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Monitoring of Alcoholic Fermentation of Onion Juice by NIR Spectroscopy: Valorization of Worthless Onions

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The valorization of vegetable byproducts is one of the main objectives of industry today. The project on which this study is based examined the potential usefulness of worthless onions (*Allium cepa* L. sp.) and overproduction to obtain several functional products with different applications in the food industry. Near-infrared (NIR) spectroscopy, combined with multivariate calibration, has been used to monitor the alcoholic fermentation of onion juice. Good results were obtained, revealing the suitability of NIR spectroscopy for controlling and optimizing this process in real time.

KEYWORDS: Alcoholic fermentation; multivariate calibration; NIR monitoring; onion; valorization

INTRODUCTION

The food industry generates huge amounts of residues during the processing and commercialization stages. Problems relating to agrofood industry waste management are as heterogeneous and varied as the large variety of different waste materials produced by different sources.

In particular, waste handling and disposal represent an extremely delicate problem for the vegetable industry. Vegetable manufacturers and merchants must comply with restrictive regulations governing the disposal of production wastes, and a significant percentage of harvested vegetables fail to meet the quality standard required for sale to customers, and so they are treated as byproducts.

Most byproducts generated by vegetable manufacturers correspond to the organic solid fraction deriving from prior treatment of vegetable raw materials to eliminate nonedible parts. This organic fraction is mainly used for animal feed, whereas only a small proportion is used for other applications (e.g., fuel), in such a way that the remaining part constitutes a waste for dump. The consignment of all these products to waste dumps represents a loss of natural resources because these materials could be used as raw materials in other industrial processes to convert them into added-value products. Recovery, recycling, and reprocessing of solid organic waste can take advantage of the geographic concentration of industries generating byproducts (*1*). Research should focus on developing and improving suitable methods for ensuring the effective use of byproducts resulting from food processing to foster sustainable development. Vegetable manufacturers generate huge amounts of byproducts. Around 50% of harvested products constitute waste for industries. In the case of onion producers, worthless onions account for 20% of total production.

Current legislation governing waste disposal aims to prevent waste production and promote waste reduction, reuse, recycling, and recovery (*2*). Moreover, future legislation based on Directive 96/61/EC on integrated pollution prevention and control establishes rules to prevent, or at least reduce, industrial emissions to the atmosphere, water, or soil, to achieve a high level of protection of the environment (*3*).

Onion (*Allium cepa* L.) belongs to the Liliaceae family (Alliaceae). Onion consumption has increased by approximately 25% in the past decade, with global production standing at 44 million tons. This increase has been due to the product's versatility as an ingredient, its easy conservation and transport, and its healthy properties extolled by doctors and other food experts (*4*−*13*).

Spain is one of the most important onion producers in Europe. In 1996, production reached 1039 thousand tons (around 23% of total production in the European Union) (*14*). In Cataluña, onion producers estimate that worthless onions account for about 15% of annual production. This percentage varies depending on the harvest, but the surplus of onions produced is normally very significant. Moreover, the current quality levels demanded by customers and the search for high-quality products are increasing the volume of worthless onions every day. Total onion waste comprises worthless onions discarded during the selection and calibration stages (irregular shape, damaged parts, noncommercial sizes), the outer fleshy layers, and the external brown leaves. Therefore, there is considerable industrial pressure to identify alternative means of onion waste processing and

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disposal. Converting the waste into useful products could be an appropriate and interesting route.

Several studies have examined the valorization of onion byproducts as potential sources of functional ingredients (*15*), as well as colorant extraction from external onion leaves (*16*) and pectin production from fruit and vegetable byproducts (*17*), whereas others have reported biological approaches for dealing with ethanol, vinegar (*18*−*22*), and lactic acid (*23, 24*) production from onions by fermentation. Onions are considered to be a favorable source for fermentation because they contain sugar and various nutrients. In particular, vinegar produced from worthless onions has strong potential for use as a new, functional condiment, owing to its high content of mineral, amino acids, and organic acids, and its specific physiological properties. Onion juice can be transformed into vinegar by a 2-fold fermentation process: the anaerobic transformation of fermentable sugars to ethanol (alcoholic fermentation) and the aerobic conversion of ethanol to acetic acid (acetic fermentation). However, vinegar production entails certain difficulties due to the relatively low concentration of sugars compared to other substrates commonly used in fermentation processes and the high concentration of antibacterial and antioxidant substances that can reduce fermentative capacity. Therefore, the control and optimization of ethanol and vinegar production from onions must carefully monitor all significant parameters involved in the corresponding fermentation process.

