetable solid wastes, sorghum and Napier grass on chemical composition. Bioresour Technol 2007;98:1270–7.
[10] Buffiere P, Loisel D, Bernet N, Delgenes JP. Towards new indicators for the prediction of solid waste anaerobic digestion properties. Water Sci Technol 2006;53:233–41.
[11] Fountoulakis MS, Drakopoulou S, Terzakis S, Georgaki E, Manios T. Potential for methane production from typical Mediterranean agro-industrial by-products. Biomass Bioenergy 2008;32:155–61.
[12] Chen T-H, Hashimoto AG. Effects of pH and substrate:inoculum ratio on batch methane fermentation. Bioresour Technol 1996;56:179–86.
[13] Angelidaki I, Sanders W. Assessment of the anaerobic biodegradability of macropollutants. Rev Environ Sci Biotechnol 2004;3:117–29.
[14] Chen Y, Cheng JJ, Creamer KS. Inhibition of anaerobic digestion process: a review. Bioresour Technol 2008;99:4044–64.
[15] Palmowski LM, Müller JA. Influence of the size reduction of organic waste on their anaerobic digestion. Water Sci Technol 2000;41:155–62.
[16] Nallathambi Gunaseelan V. Effect of inoculum/substrate ratio and pretreatments on methane yield from Parthenium. Biomass Bioenergy 1995;8:39–44.
[17] Raposo F, Banks CJ, Siegert I, Heaven S, Borja R. Influence of inoculum to substrate ratio on the biochemical methane potential of maize in batch tests. Process Biochem 2006;41:1444–50.
[18] Bellon-Maurel V, Orliac O, Christen P. Sensors and measurements in solid state fermentation: a review. Process Biochem 2003;38:881–96.
[19] Lasaridi KE, Stentiford EI. A simple respirometric technique for assessing compost stability. Water Res 1998;32:3717–23.
[20] Calmon A, Silvestre F, Bellon-Maurel V, Roger JM, Feuilloley P. Modelling easily biodegradability of materials in liquid medium-relationship between structure and biodegradability. J Environ Polym Degrad 1999;7:135–44.
[21] Barrena R, d'Imporzano G, Ponsá S, Gea T, Artola A, Vázquez F, et al. In search of a reliable technique for the determination of the biological stability of the organic matter in the mechanical–biological treated waste. J Hazard Mater 2009;162:1065–72.
[22] Wagland ST, Tyrrel SF, Godley AR, Smith R. Test methods to aid in the evaluation of the diversion of biodegradable municipal waste (BMW) from landfill. Waste Manage 2009;29:1218–26.
[23] Sánchez M, Gomez X, Barriocanal G, Cuetos MJ, Morán A. Assessment of the stability of livestock farm wastes treated by anaerobic digestion. Int Biodeter Biodegrad 2008;62:421–6.
[24] Schievano A, Pognani M, D'Imporzano G, Adani F. Predicting anaerobic biogasification potential of ingestates and digestates of a full-scale biogas plant using chemical and biological parameters. Bioresour Technol 2008;99: 8112–7.
[25] Beltrán FJ, García-Araya JF, Frades J, Álvarez P, Gimeno O. Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. Water Res 1999;33:723–32.
[26] Cossu R, Raga R. Test methods for assessing the biological stability of biodegradable waste. Waste Manage 2008;28:381–8.
[27] Sánchez A. Test methods to aid in the evaluation of the diversion of biodegradable municipal waste (BMW) from landfill. Waste Manage 2009;29: 2306–7.
[28] Ponsa S, Gea T, Alerm L, Cerezo J, Sanchez A. Comparison of aerobic and anaerobic stability indices through a MSW biological treatment process. Waste Manage 2008;28:2735–42.
[29] Hansen TL. Quantification of environmental effects from anaerobic treatment of source-sorted organic household wastes. PhD thesis. Denmark: Institute of Environment & Resources, Technical University of Denmark; 2005. p. 43.

[30] Davidsson A, Gruvberger C, Christensen TH, Hansen TL, Jansen JlC. Methane yield in source-sorted organic fraction of municipal solid waste. Waste Manage 2007;27:406–14.
