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# Modelling of olive mill wastewater characteristics

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## Abstract

A synthesis of the analytical work carried out on the characterisation of Olive Mill Wastewater (OMW) is given, covering articles published over the last 30 years, being excluded all data that didn't account phenol quantification.
Due to the wide range of the data on OMW characterisation found in the literature, results on Chemical Oxygen Demand, Biochemical Oxygen Demand, Total Solids and Volatile Solids are summarised and correlations between them and with polyphenol content are sought.
The aim of this work is to use the modelling of the analytical parameters to define working limits, in order to be able to predict and monitor successfully an OMW treatment. Scale-up from previously published data will be considered, trying to overcome the case-by-case studies found in the literature. This modelling also contributes to obtain a good experimental performance with a specific OMW.
Portuguese OMW characterisation for the aforementioned parameters is carried out, as well as the validation of the correlations found for the parameters in the literature.

# 1 Introduction

Olive Mill Wastewaters (OMW) are generated as a residue in the production of olive oil and their elimination is a major environmental problem in Mediterranean countries, where the production is very high and concentrated in a short period of time (November-February). The annual OMW production is estimated to be over $30 \times 10^6$ $m^3$ [1-3].
The composition of OMW is very variable and depends on olive variety, the ripeness of the fruit, and the extraction process (press or centrifuge) [4].
Typical OMW composition by weight is: 83-94% water, 4-16% organic compounds and 0.4-2.5% mineral salts. The organic fraction contains, among other components, 2-15% of polyphenols; divided into low-molecular weight compounds (caffeic acid, tyrosol, hydroxytirosol, p-cumaric acid, ferulic acid, syringic acid, protocatechuic acid etc.) and high molecular weight compounds (tannins, anthocianins, etc) [5-7] as well as catechol-melaninic polymers [8].
The Chemical Oxygen Demand (COD) ranges from 2 to 220 $gdm^{-3}$ [9,10]; the Biochemical Oxygen Demand ($BOD_5$) ranges from 4.3 to 93.5 $gdm^{-3}$ [11,12]; the total solids (TS) are 5.9 to 103.2 $gdm^{-3}$ [9,13]; Volatile solids (VS) are 2.4 to 89.9 $gdm^{-3}$ [9,13] and the content of polyphenols 0.1-17.5 $gdm^{-3}$ [9,14]. The high content of organic matter and polyphenols together with the very large volumes produced and the seasonality of the industry has led to considerable pollution and has limited the application of conventional methods of wastewater treatment [2]. The aim of this work is to use the modelling of the analytical parameters to define working limits, in order to be able to predict and monitor successfully an OMW treatment. We will present models based on 82 OMW characteristics.

# 2 Materials and methods

A literature survey was carried out and the parameters usually used to characterise OMW were selected. The most common parameters found were: COD, $BOD_5$, phenol, TS and VS, with phenol concentration and COD by far the most common parameters determined. The Portuguese OMW characterisation was carried out by the determination of the aforementioned parameters according to the following experimental procedure.

## 2.1 COD, TS , VS, BOD

These parameters were determined according to the procedure described in Standard Methods [15].

### 2.2 Determination of polyphenols in solution

#### 2.2.1 Folin-Denis method

Was based on oxireduction reactions between phenolic compounds and metallic ions adapted from a method describe by Duran [16].
In each centrifuge tube 3.75 mL of distilled water was added to 0.5 mL of the sample and 0.25 mL of Folin-Denis reagent (Fluka, p.a.), the solutions were yellow at this stage. After waiting 5 minutes, 0.5 mL of sodium carbonate 20% (Merck, p.a.) was mixed into solution using a vortex and left for about 10 minutes for the reaction to complete. The samples were then centrifuged for 10 minutes (Sigma 2-15 B. Braun), at 5000 rpm. The absorbance of the liquid phase was measured using a quartz cell, (optical path 1 cm) in a spectrophotometer (Hitachi U-2000) at a wavelength of 725 nm.
A standard calibration graph was prepared by plotting absorbance vs caffeic acid concentrations ranging from 0-100 ppm. Results were expressed in terms of caffeic acid equivalent as this was used as a reference substance.