In spite of their reliability, traditional methods used for off-line monitoring of fermentation processes are highly time-consuming and labor intensive and are often accompanied by complex sample preparation procedures involving large volumes of environmentally unfriendly reagents; thus, analytical cost becomes a limiting factor in routine applications. Simpler and faster methods, such as those based on spectroscopic techniques, capable of being implemented to provide real-time measurements, are a very attractive, useful, and alternative analytical tool for online monitoring and optimization of fermentation processes. In fact, several studies have reported on the online monitoring of alcoholic and acetic fermentation of several raw materials using spectroscopic measurements (*25*−*27*). In particular, near-infrared spectroscopy (NIRS) has demonstrated great potential for cost-effective real-time bioprocess monitoring. NIRS is a noninvasive and rapid technique enabling the simultaneous determination of multiple constituents from every analysis, even without any sample pretreatment, reducing operator action to a minimum, allowing untrained personnel to do routine analyses, and providing optimum flexibility while minimizing analytical costs. Nevertheless, it should be borne in mind that the actual applicability of NIRS to online process control depends crucially on chemometrics, which provides suitable tools for gathering and extracting significant information from highly overlapped and noisy NIR spectra. Partial least-squares (PLS) regression is undoubtedly the most popular and widely applied calibration technique used in NIR multivariate analysis because it generally provides robust regression models (*28, 29*).

This study focuses on the valorization of onion byproducts to promote their transformation into useful, added-value products (onion alcohol and vinegar). For this purpose, it proposes the analytical monitoring of alcoholic fermentation of onion juice using NIRS. NIR measurements were used to develop reliable PLS regression models for monitoring of the key parameters involved in the alcoholic fermentation of onion juice, which would enable the process to be controlled in real time. Onion liquor efficiently produced using this methodology could be later processed to obtain additional functional products from onion waste (such as onion vinegar).

MATERIALS AND METHODS

Medium and Strains. Red onions from the 'Figueres' variety were used as raw material for alcoholic fermentation. The product had an initial pH of 5.09 and 9.17 °Brix (concentration percentage of soluble solids content in the sample, i.e., total of all the solids dissolved in the aqueous solution). Onion juice for fermentation was obtained from worthless onions as follows. Onions were cut and the roots and stalks separated. Onions were then triturated in a vertical cutter using a 10 × 10 mm dicing grid. The pulp was then pressed with a manual crusher. The extract was adjusted to pH <4.6 by adding citric acid (0.10%), packed in heat-sealed pouches of 4 L, and pasteurized at 100 °C during 8 min.

A commercial *Saccharomyces cerevisiae* strain, Uvaferm CM, was used to inoculate the onion juice in the alcoholic batch fermentation runs.

Two fermentation runs were performed in a 20 L bioreactor (BioFlo IV, New Brunswick Scientific, Edison, NJ) furnished with a double-walled vessel with a water-jacket heater for thermostating. Processes were run without aeration (to minimize potential losses of ethanol), and agitation was controlled at 300 rpm during fermentation. The fermentor was equipped with an oxygen electrode to measure the level of dissolved oxygen and with a pH-meter to monitor the pH of the fermentation process.

The working volume was 10 L. The lyophilized strains were added to approximately 800 mL of onion juice and poured directly into the fermentor at 30 °C. No other carbohydrates or nutrients were added to the original juice from worthless onions.

Temperature was controlled during the process and set to 30 °C. The fermentation process was monitored for around 40 h to ensure the completion of the alcoholic fermentation process.

