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The potential of near infrared reflectance spectroscopy (NIRS) for the estimation of agroindustrial compost quality

L. Galvez-Sola [a], R. Moral [a], M.D. Perez-Murcia [a], A. Perez-Espinosa [a], M.A. Bustamante [a], E. Martinez-Sabater [b], C. Paredes [a,*]

[a] *Department of Agrochemistry and Environment, Miguel Hernandez University, EPS-Orihuela, Ctra. Beniel km. 3.2, 03312-Orihuela (Alicante), Spain*
[b] *Department of Agrochemistry and Biochemistry, University of Alicante, PO box 99, E-03080 Alicante, Spain*

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ABSTRACT

Composting is an environmentally friendly alternative for the recycling of organic wastes and its use is increasing in recent years. An exhaustive monitoring of the composting process and of the final compost characteristics is necessary to certify that the values of compost characteristics are within the limits established by the legislation in order to obtain a safe and marketable product. The analysis of these parameters on each composting batch in the commercial composting plant is time-consuming and expensive. So, their estimation in the composting facilities based on the use of near infrared reflectance spectroscopy (NIRS) could be an interesting approach in order to monitor compost quality. In this study, more than 300 samples from 20 different composting procedures were used to calibrate and validate the NIRS estimation of compost properties (pH, electrical conductivity (EC), total organic matter (TOM), total organic carbon (TOC), total nitrogen (TN) and C/N ratio, macronutrient contents (N, P, K) and potentially pollutant element concentrations (Fe, Cu, Mn and Zn)). The composts used were elaborated using different organic wastes from agroindustrial activities (GS: grape stalk; EGM: exhausted grape marc; GM: grape marc; V: vinasse; CJW: citrus juice waste; Alpeorujo: olive-oil waste; AS: almond skin; EP: exhausted peat; TSW: tomato soup waste; SMS: spent mushroom substrate) co-composted with manures (CM: cattle manure; PM: poultry manure) or urban wastes (SS: sewage sludge) The estimation results showed that the NIRS technique needs to be fitted to each element and property, using specific spectrum transformations, in order to achieve an acceptable accuracy in the prediction. However, excellent prediction results were obtained for TOM and TOC, successful calibrations for pH, EC, Fe and Mn, and moderately successful estimations for TN, C/N ratio, P, K, Cu and Zn.

1. Introduction

In the last decades, a rapid development of the industry has been observed and, especially, in the agroindustrial sector. This fact is mainly noticeable in several agro-food industries in the EU-25, such as in the sectors of the pork–poultry–cattle production or the horticultural crop transformation, the wine industry (EU-25 produces about 70% of the world wine production; OIV, 2009), the olive-oil industry (EU-25 represents about 74% of the world olive-oil production; IOC, 2007) and the citrus industry (EU-25 is one of the main exporters with 48% of the world total exports; FAO, 2009). Therefore, this increase in the agroindustrial production generates considerable amounts of wastes, about 222×10^6 t/year (Eurostat, 2005).

The increasing waste production from agroindustrial activities and the lack of an optimised management of these residues have led to an increase of the composting facilities, as a feasible option for waste management, coupled or not with biogas production facilities. Nowadays, the European environmental legislation includes composting as a recovery operation for organic waste (Council of the European Communities, 2008). Composting is defined as a process of aerobic thermophilic microbial degradation of wastes by populations of the indigenous microorganism which leads to a stabilised, mature, deodorised, hygienic product, free of pathogens and plants seeds, rich in humic substances, easy to store and marketable as organic amendment or fertiliser (Haug, 1993).

Composts can be used to improve soil structure, increase soil organic matter, provide some plant nutrients and enhance plant growth (Paredes et al., 2005). However, the use of immature compost can produce adverse effects in the environment, as a consequence of the production of phytotoxic compounds (Tang et al., 2006), dispersion of potentially pathogenic microorganisms (Hassen et al., 2001; Bustamante et al., 2008), nitrogen immobilisation (Kotaro et al., 2005), especially in the case of immature compost with high value of C/N ratio, and deficiency of oxygen concentrations (Chikae et al., 2007). In addition, the composting of organic wastes with notable

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* Corresponding author.
E-mail address: c.paredes@umh.es (C. Paredes).

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contents of potentially toxic elements can limit the agricultural use of the composts obtained (Perez-Murcia et al., 2006). So, the European and the Spanish Government Departments have elaborated different laws and regulations to limit the pollutant dispersion from the compost application into the soil (European Commission, 2001; BOE, 2008). These legislations establish the limit of organic matter and heavy metal contents, pathogenic microorganism levels and C/N ratio values for composts. Moreover, in the Spanish legislation related to fertilisers, the nutrient content of compost must be declared, in order to fit the correct application dose to each crop and thus, avoiding contamination of watersheds by nutrient-surplus (BOE, 2008).

The determination of all parameters established by the legislation for marketable composts is time-consuming and expensive. Consequently, a more convenient and reliable method is necessary for the management and the traceability of the composting process, as well as to evaluate the different requirements demanded by the legislation for compost.

Near infrared reflectance spectroscopy (NIRS) is an emerging tool for environmental analyses. NIRS is a non-destructive technique, with an easy sample preparation and management (no reagents are required), rapid (1 min per spectrum) and inexpensive. Near infrared radiation (700–2500 nm) is absorbed by various bonds, such as C–H, C–C, C=C, C–N, and O–H, characteristics of organic matter (Ludwig and Khanna, 2001). In NIR spectra the different constituents have broad overlapping bands and therefore, NIRS measurements have to be calibrated against samples with known chemical composition in order to extract the desired information (Gislum et al., 2004). Mineral composition in an organic matrix can be measured by NIRS owing to the association between the mineral concentrations and spectral features, this being due to the association between minerals and organic functional groups or the organic matrix (Huang et al., 2008).

