Determination of the Geographical Origins of Olive Mill Wastewater: FTMIR Spectroscopy and Chemometric Algorithms for Accurate Classification

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Received: August 06, 2024; Accepted: September 27, 2024
DOI: 10.17721/moca.2024.206-212
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The present research studies the geographical classification of olive mill wastewater (OMWW) samples using FT-MIR spectroscopy and chemometric recognition algorithms. The study focuses on samples collected from two regions in Morocco: BeniMellal-Khenifra and Fes-Meknes. Principal Component Analysis (PCA) has been applied to the spectral data, revealing distinct clustering of OMWW samples based on their geographical origin. Additionally, Partial Least Squares Discriminant Analysis (PLS-DA) has been employed to develop a classification model for accurate sample categorization. The PLS-DA model presented high sensitivity and specificity, achieving perfect classification rates during the calibration phase. Validation results show the model's capability to accurately identify the majority of samples, with a minor misclassification. These results confirm the potential of FTMIR spectroscopy and chemometric recognition algorithms for authentication, and traceability in the olive oil industry. Further research can explore the extension of this methodology to other regions and agricultural by-products, incorporating advanced machine learning algorithms for enhanced classification accuracy. Overall, the present study contributes to enhance environmental waste management research by addressing OMWW disposal concerns and promoting sustainable practices on the valuation possibilities.

Keywords: Olive Mill Wastewater (OMWW), FTMIR, data analysis, traceability, classification and discrimination

Introduction

Olive oil is widely recognized as a primary fats source in the Mediterranean diet that plays a significant role in the culinary habits of Mediterranean countries. It possesses health-promoting properties thanks to its abundant content of unsaturated fatty acids. However, the production of olive oil is accompanied by a notable amount of a by-product known as olive mill wastewater (OMWW) that is generated in substantial quantities during a specific timeframe, typically spanning from October to December. Morocco, being the sixth largest producer of olive oil, generates an estimated annual volume of over 250,000 m^3 of olive mill wastewater (OMWW) [1].

These OMWW possess detrimental characteristics including pollution, phytotoxicity, and antimicrobial properties, making them a significant environmental concern in the olive oil production industry [2]. Various methods have been suggested to address the challenges posed by olive mill wastewater (OMWW). These methods include evaporation ponds, thermal concentration, physico-chemical and biological treatments, and the direct use of OMWW as an organic fertilizer in agricultural soils. Nevertheless, the two most commonly employed techniques today involve the direct application of OMWW to agricultural soils and their storage in evaporation ponds, resulting in the production of sludge [3].

For better understanding of this olive oil by-product several studies were conducted on physicochemical composition of OMWW. It is typically characterized as a dark brown to deep black discharge, exhibiting acidity and a high pollution load primarily due to substantial amounts of suspended solids and a substantial organic content. This organic content comprises polysaccharides, sugars, polyphenols, polyalcohols, tannins, proteins, organic acids and lipids [4-6]. Additionally, OMWW contains significant quantities of mineral salts, particularly potassium, phosphate and sodium [7,8]. Although limited in scope, the microbiological analysis of OMWW has revealed the presence and isolation of numerous species from yeast, fungal, and bacterial populations within these effluents [9-12]. The chemical composition of OMWW is influenced by uncontrolled multiple factors such as olive cultivars, fruit ripening, harvesting period, storage conditions, farming methods, production origin, climatic conditions and oil extraction technology [13-18]. In fact, several studies have been carried on olive by-products as OMWW, namely in terms of biological applications of their polyphenolic compounds content [19-24].

In the present study, we develop rapid FTMIR spectroscopic method combined with chemometric tools that could be able to discriminate and classify Olive Mill Wastewater samples collected from different provinces in the two Moroccan regions Beni Mellal-Khenifra and Fes-Meknes.

Material and methods

Sampling

Calibration (40) and validation (16) samples of OMWW were collected from different industrial olive oil facilities in different provinces in the two regions: Beni Mellal–Khénifra (Khouribga,Azilal, Beni Mellal and Fkih Ben Saleh) and Fes-Meknes (Taounat, Fes, Sefrou, Meknes and El Hajeb) (Table 1).

Table 1. Geographical origins of the collected samples.

