

Components Analysis of Biochar Based on Near Infrared Spectroscopy Technology



XIE Yue^{1,2,3}, LI Fei-Yue^{1,2}, FAN Xing-Jun¹, HU Shui-Jin³, XIAO Xin^{1,*}, WANG Jian-Fei¹

¹ College of Resources and Environment, Anhui Science and Technology University, Fengyang 233100, China

² Key Laboratory of Bio-organic Fertilizer Creation, Ministry of Agriculture, Bengbu 233000, China

³ Department of Plant Pathology, North Carolina State University, Raleigh, NC 27695, USA

Abstract: This study aims to establish a rapid quantitative analysis method for biochar based on near infrared spectroscopy (NIRS) technology. Near infrared spectra of 163 samples in the 10000–3800 cm⁻¹ (1000–2632 nm) range were collected, and the contents of fixed carbon (FC), volatile matter (VM) and ash of samples were also analyzed. A partial least square (PLS) model for FC, VM and Ash was established after the model spectral ranges were optimized, the optimal factors were determined, and the raw spectra were pretreated by multiple scatter correction and second derivative (MSC + SD) method. Finally, the prediction performance of predictive model was evaluated. The results showed that the PLS model had a good prediction ability, and the predicted coefficient R^2_p of actual values vs prediction values for FC, VM and ash were 0.9423, 0.9517 and 0.9265, respectively. Root mean square error of prediction (RMSEP) was 0.1074, 0.1201 and 0.1243, and ratios of prediction to deviation (RPD) were 3.51, 4.28 and 2.03, respectively. The PLS model had good accuracy and precision for both of FC and VM, and could be used as a quantitative method for FC and VM contents analysis. Nevertheless, PLS model need to improve the precision for Ash analysis according to RPD value. This method provides a fast and effective technical means for the quantitative analysis of biochar components.

Key Words: Near infrared spectroscopy; Spectrum; Biochar; Fixed carbon; Volatile matter; Ash

1 Introduction

Biochar is a new type of carbon material, and is an aromatized substance produced by low-temperature pyrolysis of organic raw materials under anaerobic or oxygen-limited condition^[1]. In recent years, biochar materials have shown significant potential in the fields of environmental science and agriculture. However, the primary issue in various applications of biochar is the analysis of biochar composition. Generally, the components of biochar from different sources can be divided into three types: fixed carbon (FC), volatile matter (VM) and ash^[2]. For the quantitative analysis of biochar composition, traditional analysis techniques are usually costly and time-consuming. Therefore, because of the numerous applications of biochar in various fields, reliable,

rapid and low-cost methods to analyze the FC, VM and ash contents are highly desirable.

Near-infrared spectroscopy (NIRS) is a modern spectroscopic technique for the low-cost, rapid and non-destructive measurement of the contents of substances and has been widely used in food, agriculture, medicine, textiles, environment and other fields^[3–8]. Our research group used NIRS to achieve the quantitative analysis of ferulic acid in soil sustaining the continuous cropping of *Chrysanthemum morifolium* (Ramat) cv. Chuju^[9]. Huang *et al*^[10] used NIRS to predict the contents of FC and VM in straw and achieved simultaneous determination of straw components. Some researchers applied NIRS in the study of carbon materials, constructed NIRS-based prediction model, and quantitatively analyzed FC, VM and ash contents of coal, and the analysis

Received 11 July 2017; Accepted 1 February 2018

*Corresponding author. E-mail: xiaoxin8088@126.com

This work was supported by the National Natural Science Foundation of China (Nos. 21607002, 41705107) and the Natural Science Foundation of Anhui Province, China (Nos. 1508085QD74, 1604a0702011, 160307011102).

Copyright © 2018, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. Published by Elsevier Limited. All rights reserved.

DOI: 10.1016/S1872-2040(17)61081-8

results were accurate and reliable^[11,12]. Yang *et al.*^[13] measured ash, VM, and FC contents, as well as the calorific value of the three types of biochar samples, using a NIRS technique in the visible and shortwave NIRS range of 28571–9091 cm^{-1} (350–1100 nm), preliminarily demonstrating the advantages of NIRS in the compositional analysis of biochar samples. However, they did not analyze the biochar sample over the full NIRS range in their work, and sample information located in the longwave NIRS range of 9091–3959 cm^{-1} (1100–2525 nm) was missing. The overtone and combination absorption bands of the vibrations of hydrogen-containing groups in the aromatic substances of the biochar components are mainly found in the longwave NIRS region^[14], and there is less information present in the shortwave NIRS range. Therefore, the information in the longwave NIRS range is necessary for the quantitative analysis of biochar samples.