Obviously, there are multiple factors related to the raw material used as a substrate for alcoholic fermentation (i.e., onion juice), including onion variety, geographic origin, year of harvest, and/or juice extraction procedure, which may have a significant impact on the composition of the fermentation medium and, therefore, modify the concentration ranges of the different analytes modeled and alter measured spectra. Nevertheless, it should be noted that the aim of this study was not to provide definitive and immutable NIR calibration models for real-time monitoring of alcoholic fermentation of onion juice by introducing and modeling all possible sources of variation in the medium composition within the calibration set, but rather to perform a feasibility study to propose a strategy capable of predicting the relevant parameters involved in the fermentation process studied and verify its reliability and effectiveness. To confirm the chemical homogeneity in terms of composition of the onion juice used as raw material in the present work, data from two fermentation runs were treated by a preliminary ANOVA, which showed that the variation between different fermentation batches was not significant. Thus, it should be noted that the validity and applicability of the calibration models developed to real-time monitoring of alcoholic fermentation of onion juice is limited to fermentation processes performed under conditions similar to those used in this study.

Online NIR Measurements. NIR spectra were online recorded on a near-infrared spectrophotometer NIRSystem 5000 (Foss NIRSystems, Raamsdonksveer, The Netherlands) equipped with a liquid analyzer module, using a 2 mm flow cell. The instrument was controlled by a compatible PC using the Vision v. 2.22 software package for data acquisition. NIR spectra were collected directly from noncentrifuged fermentation samples, at regular time intervals (45 min). Each spectrum was obtained from 32 scans performed at 2 nm intervals over the wavelength range of 1100−2500 nm. When NIRS is applied to liquid samples, temperature control is essential to assess spectra reproducibility. The heater of the liquid analyzer module was set to maintain the temperature of the sample at a constant 43 °C (*30*). The software was programmed to hold the flow cell inside the liquid analyzer module for 105 s before scanning to allow the sample to reach the desired temperature.

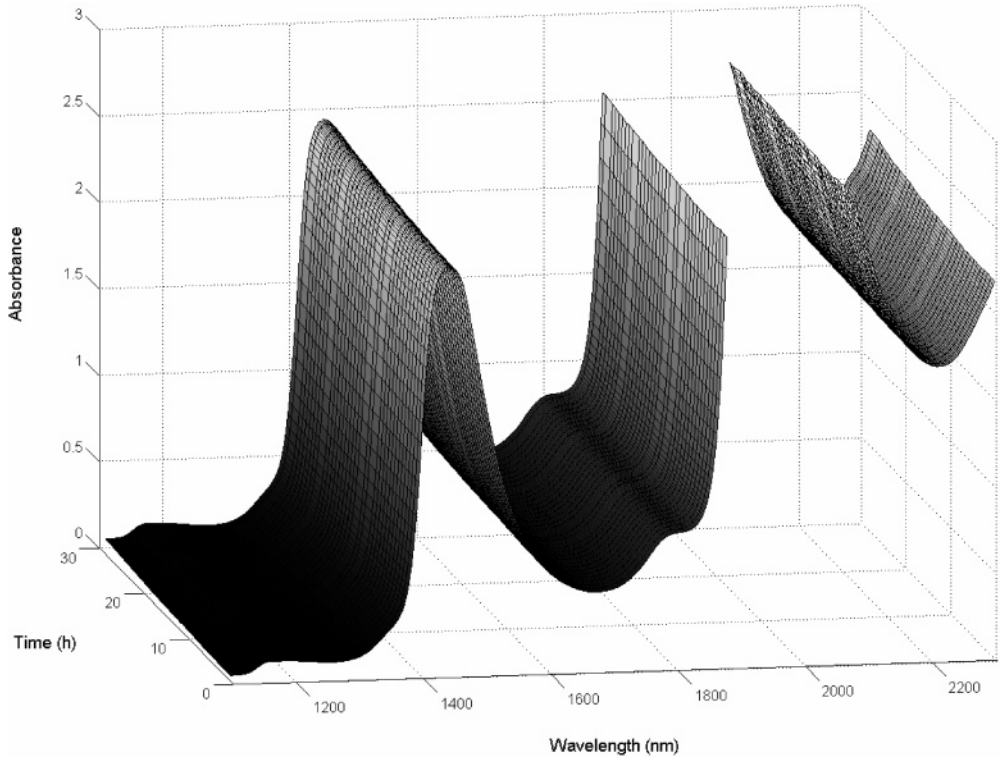

Figure 1. Evolution of absorbance NIR spectra during an alcoholic fermentation run.