Several studies of compost or organic wastes using NIRS have shown that NIRS could be an effective management method. For example, NIRS technology has been used to determinate physico-chemical parameters and nutrient metal contents in animal manure compost (Malley et al., 2005; Huang et al., 2008), carbon and nitrogen contents in sewage sludge and green waste compost (Albrecht et al., 2008), nitrogen content in poultry manure compost (Fujiwara and Murakami, 2007), physico-chemical parameters, organic matter, total organic carbon and concentrations of different nitrogen forms and cell wall fractions of sewage sludge compost (Vergnoux et al., 2009), heavy metal contents in sewage sludge (Moral et al., 2007) and compost (Galvez-Sola et al., 2009a), nitrogen content in sewage sludge (Gálvez-Sola et al., 2009b), humic acid from sewage sludge (Polak et al., 2005), mushroom compost (Sharma et al., 2000), nutrient composition of layer manure (Xing et al., 2008) and fattening pig manure (Yang et al., 2006). However, very little is known about the use of the NIRS for the management and the traceability of the composting process of agroindustrial composts.

Therefore, the main purpose of this study was to explore the feasibility of analyzing parameters limited by the legislation for compost (pH, EC, TOM, TOC, C/N ratio and macronutrient and potentially toxic element contents) on a wide survey of agroindustrial composts using near infrared spectroscopy (NIRS).

2. Materials and methods

2.1. Compost samples

Three hundred and five different samples were used in this study from 20 different composting piles elaborated using several residues, but including in all the cases wastes from the winery and distillery industry (Table 1). Twelve piles were made using the turning composting system (LS, low scale) (500 L commercial composters, with natural aeration), and the rest was composted in a semi-industrial scale (HS, high scale) (5000 kg) by the Rutgers static pile composting system with temperature control and forced aeration. In all the scenarios, the bio-oxidative phase of composting was considered finished when the temperature of the pile was stable and near to that of the surrounding atmosphere and then, the piles were allowed to mature for two months. The moisture of the piles was controlled weekly by adding the necessary amount of water to obtain a moisture content not less than 40%. Samples were obtained by mixing subsamples coming from seven different zones of the piles and they were collected every week. The number of samples used in each composting pile is shown in Table 1.

2.2. Analytical methods

All samples were ground, dried at 105 °C and stored prior to their analysis. The electrical conductivity (EC) and pH of the compost samples were determined in a 1:10 (w/v) water extract; total organic matter content (TOM) was determined by loss on ignition at 430 °C for 24 h (Navarro et al., 1993). Total organic carbon (TOC) and total nitrogen (TN) were determined by dry combustion at 950 °C using a Leco TruSpec C–N Elemental Analyzer (Leco Corp., St. Joseph, MI, USA) according to Navarro et al. (1991) and Paredes et al. (1996). After $HNO_3/HClO_4$ digestion, P was assessed colorimetrically as molybdovanadate phosphoric acid (Kitson and Mellon, 1944), K was determined by flame photometry (Jenway PFP7 Flame Photometer, Jenway Ltd., Felsted, Dunmow, Essex, UK) and Fe, Cu, Mn and Zn by atomic absorption (Varian 220FS Atomic Absorption Spectrometer, Varian Inc., Melbourne, Australia). All analytical determinations were done in quadruplicate.

2.3. NIRS analysis

NIRS analyses were performed using a FT-NIR spectrometer (MPA, Bruker Optik GmbH, Germany) in the range of wave number from 12,000 to 3800 cm^{-1} (830–2600 nm) with a step of 8 cm^{-1}. Each sample was scanned three times using Opus software (version 6, ©Bruker Optik), recording absorbance, as log 1/R, where R is reflectance, for a total of 64 scans per sample. The three spectra of each sample were averaged. Fig. 1 shows the NIRS spectra of the compost samples.

The validation step was carried out using the full cross-validation method, following the leave-one-out procedure. This method was used to ensure the predictive ability and to avoid over-fitting of the data (Martens and Næs, 1989). With cross-validation, the same samples are used both for the calibration and the validation step and the outlier samples were not omitted. A sample is removed from the calibration data set and the model is calibrated on the remaining data points. The value for the removed sample is predicted and the prediction residual is computed. The process is repeated with another sample of the calibration set, and so on until every object has been removed once; then all prediction residuals are combined to compute the validation residual variance and root mean square error of cross validation (RMSECV).

Analytical data of the samples are shown in Table 2. Partial least square regression (PLSR) was used for calibration. To ensure a good correlation between the spectral data and the concentration values, different spectra pre-treatments were tested:

- Vector Normalization (VN): normalizes a spectrum by an initial calculation of the average intensity value and subsequent subtraction of this value from the spectrum. Then, the addition of the squared intensities is calculated and the spectrum is divided by the square root of this addition.
- Multiplicative Scatter Correction (MSC): performs a linear transformation of each spectrum for it to best match the mean spectrum of the whole set.
- First Derivative (FD): calculates the first derivative of the spectrum. This method emphasises steep edges of a peak. It is used to emphasise pronounced, but small features over a broad background. Spectral noise is also enhanced.