Region	Province	Calibration Samples	Validation Samples
Beni Mellal - Khénifra	Khouribga	8	2
	Azilal	4	2
	Beni Mellal	7	2
	Fkih Ben Saleh	8	4
Fes - Meknes	Taounat	2	1
	Fes	3	1
	Sefrou	2	1
	Meknes	5	3
	El Hajeb	1	-
Total		40	16

The OMWW collected were produced during the olive oil crushing period from October 2021 to January 2022 and then stored at 4 °C.

ATR-FTMIR Spectroscopy

The analysis of the samples was performed by the TENSOR 27 ATR-FTMIR spectrometer equipped with a horizontal ATR accessory by a Germanium crystal. Using a micropipette, each well homogenized OMWW sample was deposited on the crystalline surface of the ATR accessory. For each analysis, the ATR accessory is cleaned by an ethanol solution. The spectra were recorded in absorbance mode, collected between 4000 cm^{-1} and 400 cm^{-1}, with 32 scans and a 4 cm^{-1} resolution.

Multivariate Analysis

Previous studies, on olive oil produced in Morocco, have already used the coupling between spectroscopic methods, in particular FTMIR, on the one hand and methods of multivariate analysis on the other hand [25-29]. The results of these studies have motivated us to investigate into such a coupling not to olive oil as one of the products of the olive tree but rather to OMWW as one of the by-products of this plant. So, we have used various statistical techniques in the present study to process and evaluate spectral data obtained by ATR-FTMIR spectroscopy. To explore and represent the data set, we first applied Principal Component Analysis (PCA). PCA allows us to search for directions of maximum dispersion in order to synthesize new variables and represent the data in a reduced-dimensional space. In addition to reducing data size, this method is frequently used to clean up data by identifying outliers. It is also an effective tool for identifying groups of individuals that behave similarly in terms of measured variables.

At the second step the principal components are used in a Partial least squares regression analysis. PLS regression is a modern method in chemometrics that enhance and couple the characteristics of principal component analysis and multiple regressions. Its objective is to predict or examine a group of dependent variables using a set of independent variables or predictors. This prediction is achieved by extracting a collection of orthogonal factors known as latent variables from the predictors that possess optimal predictive capability.

In the present study, PLS-DA was applied to find what were the variables that effectively discriminate within samples groups based on their FTIR spectra (X data block) according to their maximum covariance with a geographical location indicated by a class relevance variable (Y data block).

PLS-DA aims to determine whether a sample's spectrum corresponds to a specific geographical location, categorized as binary values of zero (0) and one (1).

The statistical processing of the data was carried out using The Unscramble Version X 10.4 software.

Results and discussion

FTMIR Analysis

The FTMIR absorption spectra of the collected samples are presented in Fig. 1.

The FTMIR spectra show a similar appearance to that of water that is the major component of OMWW but it also contains weak absorbance's corresponding to functional groups that characterize the olive oil compounds (Table 2).

The visual observation of the ATR-FTMIR spectra of these 40 samples cannot be used to determine the similarities between individuals to differentiate between OMWW coming from different geographical origins.

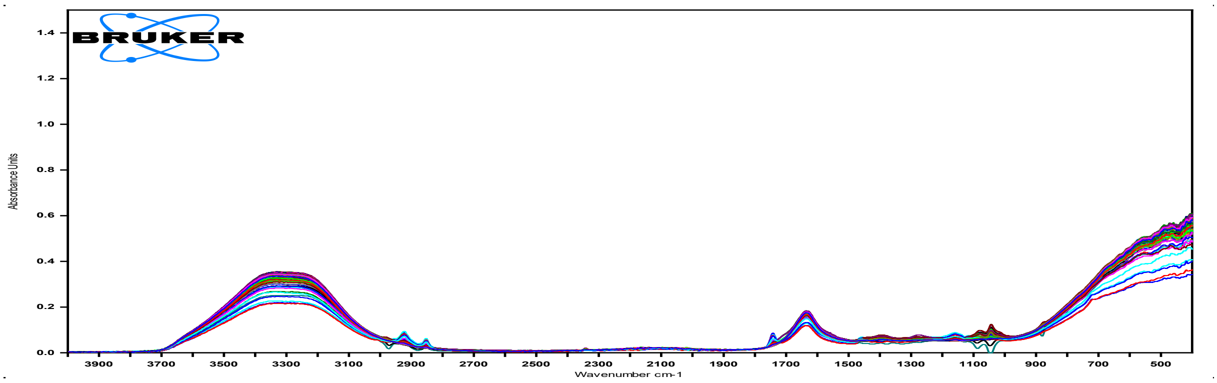

Fig. 1. ATR-FTMIR spectra of the collected OMWW samples.