To avoid potential interferences, automated clean cycles were performed between the collection of each spectrum [the sample cell was cleaned with diluted sodium hypochlorite chlorine (10%)]. **Figure 1** shows the NIR spectra of onion samples at different stages during alcoholic fermentation.

Reference Methods and Instrumentation. Samples from the bioreactor were centrifuged at 20 °C and 11000 rpm for 10 min. The supernatant was used to determine sugar and ethanol contents.

Sugars (fructose, glucose, and sucrose) were determined by high-performance liquid chromatography measurements. A modular apparatus, comprising a complete HP 1050 series system and a refractive index detector HP 1047A, was used. The column used was a Zorbax SB-C18, 250 mm × 4.6 mm i.d. with 5 μm particle size (Hewlett-Packard GmbH, Waldbronn, Germany). The Stable bond (SB) packing was suitable for working at low pH values and prevented tailing. Operating temperature was 25 °C. Mobile phase was 0.009 M potassium dihydrogen phosphate (adjusted to pH 2.06 with phosphoric acid)/methanol (92:8, v/v) at a flow rate of 0.64 mL·min^{-1} at 25 °C and a working pressure of 90 bar (1 bar = 10^5 Pa). Detection was performed by measuring the UV absorption at 210 nm. A previous multiwavelength detection study (190−280 nm) was performed to select the optimal absorbance wavelength. All solutions, standards, and samples were filtered prior to their injection in the chromatographic system through a 0.7 μm pore size glass fiber filter (Whatman GF/F, Whatman International Ltd., Maidstone, U.K.).

Ethanol was determined by gas chromatography in a Hewlett-Packard 5890 series II gas chromatograph with flame ionization detection (FID) and *n*-propanol as internal standard. Chromatographic conditions used for the analysis of this compound can be found in **Table 1**.

Total biomass concentration was measured using a Neubauer counting chamber. The number of viable yeasts was determined by a technique that identified nonvital cells stained by methylene blue phenicated solution. Viable concentration was calculated as the difference between total and nonviable cells (stained).

Data Set and Data Processing. The samples used to develop and validate the calibration models were directly obtained from the fermentation system. Overall two fermentation runs were conducted. Thus, the data set used in the present study comprised 98 samples, with approximately 50% belonging to each fermentation run. Each sample taken from the fermentor was then analyzed to obtain both its corresponding NIR spectrum and the reference values for all parameters to be modeled at a later stage. Chemometric analysis was performed using MATLAB software (*31*).

Table 1. Features of the Chromatographic Method Used To Assay Ethanol

column	Supelcowax 10 (30 m, ∅ 32 mm)
detector	FID
injector temperature	200 °C
detector temperature	250 °C
temperature program	40–150 °C, 18 °C·min^{-1}; 150 °C, 2 min
carrier gas	He, constant flow rate at 1.0 mL·min^{-1}
split	1:30

Two segments of the whole wavelength range of 1100−2500 nm were removed in all spectra: first, the region from 1880 to 2080 nm due to signal saturation caused by the strong combination band of O−H bonds from water (1950 nm); and, second, the zone from 2300 to 2500 nm due to its very low signal/noise ratio.

PLS regression was used to develop separate calibration models between NIR measurements within the above-mentioned wavelength range and each considered parameter of alcoholic fermentation (ethanol, biomass, pH, fructose, glucose, and total sugars). Different preprocessing methods were tested to find models with as high a predictive ability as possible.

For each calibration, different training and test data sets were generated to provide a more robust estimate of the predictive ability of the constructed models (*32*, *33*). For this purpose, a total of 20 PLS runs were performed with different random external test sets accounting for 30% of original data, in such a way that the final error measurements associated with each model were calculated as the mean values for the 20 different calibration runs performed. The suitable complexities of the models developed were chosen according to the validation results.