## 3 Results and discussion

The modelling of OMW characteristics was studied using two different strategies, an exhaustive bibliographic research was carried out and 42 values of OMW characterisation were encountered and used for the model development, the second approach was the validation of the model proposed by the introduction of 40 values from Portuguese OMW characterisation.
It is important to take into account that the values collected from the bibliographic survey concern different OMW source countries, different fruit varieties and ripeness, different extraction systems (pressing and centrifuging) and were evaluated by the application of different analytical techniques. For the Portuguese case the same aforementioned variables were considered, in this case the source country was obviously the same and the analytical procedures for OMW characterisation.
The bibliographic references found in literature are summarised in Table 1 and those for the Portuguese case in Table 2.

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Table 1. Bibliographic References found in literature for OMW characterisation

| Year of publication | Bibliographic Reference |
|---|---|
| 1988 | [33]$^{2}$ |
| 1989 | [37]$^{2}$, [40]$^{2}$ |
| 1990 | [31]$^{1}$, [38]$^{1}$, [44]$^{1}$ |
| 1991 | [12]$^{2}$, [18]$^{1}$, [19]$^{1}$, [42]$^{3}$ |
| 1992 | [22]$^{1}$, [25]$^{1}$, [26]$^{1}$, [28]$^{1}$ |
| 1993 | [13]$^{3}$, [14]$^{3}$, [34]$^{2}$, [43]$^{1}$, [46]$^{5}$ |
| 1994 | [9]$^{1}$ |
| 1995 | [17]$^{1}$, [21]$^{1}$ |
| 1996 | [20]$^{2}$, [35]$^{2}$ |
| 1997 | [29]$^{1}$, [45]$^{4}$ |
| 1999 | [11]$^{1}$, [36]$^{2}$, [39]$^{2}$ |
| 2000 | [23]$^{1}$, [24]$^{1}$, [27]$^{1}$, [30]$^{1}$, [47]$^{7}$ |
| 2001 | [32]$^{4}$, [41]$^{1}$ |
| 2002 | [10]$^{6}$ |

Note: Source Countries: $^{1}$Spain, $^{2}$ Italy, $^{3}$ France, $^{4}$ Greece, $^{5}$ Tunisia, $^{6}$ Portugal, $^{7}$ different countries

Table 2. Bibliographic References survey OMW characterisation in Portugal

| Year of publication | Bibliographic Reference |
|---|---|
| 2002 | [10], [48] |

Note: Beside the bibliographic references, OMW characterisation values from 2002/2003 campaign were considered

### 3.1 Model development

For this issue the Portuguese and the literature values are plotted as is in Figure 1, along with the best fit that was a second-degree polynomial function, being the correlation parameter ($R^2$), 0.5613 for all values.

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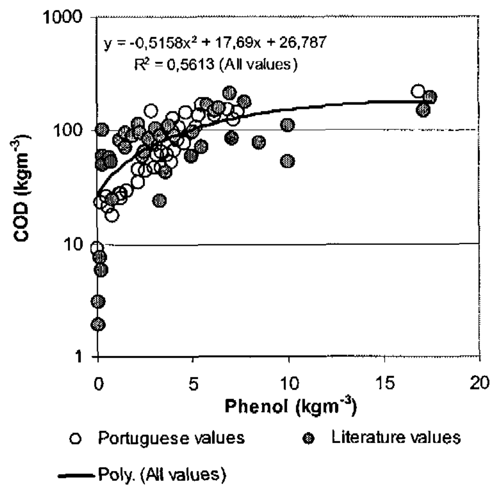


Figure 1:Second-degree polynomial function applied to all values

As the large number of points cannot be readily distinguished from one another, the values were ordered ascending for phenol concentrations and average values for fixed intervals of phenol and COD were determined and plotted in Figure 2.

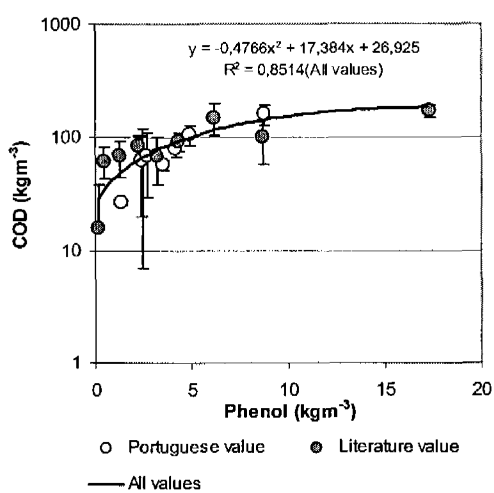


Figure 2:Second-degree polynomial applied to average values

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Bearing in mind the application of the model to several OMW in a collective OMW treatment plant, the model applied to average values is preferable to be used. For average values the same second-degree polynomial function fitted and the $R^2$ increased to 0.8514 for all values.