Table 2. Characteristics of the ATR-FTMIR spectrum of OMWW [30, 31].

Wavenumber in cm^{-1}	Corresponding functional groups
Large and intense band at 3300	Elongation of O-H (phenol)
band at 2920	Elongation of C-H (saturated and aromatic)
pic at 1720	Elongation of C=O (Ketones)
band at 1630	Elongation of C=C unconjugated double bond

Principal Component Analysis

A preliminary examination of the spectral data collected was carried out by principal component analysis using the 400–4000 cm^{-1} FTMIR spectral range, in order to represent the data in a reduced dimensional space. The PCA results (Fig. 2) show that three principal components explain 97% of the total variance in the spectral data, accounting for 85, 8 and 4 % of the total variance in the raw data respectively.

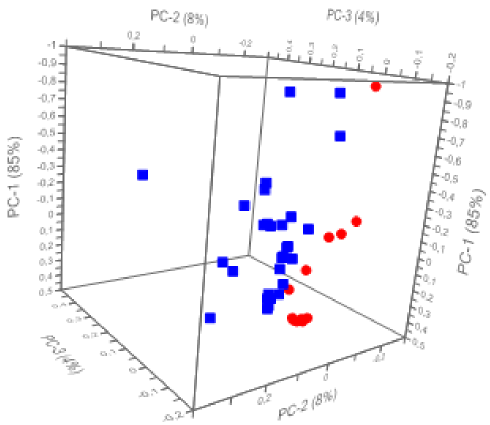

Fig. 2. 3D PCA score plot of ATR-FTMIR spectra at the PC1, PC2 and PC3on olive mill wastewater from two different regions (Beni Mellal-Khenifra - blue, and Fes-Meknes - red).

The observation of the score plot shows that there is a clustering of OMWW based on the geographical origin of the samples. The PCA also determines that the samples clustered in two groups, the first group is representative of the Beni Mellal–Khenifra region while the second one concerns the Fes-Meknes region. We have compared the results of the present work, in terms of classification between OMWW samples from the same region, to those that have been published in the literature. So, the PCA has been used by various previous works which have been able to classify according to the geographical and varietal origins of samples of olive oil from Morocco [32,35]. Indeed, thanks to PCA El orche et al. were able to carry out the classification of olive oil in the Beni Mellal-Khenifra region [32] while Zeroual and al. have done so over the Fes-Meknes region and other regions in Morocco [33-35].

Partial Least Squares Discriminate Analysis

To develop a classification model capable of accurately categorizing samples based on their geographical origin, we employed Partial Least Squares Discriminant Analysis (PLS-DA) on spectroscopic data. PLS-DA is a robust multivariate statistical technique that combines the power of partial least squares regression with discriminant analysis. By leveraging the inherent patterns and relationships present in the spectroscopic data, PLS-DA enables us to extract meaningful features and create a predictive model. Through this approach, we aim to achieve a high level of accuracy in classifying samples based on their origin, facilitating various applications such as authentication and traceability. When analyzing the score plot (Fig. 3), we can observe distinct clusters or well-separated groups representing samples of different origins. This high level of classification in the score plot implies that the PLS-DA model has effectively learned and utilized the spectral information to differentiate samples according to their origin. It suggests that the model has extracted informative features from the spectroscopic data, allowing it to accurately classify samples based on the unique spectral signatures associated with each geographical origin.

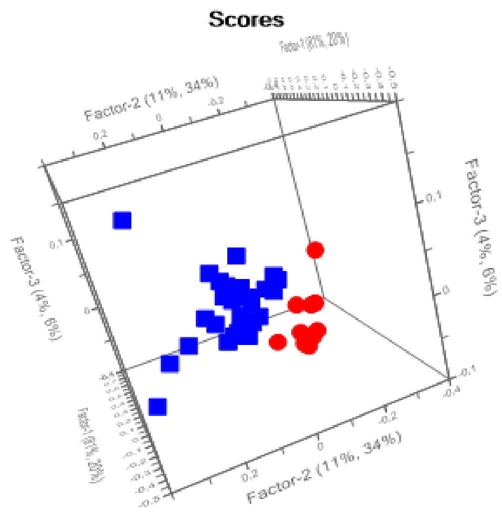

Fig. 3. PLS-DA score plot of ATR-FTMIR spectra at the PC1, PC2 and PC3 on olive mill wastewater from two different regions (Beni Mellal-Khenifra - blue, and Fes-Meknes - red).