The quality of the results provided by the different PLS regression models constructed were evaluated by testing and comparing the predictive ability of the respective models. In this way, a useful index for evaluating the quality of the results of a PLS calibration model is

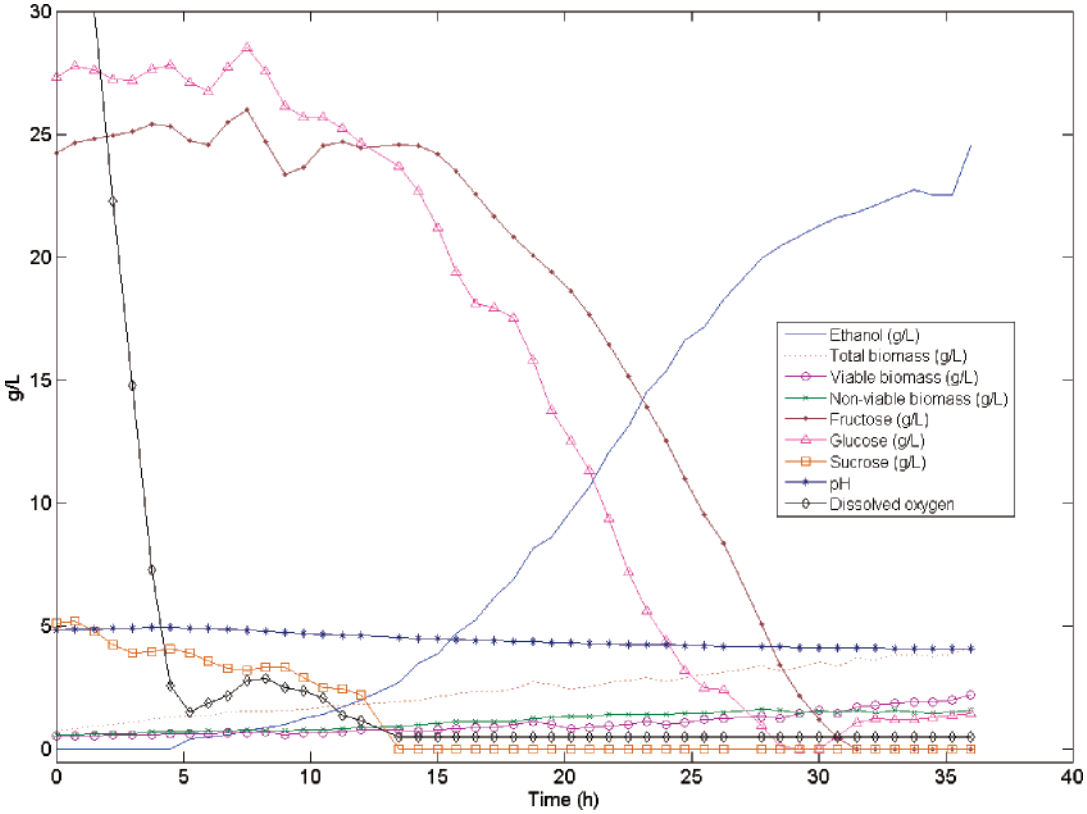

Figure 2. Variation of physicochemical parameters during the fermentation process.

the root-mean-square error (RMSE) in percentage of residuals obtained, defined as

$$\%\mathrm{RMSE} = \frac{\sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n}}}{y_{i,\max} - y_{i,\min}} \times 100 \qquad (1)$$

where y_i is the reference response value, $\hat{y}_i$ the predicted response value, and n the total number of samples in the sample set. RMSE is termed root-mean-square error in calibration (RMSEC) for the calibration set and root-mean-square error of prediction (RMSEP) for the prediction (test) set. One advantage of using RMSE values expressed in percentage terms is that results obtained from different response variables, not directly comparable in terms of dimensionality, can be contrasted.