The low frequency of phenol values together with the absence of values in some intervals for high phenol concentration, led us to represent the model until the phenol concentration of 8 $kgm^{-3}$, as is presented in Figure 4.

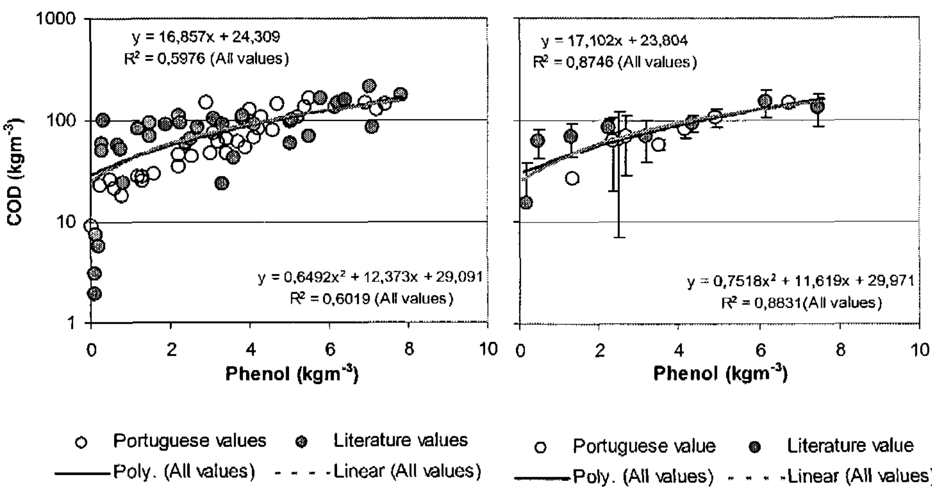


Figure 3: Linear and Second-degree polynomial functions applied to A) all values B) all average values; until 8 $kgm^{-3}$ for phenol concentration.

The main feature in these representations is that for this range both second degree polynomial and linear functions fit well and the $R^2$ is very similar for both of them, however the increase of phenol content in OMW the COD doesn't follow this increase and gets to a saturation point as was demonstrated by the polynomial function for high phenol content (Figures1 and 2). Although linearity is observed for low phenol concentrations, the second-degree polynomial model is preferable because it fits well for high and low concentrations.

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# 4 Conclusions and future work

Despite the fact that the OMW characteristics were obtained from different countries, with different olive varieties, from different years, from mills with different extraction processes and were obtained using different techniques in different laboratories, a good correlation between COD and phenols is found using second-degree polynomial function.
The model developed may be useful not only for OMW treatment plant conception but also for monitoring it as allows less time consumption on analytical work. When considering a collective OMW treatment plant is plausible to use the model developed from the overall average values. In the future, the models will be completed with more OMW characterization values and their optimization will be pursued.

# References


[1] Hamdi, M., Future prospects and constraints of olive mill wastewaters use and treatment: A review. *Bioprocess Engineering*, **8**:209-214, 1993.

[2] Yesilada O., Fiskin K., Yesilada E., The use of white rot fungus *Funalia trogii (Malatya)* for the decolourization and phenol removal from olive mill wastewater. *Environmental Technology*, **16**:95-100, 1995.

[3] Paredes C., Bernal M., Roig A., Cegarra J., Sánchez-Monedero M., Influence of the bulking agent on the degradation of olive mill wastewater sludge during composting. *International Biodeterioration & Biodegradation*, **38**:205-210, 1996.

[4] Lopez M., Ramos-Cormenzana A., Xanthan production from olive-mill wastewaters. *International Biodeterioration & Biodegradation,* **38**:263-270, 1996.

[5] Cabrera F., López R., Martinez-Bordiú A., Dupuy de Lome E., Murillo J.M., Land treatment of olive oil mill wastewater. *International Biodeterioration & Biodegradation*, **38**:215-225,1996.

[6] Fiestas Ros de Ursinos J., Borja-Padilla R., Biomethanization. *International Biodeterioration & Biodegradation,* **38**:145-153, 1996.

[7] Chung K., Wei C., Johnson M., Are tannins a double-edged sword in biology and health?. *Trends in Food Science and Technology*, **9**:168-175, 1998.