[31] Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi S, Pavlostathis SG, Rozzi A, et al. The IWA anaerobic digestion model N°1 (ADM1). Water Sci Technol 2002;45:65–73.
[32] Cavaleiro AJ, Pereira MA, Alves M. Enhancement of methane production from long chain fatty acid based effluents. Bioresour Technol 2008;99:4086–95.
[33] Angelidaki I, Ahring BK. Effects of free long-chain fatty-acids on thermophilic anaerobic-digestion. Appl Microbiol Biotechnol 1992;37:808–12.
[34] Neves L, Gonçalo E, Oliveira R, Alves MM. Influence of composition on the biomethanation potential of restaurant waste at mesophilic temperatures. Waste Manage 2008;28:965–72.
[35] Hansen KH, Angelidaki I, Ahring BK. Anaerobic digestion of swine manure: inhibition by ammonia. Water Res 1998;32:5–12.
[36] Lissens G, Thomsen AB, De Baere L, Verstraete W, Ahring BK. Thermal wet oxidation improves anaerobic biodegradability of raw and digested biowaste. Environ Sci Technol 2004;38:3418–24.
[37] Neves L, Ribeiro R, Oliveira R, Alves MM. Enhancement of methane production from barley waste. Biomass Bioenergy 2006;30:599–603.
[38] Scherer PA, Schultz KU, Meyer-Pittrof R. Comparison of methods to characterize the degradation rate of organic matter during solid state fermentation. In: Behrens D, editor. DECHEMA Biotechnology Conferences. Weinheim, Germany: Wiley; 1990. p. 661–5.
[39] Van Soest PJ, Robertson JB, Lewis BA. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. J Dairy Sci 1991;74:3583–97.
[40] Chandler JA, Jewell WJ, Gossett JM, Vansoest PJ, Robertson JB. Predicting methane fermentation biodegradability. Biotechnol Bioeng 1980;22:93–107.
[41] El Hajjouji H, Fakharedine N, Ait Baddi G, Winterton P, Bailly JR, Revel JC, et al. Treatment of olive mill waste-water by aerobic biodegradation: an analytical study using gel permeation chromatography, ultraviolet–visible and Fourier transform infrared spectroscopy. Bioresour Technol 2007;98:3513–20.
[42] Domeizel M, Khalil A, Prudent P. UV spectroscopy: a tool for monitoring humification and for proposing an index of the maturity of compost. Bioresour Technol 2004;94:177–84.
[43] Sellami F, Hachicha S, Chtourou M, Medhioub K, Ammar E. Maturity assessment of composted olive mill wastes using UV spectra and humification parameters. Bioresour Technol 2008;99:6900–7.
[44] Zbytniewski R, Buszewski B. Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 1. Chemical and spectroscopic properties. Bioresour Technol 2005;96:471–8.
[45] Fogelman S, Zhao HJ, Blumenstein M. A rapid analytical method for predicting the oxygen demand of wastewater. Anal Bioanal Chem 2006;386:1773–9.
[46] Brookman SKE. Estimation of biochemical oxygen demand in slurry and effluents using ultra-violet spectrophotometry. Water Res 1997;31:372–4.
[47] Garimella Purna SK, Prow LA, Metzger LE. Utilization of front-face fluorescence spectroscopy for analysis of process cheese functionality. J Dairy Sci 2005;88:470–7.
[48] Moreira AB, Dias ILT, Neto GO, Zagatto EAG, Kubota LT. Solid-phase fluorescence spectroscopy for the determination of acetylsalicylic acid in powdered pharmaceutical samples. Anal Chim Acta 2004;523:49–52.
[49] Reynolds DM, Ahmad SR. Rapid and direct determination of wastewater BOD values using a fluorescence technique. Water Res 1997;31:2012–8.
[50] Miikki V, Senesi N, Hanninen K. Characterization of humic material formed by composting of domestic and industrial biowastes. Part 2. Spectroscopic evaluation of humic acid structures. Chemosphere 1997;34:1639–51.