RESULTS AND DISCUSSION

NIR Spectral Features and Fermentation Evolution. The previously pasteurized onion juice with a total content of sugars of approximately 60 g/L was inoculated with a starter culture deriving from the pure yeast culture described above. *S. cerevisiae* transforms sugars into ethanol and carbon dioxide. The evolution of onion juice composition and that of pH in the culture medium through alcoholic fermentation are shown in **Figure 2**. At the beginning of fermentation, onion juice contained 25 g/L of fructose, 27 g/L of glucose, and a concentration of 5 g/L of sucrose. During the first stages of fermentation, there was a decrease in sucrose content, whereas fructose and glucose concentrations fell only slightly. The concentrations of fructose and glucose started to decrease when sucrose hydrolysis and consumption had ended (sucrose is first decomposed to glucose and fructose by cellular invertase and then used by the yeast). Ethanol concentration increased over the 40 h of fermentation until there were no sugars in the medium. There was a positive, almost linear evolution of total biomass during fermentation. Viable and nonviable biomass increased as well. Another noteworthy observation was the acidification of fermentation medium during alcoholic fermentation, in response to the formation of organic acids as secondary nondesired metabolites in the fermentation processes, as a result of the high pH levels in onion juice (pH >3.5) (*34*).

Table 2. Ranges of Analytical Parameters in the Sample Set

analyte	min	max	av
ethanol ($g \cdot L^{-1}$)	0	24.52	9.60
total biomass ($g \cdot L^{-1}$)	0.77	4.16	2.42
pH	4.08	4.96	4.47
dissolved oxygen (DO) (% saturation)	0.5	46.3	2.4
fructose ($g \cdot L^{-1}$)	0	25.98	16.12
glucose ($g \cdot L^{-1}$)	0	28.53	14.84
sucrose ($g \cdot L^{-1}$)	0	5.22	0.83
total sugars ($g \cdot L^{-1}$)	1.03	57.71	32.29

NIR spectra of samples collected at different times during alcoholic fermentation (**Figure 1**) exhibited an increase in absorbance as the fermentation process progressed and ethanol was produced. The dominant feature observed in the raw spectra was the water absorption band (major component in onion juice) at approximately 1450 nm. In the subsequent calibration step, no attempts were made to select specific spectral bands that could be used to construct the calibration models, but the whole spectra were used (once the saturated/noisy regions had been discarded) to retain all of the information available in the block of predictors and to take advantage of their synergy, taking into account the complexity of the fermentation medium. However, we were able to detect and identify certain changes in spectra that can be ascribed to specific relevant compounds.

The spectral region from 1150 to 1250 nm contained absorptions owing to the second overtone of C−H stretching, whereas the 1350−1650 nm region included the first overtone of O−H stretching in water and sugars (≈1450 nm changes in spectra with time from the 1660−1780 and 2200−2300 nm

Table 3. Descriptive Statistics of Calibration and Validation Sets for Different Response Variables

analyte	spectra preprocessing	PLS factors	mean %RMSEC	std %RMSEC	mean %RMSEP	std %RMSEP
ethanol	centered	3	1.48	0.14	1.91	0.23
total biomass	first derivative	6	3.04	0.15	4.62	0.57
ph	MSC	5	4.35	0.24	6.87	0.74
fructose	autoscaled	4	4.25	0.24	5.59	0.58
glucose	autoscaled	3	3.33	0.17	3.67	0.43
total sugars	centered	3	2.60	0.15	2.85	0.44

Table 4. Figures of Merit for the Relationship between NIR Computed Values and the Corresponding Reference Values for Each Modeled Fermentation Parameter[a]

analyte	slope	intercept	R^2
ethanol	0.996 ± 0.010	0.037 ± 0.120	0.998
total biomass	0.979 ± 0.027	0.052 ± 0.073	0.982
pH	0.972 ± 0.032	0.132 ± 0.149	0.974
fructose	0.981 ± 0.026	0.307 ± 0.489	0.983
glucose	0.988 ± 0.021	0.199 ± 0.404	0.989
total sugars	0.994 ± 0.016	0.217 ± 0.620	0.994

[a] Symbol ± denotes the 95% confidence interval.

regions can be ascribed, respectively, to the first overtone for the C−H bonds and to the combination bands for the −OH group in ethanol structure; for this reason, absorbance increased as ethanol concentration rose).

Calibration Results. Several parameters were controlled during alcoholic fermentation. Ethanol, dissolved oxygen pH, sugars, total, and viable and nonviable biomass were crucial parameters that describe the alcoholic fermentation process. **Table 2** shows the concentration ranges spanned by the fermentation samples used for calibration and validation of the models developed in the present study for all parameters controlled during the fermentation process.