In this study, 163 biochar samples were prepared from plant-based and solid-waste-based sources, and a quantitative analysis of the biochar samples was performed for the first time in the longwave NIRS range of 10000–3800 cm^{-1} (1000–2632 nm). Partial least squares (PLS) method was used to construct a NIRS data-based model to predict the contents of FC, VM and ash in the samples of the validation set, to provide a fast and reliable quantitative analysis method for biochar research.

2 Experimental

2.1 Acquisition of original NIR spectra

Experiments were conducted using an ANTARIS NIRS Analyzer (Thermo Nicolet Com, USA) with an integrating sphere module and TQ Analyst processing software (Thermo Nicolet Com, USA). The instrument was preheated for 1 h, and each spectral band was scanned in the range of 10000–3800 cm^{-1} (1000–2632 nm), with a total of 64 scans and a gain of 2 times at a resolution of 4 cm^{-1} . Each sample was loaded into a sample holder to 1/3 full and was scanned three times, and the data were saved in $\lg(1/R)$ form. Temperature in the test room was 23 °C, and the relative humidity was controlled at approximately 45%.

2.2 Collection and preparation of biochar samples

The raw materials used to prepare the biochar samples in this experiment were rice straw, wheat straw, tobacco stalk, corn stalk, cotton stalks, oak, mahogany, bamboo, willow branches, leaves, grass, pig manure, cow manure, chicken manure, horse manure, municipal sludge, coconut shells, waste paper, orange peel, and banana peel. These 20 types of raw materials represent the current plant-based and solid-waste-based organic sources used to prepare biochar samples. All raw materials were washed, air dried, oven dried

and crushed, followed by being placed in a self-made porous fused alumina container that was filled with nitrogen to protect the samples. In a muffle furnace, heating took place over a range of 200–600 °C in 50 °C increments for a total of 9 temperature treatments. For each treatment, the sample underwent pyrolysis in the muffle furnace for 2 h; then, all temperature was maintained for 1 h, and the biochar samples were finally achieved. After preparation, the samples were immediately transferred to a desiccator containing self-indicating silica gel for storage. A total of 163 valid biochar samples were collected, and each sample was divided into two equal aliquots: one for analysis and one for back-up. All biochar preparations were completed at the Soil Ecology Laboratory at North Carolina State University (USA).

2.3 Biochar composition analysis

The contents of FC, VM and ash in the biochar samples were determined according to GB/T28731-2012 “Industrial Analysis Method for Solid Biomass Fuel”^[15], and the analytical results were expressed as the mass percentage. Each biochar component was calculated according to equation (1):

$$\text{FC} (\%) = 1 - \text{VM} (\%) - \text{Ash} (\%) \quad (1)$$

2.4 NIRS data analysis and model construction

The samples were randomly divided into a calibration set (100) and a validation set (the remaining samples after the removal of abnormal samples). The processing of the NIRS data collected in the experiment and the model construction was performed using TQ Analyst software. First, the test for abnormal samples was carried out using three criteria: a studentized residual, a sample standard leverage and the Mahalanobis distance. Subsequently, the optimal spectral ranges for FC, VM and ash for the sample were selected, followed by the pretreatment of the original spectra of the samples. After the optimum number of factors was determined, the PLS method was adopted to establish the NIRS data-based quantitative mathematical model. The validation correlation coefficient (R_{cv}^2) and root mean square error of cross-validation (RMSECV) were used to optimize the parameters, and the accuracy of the model was evaluated using cross-validation method^[14,16].

2.5 Validation of the quantitative mathematical model

After the mathematical model was constructed, the predictive accuracy and stability of the model were evaluated by cross-validation method, and the related evaluation indexes were the predicted coefficient (R_p^2), RMSEP and relative predictive error (RPD). The evaluation criteria were that if the RMSEP value was smaller and the R_p^2 value was closer to 1, the predictive ability of the model was strong. When the $\text{RPD} \geq$

Download English Version:

<https://daneshyari.com/en/article/7563941>

Download Persian Version:

<https://daneshyari.com/article/7563941>

[Daneshyari.com](https://daneshyari.com)