[51] Castaldi P, Alberti G, Merella R, Melis P. Study of the organic matter evolution during municipal solid waste composting aimed at identifying suitable parameters for the evaluation of compost maturity. Waste Manage 2005;25:209–13.
[52] Smidt E, Lechner P, Schwanninger M, Haberhauer G, Gerzabek MH. Characterization of waste organic matter by FT-IR spectroscopy: application in waste science. Appl Spectrosc 2002;56:1170–5.
[53] Smidt E, Schwanninger M. Characterization of waste materials using FTIR spectroscopy: process monitoring and quality assessment. Spectr Lett 2005;38:247–70.
[54] Meissl K, Smidt E, Schwanninger M. Prediction of humic acid content and respiration activity of biogenic waste by means of Fourier transform infrared (FTIR) spectra and partial least squares regression (PLS-R) models. Talanta 2007;72:791–9.
[55] Pasquini C. Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. J Braz Chem Soc 2003;14:198–219.
[56] Hongqiang L, Hongzhang C. Near-infrared spectroscopy with a fiber-optic probe for state variables determination in solid-state fermentation. Process Biochem 2008;43:511–6.
[57] Bruno-Soares AM, Murray I, Paterson RM, Abreu JMF. Use of near infrared reflectance spectroscopy (NIRS) for the prediction of the chemical composition and nutritional attributes of green crop cereals. Anim Feed Sci Technol 1998;75:15–25.
[58] Sanderson MA, Agblevor F, Collins M, Johnson DK. Compositional analysis of biomass feedstocks by near infrared reflectance spectroscopy. Biomass Bioenergy 1996;11:365–70.
[59] Thuries L, Bastianelli D, Davrieux F, Bonnal L, Oliver R, Pansu M, et al. Prediction by near infrared spectroscopy of the composition of plant raw materials from the organic fertiliser industry and of crop residues from tropical agrosystems. J Near Infrared Spectrosc 2005;13:187–99.
[60] Gonzalez-Martin I, Alvarez-Garcia N, Hernandez-Andaluz JL. Instantaneous determination of crude proteins, fat and fibre in animal feeds using near infrared reflectance spectroscopy technology and a remote reflectance fibre-optic probe. Anim Feed Sci Technol 2006;128:165–71.
[61] Park RS, Agnew RE, Gordon FJ, Steen RWJ. The use of near infrared reflectance spectroscopy (NIRS) on undried samples of grass silage to predict chemical composition and digestibility parameters. Anim Feed Sci Technol 1998;72:155–67.
[62] Adesogan AT, Owen E, Givens DI. Prediction of the in vivo digestibility of whole crop wheat from in vitro digestibility, chemical composition, in situ rumen degradability, in vitro gas production and near infrared reflectance spectroscopy. Anim Feed Sci Technol 1998;74:259–72.
[63] Lovett DK, Deaville ER, Mould F, Givens DI, Owen E. Using near infrared reflectance spectroscopy (NIRS) to predict the biological parameters of maize silage. Anim Feed Sci Technol 2004;115:179–87.
[64] Faughey GJ, Sharma HSS. A preliminary evaluation of near infrared spectroscopy for assessing physical and chemical characteristics of flax fibre. J Near Infrared Spectrosc 2000;8:61–9.
[65] Ben-Dor E, Inbar Y, Chen Y. The reflectance spectra of organic matter in the visible near-infrared and short wave infrared region (400–2500 nm) during a controlled decomposition process. Remote Sens Environ 1997;61:1–15.
[66] Gillon D, Joffre R, Ibrahima A. Can litter decomposability be predicted by near infrared reflectance spectroscopy? Ecology 1999;80:175–86.
[67] Herrero M, Murray I, Fawcett RH, Dent JB. Prediction of the in vitro gas production and chemical composition of kikuyu grass by near-infrared reflectance spectroscopy. Anim Feed Sci Technol 1996;60:51–67.