[8] Ranalli A., El efluente de las almazaras: propuestas para su utilización y depuración con referencias a la normativa italiana (primera parte). *Olivae*, **37**:30-39, 1991.

[9] Alba, J. *Nuevas tecnologías para la obtención del aceite de oliva*, Fruticultura Profesional (Suplemento), **62**, 85-95, 1994.

[10] Passarinho P., Destoxificação de águas ruças, PhD Thesis, Instituto Superior Técnico, Universidade Técnica de Lisboa, 2002

[11] Benitez, F.J., Beltran-Heredia, J., Torregrosa, J. & Dominguez, J.R. *Aerobic treatment of black olive oil wastewater and the effect of an ozonation stage,* Bioprocess Engineering, **20**, 355-361, 1999.

[12] Saviozzi, A., Levi-Minzi, R., Riffaldi, R. & Lupetti, A. *Effeti dello spandimento di acque di vegetacione sul terreno agrario*, Agrochimica, **35(1-3)**, 135-147, 1991.

[13] Hamdi, M. *Thermoacid precipitation of darkly coloured polyphenols of olive mill wastewater*, Environmental Technology, **14**, 495-500, 1993.

[14] Hamdi, M. *Future prospects and constrains of olive mill wastewater use and treatment. A review,* Bioprocess Engineering , **8**, 209-214, 1993.

[15] APHA (American Public Health Association), *Standard Methods for the examination of water and wastewater*, edited by Eaton A., Clesceri L., Greenberg A., 19th edition, Washington, D.C., 1995.

[16] Durán M, Padilla B, Martin A, Fiestas Ros de Ursinos A. & Mendoza J, Biodegradación de los compuestos fenólicos presentes en el alpechin. *Grasas Y Aceites*, **42** (4):271-276, 1991.

[17] Borja, R., Martín, A., Alonso, V., García, I. & Banks, C.J. Influence of different aerobic pretreatments on the kinetics of anaerobic digestion of olive mill wastewater, *Wat. Res.*, **29**, 489-495, 1995.

[18] Borja Padilla, R., Martín Martín, A., Maestro Durán, R., Alba Mendonza, J. & Fiestas Ros de Ursinos,J. A. Cinética del proceso de depuración anaerobia de alpechín previamente biotratado via anaeróbia, *Grasas y Aceites*, **42**, 194-210, 1991.

[19] Maestro Durán, R., Borja Padilla, R., Martín Martín, A., Fiestas Ros de Ursinos, J.A. & Alba Mendonza, J. Biodegradación de los compuestos fenólicos presentes en el alpechín, *Grasas y Aceites*, **42**, 271-276, 1991.

[20] Amirante, P. & Montervino, A. Depuración por concentración térmica de los efluentes de las almanzares y compostización del concentrado. Una experiencia en Apulia, *OLIVAE*, **63**, 64-68, 1996.

[21] Borja, R., Alba, J., Garrido, S.E., Martinez, L., García, M.P., Incerti, C. & Ramos-Cormenzana, *A.* Comparative study of anaerobic digestion of olive mill wastewater (OMW) and OMW previously fermented with Aspergillus terreus. *Bioprocess Engineering*, **13**, 317-322, 1995.

[22] Borja Padilla, R., Martín Martín, A., Durán Barrantes, M.M. & Maestro Durán, R. Estudio cinético comparativo del proceso de digestión anaerobia del alpechín en los intervalos mesofílicos y termofílicos de temperatura. *Grasas y Aceites*, **43**, 341-346, 1992.

[23] Rivas, F.J., Béltran, F.J., Gimeno, O. & Frades, J. Joint aerobic biodegradation of wastewater from table olive manufacturing industries and urban wastewater, *Bioprocess Engineering*, **23**, 283-286, 2000.

[24] García García, I., Jiménez Peña, P.R., Bonilla Venceslada, J.L., Martín Martín, A., Martín Santos, M.A. & Ramos Gómez, E. Removal of phenol compounds from olive mill wastewater using Phanerochaete chrysosporium, Aspergillus niger, Arpergillus terreus and Geotrichum candidum, *Process Biochemistry*, **35**, 751-758, 2000.

[25] Borja Padilla, R., Alba Mendonza, J. & Durán Barrantes, M.C. Influencia de los coadyuvantes tecnológicos utilizados en el proceso de elaboración de aceite de oliva sobre la cinética del proceso de digestión anaerobia del alpechín, *Grasas y Aceites*, **43**, 204-211, 1992.