Different PLS regression models were calculated using NIR variables as predictor variables and the respective reference values determined for each fermentation parameter to be modeled and predicted (i.e., ethanol, total biomass, pH, fructose, glucose, and total sugars). Viable and nonviable biomasses were not separately calibrated because NIR technology was able to measure turbidity but not to distinguish between live and dead yeasts. Note that the narrow concentration range covered by sucrose during fermentation (compared to the rest of absorbing sugars present in the medium) would cause a calibration model separately developed for determining this parameter to be a poor approximation in terms of model quality and reliability. For this reason and considering that total sugar content was simply computed as the sum of the glucose, fructose, and sucrose concentrations for each fermentation sample, it was decided to address the problem of accurately predicting sucrose concentration with an indirect calibration procedure. Thus, a highly reliable NIR calibration model was developed for monitoring total sugar concentration so that the subsequent combination of total sugar prediction provided for each sample with the corresponding glucose and fructose contents predicted by the respective regression models developed would allow a more accurate determination of sucrose concentration to be obtained.

The nonsaturated regions of the whole spectra of samples taken from the fermentor during alcoholic fermentation were considered in order to build the calibration models according to the iterative PLS calibration procedure described previously (20 PLS regression cycles were carried out using different random calibration and test sets, in such a way that an average PLS model was subsequently computed). **Table 3** summarizes the results obtained in both calibration and prediction to model each alcoholic fermentation parameter, after selection of the most suitable data pretreatment and model complexity. Standard deviations of both RMSEC and RMSEP values obtained in the 20 PLS runs performed with different random external test sets for each response studied were also provided to better illustrate, together with the mean error measurement associated with each model (in both calibration and prediction), the robustness and stability of the validation process applied. **Table 4** shows the slope, intercept, and determination coefficient (R^2 value) between the NIR computed values and the respective reference values for each modeled fermentation parameter, which may be used as additional statistical measurements to better evaluate model performances. Prediction intervals at the 95% confidence level were computed for each regression model to properly estimate reliability and uncertainty. Likewise, the plot showing the root-mean-square error in percentage terms, in both calibration and prediction (RMSEC and RMSEP), versus the number

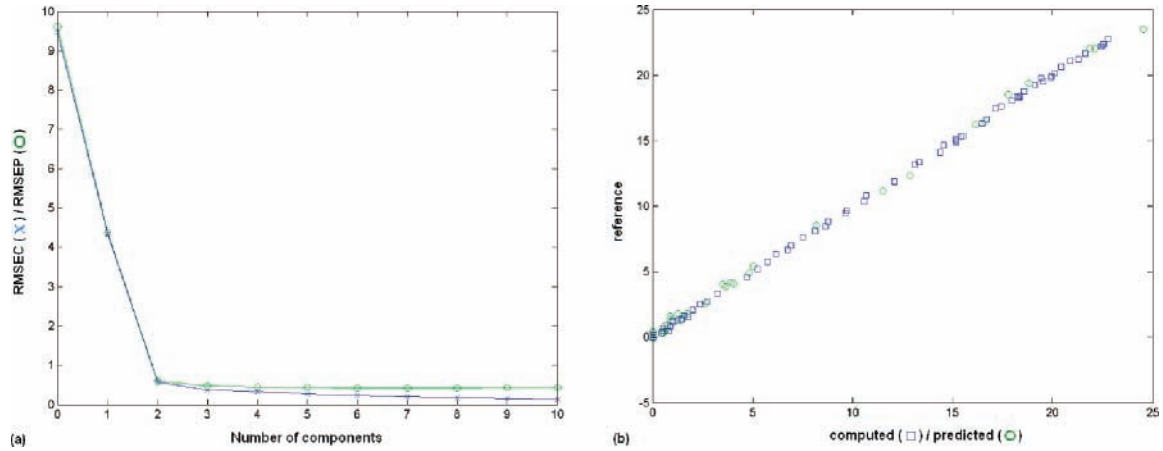

Figure 3. Calibration model for ethanol: (**a**) RMSEP and RMSEC values versus number of components in the model; (**b**) computed and predicted values versus reference values.