[68] Herrero M, Jessop NS, Fawcett RH, Murray I, Dent JB. Prediction of the in vitro gas production dynamics of kikuyu grass by near-infrared reflectance spectroscopy using spectrally-structured sample populations. Anim Feed Sci Technol 1997;69:281–7.
[69] Andres S, Calleja A, Lopez S, Gonzalez JS, Rodriguez PL, Giraldez FJ. Prediction of gas production kinetic parameters of forages by chemical composition and near infrared reflectance spectroscopy. Anim Feed Sci Technol 2005;123:487–99.
[70] Sousa AC, Lucio M, Bezerra OF, Marcone GPS, Pereira AFC, Dantas EO, et al. A method for determination of COD in a domestic wastewater treatment plant by using near-infrared reflectance spectrometry of seston. Anal Chim Acta 2007;588:231–6.
[71] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Org Geochem 1999;30:1479–93.
[72] Jarde E, Mansuy L, Faure P. Characterization of the macromolecular organic content of sewage sludges by thermally assisted hydrolysis and methylation-gas chromatography–mass spectrometer (THM-GC/MS). J Anal Appl Pyrolysis 2003;68–69:331–50.
[73] Parnaudeau V, Dignac M-F. The organic matter composition of various wastewater sludges and their neutral detergent fractions as revealed by pyrolysis–GC/MS. J Anal Appl Pyrolysis 2007;78:140–52.
[74] Alves A, Schwanninger M, Pereira H, Rodrigues J. Analytical pyrolysis as a direct method to determine the lignin content in wood. Part 1. Comparison of pyrolysis lignin with Klason lignin. J Anal Appl Pyrolysis 2006;76:209–13.
[75] Syverud K, Leirset I, Vaaler D. Characterization of carbohydrates in chemical pulps by pyrolysis gas chromatography/mass spectrometry. J Anal Appl Pyrolysis 2003;67:381–91.
[76] Page DW, van Leeuwen JA, Spark KM, Mulcahy DE. Pyrolysis characterisation of plant, humus and soil extracts from Australian catchments. J Anal Appl Pyrolysis 2002;65:269–85.
[77] Smidt E, Eckhardt KU, Lechner P, Schulten HR, Leinweber P. Characterization of different decomposition stages of biowaste using FT-IR spectroscopy and pyrolysis–field ionization mass spectrometry. Biodegradation 2005;16:67–79.
[78] Sato H, Furuhashi M, Yang D, Ohtani H, Tsuge S, Okada M, et al. A novel evaluation method for biodegradability of poly(butylene succinate-co-butylene adipate) by pyrolysis–gas chromatography. Polym Degrad Stab 2001;73:327–34.
[79] Roig B, Thomas O. Rapid estimation of global sugars by UV photodegradation and UV spectrophotometry. Anal Chim Acta 2003;477:325–9.
[80] Roig B, Gonzalez C, Thomas O. Measurement of dissolved total nitrogen in wastewater by UV photooxidation with peroxodisulphate. Anal Chim Acta 1999;389:267–74.
[81] Castillo L, El Khorassani H, Trebuchon P, Thomas O. UV treatability test for chemical and petrochemical wastewater. Water Sci Technol 1999;39:17–23.
[82] Muret C, Pouet MF, Touraud E, Thomas O. From UV spectra to degradability of industrial wastewater/definition and use of a "shape factor". Water Sci Technol 2000;42:47–53.
[83] Knol W, Vandermost MM, Waart JD. Biogas production by anaerobic digestion of fruit and vegetable waste—preliminary-study. J Sci Food Agric 1978;29:822–30.
[84] Chynoweth DP, Turick CE, Owens JM, Jerger DE, Peck MW. Biochemical methane potential of biomass and waste feedstocks. Biomass Bioenergy 1993;5:95–111.
[85] Nallathambi Gunaseelan V. Biochemical methane potential of fruits and vegetable solid waste feedstocks. Biomass Bioenergy 2004;26:389–99.
[86] Cho JK, Park SC, Chang HN. Biochemical methane potential and solid state anaerobic digestion of Korean food wastes. Bioresour Technol 1995;52:245–53.