The obtained confusion matrix from the calibration results of the PLS-DA model provides valuable insights into its performance (Table 3). The matrix reveals that all samples belonging to Class 1 (Beni Mellal-Khenifra) were accurately classified, resulting in a sensitivity of 100%. Similarly, all samples of Class 2 (Fes-Meknes) were correctly identified, leading to a specificity of 100%. These high values indicate that the model effectively distinguished between the two classes and displayed a strong capability to correctly classify samples based on their geographical origin.

Furthermore, the Correct Classification Rate (CCR) of 100% demonstrates the overall accuracy of the PLS-DA model on the given dataset. This indicates that the model achieved flawless classification, correctly assigning all samples to their respective origins. These remarkable results emphasize the robustness and reliability of the PLS-DA model when applied to spectroscopic data for classification purposes.

Analyzing the confusion matrix, we can draw valuable insights into the performance of the PLS-DA model in classifying samples during the validation phase.

The sensitivity of 100% indicates that all samples belonging to Class 1 (Beni Mellal-Khenifra) were correctly identified by the model. This means that the model accurately detected and classified all samples originating from Class1 (Beni Mellal-Khenifra). Similarly, the specificity of 83.33% suggests that the model correctly classified a majority of the samples from Class 2 (Fes-Meknes) (Table 4). However, it did misclassify one sample from Class 2 (Fes-Meknes) as Class 1 (Beni Mellal-Khenifra).The Correct Classification Rate (CCR) measures the overall accuracy of the model and takes into account both true positives and true negatives. In this case, the CCR is calculated by summing the true positives and true negatives and dividing it by the total number of samples. Therefore, the CCR is approximately 93.75%. This indicates that the model achieved a high overall accuracy in classifying the samples during the validation phase.

These results demonstrate the effectiveness of the PLS-DA model in correctly identifying the majority of samples from both Class 1 (Beni Mellal-Khenifra) and Class 2 (Fes-Meknes). While the specificity value indicates a small misclassification, the model exhibited a strong sensitivity and a high overall accuracy (CCR) in classifying the samples based on their geographical origin. Thus the results of the present work, in terms of discrimination between OMWW samples from the same region, are comparable to those of previous work on virgin olive oil in France [36,37] and olive products in Morocco [38-41]. PLS-DA model showed a high sensitivity, indicating accurate identification of Class 1 (BeniMellal- Khenifra) samples. The specificity value suggests a mostly correct classification of Class 2 (Fes-Meknes) samples, with a minor misclassification. The CCR value reflects the overall accuracy of the model in classifying the samples during the validation phase. These results emphasize the model's capability to effectively classify samples based on their geographical origin that can have significant applications including authentication, and traceability.

Table 3. Confusion matrix of calibration results obtained by PLS-DA for the dataset.

Origin	1	2	Specificity (%)	Sensitivity (%)	CCR (%)
1	27	0	100	100	100
2	0	13			

Table 4. Confusion matrix of validation results obtained by PLS-DA for the dataset.

Origin	1	2	Specificity (%)	Sensitivity (%)	CCR (%)
1	10	1	83.33	100	93.75
2	0	5			

Conclusion

The present study has shown the successful application of FTMIR spectroscopy coupled to chemometric recognition algorithms, namely PCA and PLS-DA, to perform a geographical classification of olive mill wastewater (OMWW) samples from two geographical areas. The PCA analysis revealed distinct clustering of OMWW samples based on their geographical origin, while the PLS-DA model achieved high accuracy in accurately classifying samples according to their origin. These results highlight the potential of this approach for authentication, and traceability purposes in industries related to olive oil production. By effectively utilizing spectral data and extracting meaningful features, this methodology offers valuable insights into the classification and traceability of OMWW samples, addressing environmental concerns and supporting sustainable practices in the olive oil industry. Further research could explore the expansion of this methodology to a broader range of geographical regions and investigate its applicability to other by-products in the agricultural and food processing sectors. Additionally, integrating complementary analytical techniques and exploring advanced machine learning algorithms could further enhance the accuracy and efficiency of classification models. These advancements would contribute to improved environmental management, ensuring proper disposal of OMWW, and supporting sustainable practices in the olive oil industry and even other products or by-products.

Acknowledgments

The authors thank all the people who participated in this work.

Funding

No financial aid is applicable

Conflicts of Interest

All authors declare no conflict of interest.

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