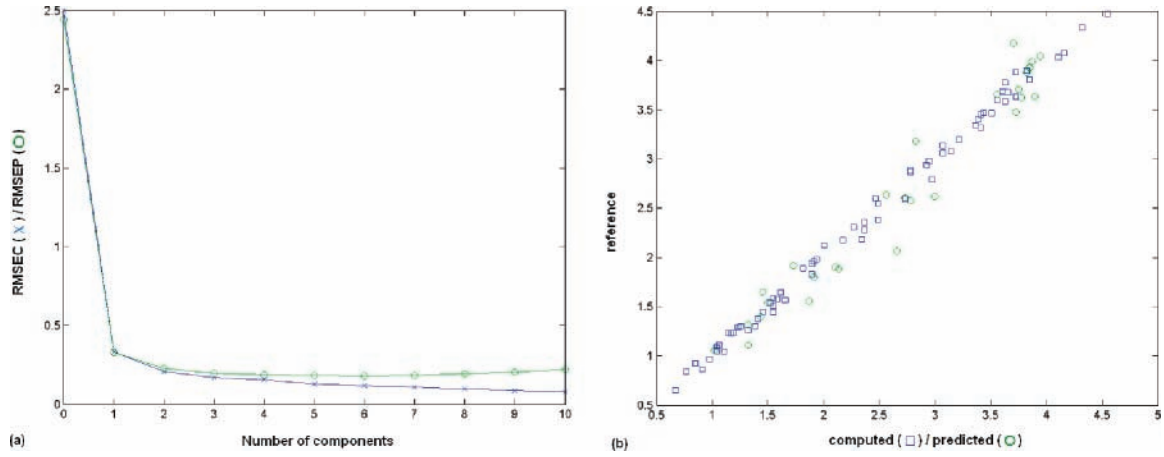

Figure 4. Calibration model for total biomass: (**a**) RMSEP and RMSEC values versus number of components in the model; (**b**) computed and predicted values versus reference values.

of components in the model, and the correlation plots between computed (□)/predicted (○) values and reference response values were also obtained for use as additional tools to evaluate model performance. Thus, **Figures 3** and **4** show these types of diagnostic plots for ethanol and total biomass, respectively. Although several preprocessing methods were applied to NIR data to test their effect on the quality of the final regression models—including mean-centering, autoscaling, first and second derivatives, orthogonal signal correction, multiplicative signal correction (MSC), and standard normal variate (SNV)—it can be observed that complex pretreatments of spectral data were not needed to obtain the best possible results for all modeled physicochemical variables. The selection of the optimal number of PLS factors to be included in the model development was based on the results obtained in validation. The calibration (prediction) errors for all studied parameters ranged from 1.48% RMSEC (1.91% RMSEP) in the case of ethanol to 4.35% RMSEC (6.87% RMSEP) for pH. The higher RMSE values obtained when pH was used as a response variable (compared to other descriptors) may be attributed to the small variation range of pH during alcoholic fermentation. The results obtained for total biomass (3.04% RMSEC and 4.62% RMSEP) may be considered to be very successful (even though it was one of the parameters showing higher errors), bearing in mind the great difficulties in measuring biological variables in such a complex system. The best results were obtained for ethanol and total sugars (product and substrate of alcoholic fermentation, respectively), as was expected considering the wider range of values for these compounds during fermentation and the high correlation between the NIR signal and the chemical features of both species. Therefore, in view of the high predictive ability in both calibration and validation displayed by all of the proposed regression models, they may be recommended as suitable tools for real-time monitoring of the evolution of the main parameters involved in the alcoholic fermentation of onion juice.

In short, the objective of the present study was to examine ethanol production from juice extracted from worthless onions via alcoholic fermentation as a strategy for obtaining high-value-added products from onion waste. To evaluate the feasibility of this approach, it is essential to develop a suitable tool for monitoring of such a fermentation process. The results reported in this study show that NIR spectroscopy, in combination with multivariate calibration, may be applied for real-time monitoring of crucial parameters in the alcoholic fermentation of onion juice, in spite of the high complexity inherent in the study of biological systems. Use of the high-quality regression models proposed would enable fast, nondestructive, accurate, and near-real-time determination of key parameters involved in fermentation, which is crucial for the control and global optimization of the process and for ensuring the effective conversion of onion waste into commercially valuable food ingredients.

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