[26] Borja Padilla, R., Alba Mendonza, J. & Luque González, M. Depuración aerobia de los efluentes resultantes del proceso de biometanización del alpechín, *Grasas y Aceites*, **43**, 20-25, 1992.

[27] Heredia Alonso, J.B., Torregrosa Antón J., García Rodríguez, J. & Domínguez Vargas, J.R. Tratamiento con ozono de las aguas residuales de almazara. *Grasas y Aceites*, **51**, 301-306, 2000.

[28] Borja Padilla, R., Martín Martín, A., Durán Barrantes, M.M. Estudio cinético del proceso de biometanización de alpechín de almanzara clásica previamente sometido a tratamiento aerobio con Geotrichum Candida. *Grasas y Aceites*, **43**, 82-86, 1992.

[29] Javier Benitez, F., Beltrán-Heredia, J., Torregrosa, J. & Acero, J.L. Treatment of wastewaters from olive oil mills by UV radiation and by combined ozone-UV radiation, *Toxicological and Environmental Chemistry*, **61(1-4)**, 173-185, 1997.

[30] Heredia Alonso, J.B., Torregrosa Antón, J., García Rodríguez, J., Ramos Viseas, M.P. & Domínguez Vargas, J.R. Tratamiento biológico aerobio de alpechín depurado previamente con ozono, *Grasas y Aceites*, **51**, 332-339, 2000.

[31] Borja Padilla, R., Martín Martín, A. & Fiestas Ros de Ursinos, J.A. Estudio cinético de la depuración anaerobia del alpechín en presencia de diversos soportes para la inmovilización de los microorganismos responsables del proceso, *Grasas y Aceites*, **41**, 347-356, 1990.

[32] Aktas, E.S., Imre, S., Ersoy, L. Characterization and Lime Treatment of olive mill wastewater, *Wat. Res.*, **9**, 2336-2340, 2001.

[33] Giovacchino, L.D., Mascolo, A. & Seghetti, L. Sulle caratteristiche delle acque di vegetacione delle olive, Nota II, *La Rivista Della Sostanza Grasse*, **65**, 481-487, 1988.

[34] Bonari, E., Macchia, M., Angelini, L.G. & Ceccarini, L. The waste waters from olive oil extraction: their influence on germinative characteristics of somo cultivated and weed species, *Agricoltura Mediterranea*, **123**, 273-280, 1993.

[35] Beccari, M., Bonemazzi, F., Majone, M. & Riccardi, C. (1996) Interactions between acidogenesis and methanogenesis in the anaerobic treatment of olive oil mill effluents, *Wat. Res.*, **30**, 183-189, 1996.

[36] Catalano, L., Franco, I., Nobili, M. & Leita, L. Polyphenols in olive mill waste waters and their depuration plant effluents: a comparison of the Folin-Ciocalteau and HPLC methods. *Agrochimica,* **43(5-6)**, 193-205,1999.

[37] Rannali, A. Fermenti selezionati nel trattamento biologicoi delle acque reflue dei frantoi, *Industrie Alimentari*, **28**, 141-148, 1989.

[38] Fiestas, J.A., Martín, A. & Borja, R. Influence of immobilization supports on the kinetic constant of anaerobic purification of olive mill wastewater, *Biological Wastes*, **33**, 131-142, 1990.

[39] Becari, M., Caricci, G., Majone, M. & Torrisi, L. Role of lipids and phenolic compounds in the anaerobic treatment of olive oil mill effluents, *Environmental Technology*, **20**, 105-110, 1999.

[40] Fernandéz, A.G. & García, P.G. Purificación de aguas residuales ricas en polifenoles: aplicación de la oxidación húmeda a los efluentes acuosos derivados de las industrias olivareras,*Grasas y Aceites*, **40**, 291-295, 1989.

[41] Rivas, F.J., Béltran, F.J., Gimeno, O. & Frades, J. Treatment of olive oil mill wastewater by Fenton's reagent, *J. Agric. Food Chem.*, **49**, 1873-1880, 2001.

[42] Hamdi, M. & Garcia, J.L. Comparison between anaerobic filter and anaerobic contact process for fermented olive mill wastewater, *Bioresource Technology*, **8**, 23-29, 1991.

[43] Martinez Nieto, L., Garrido Hoyos, S.E., Camacho Rubio, F., Garcia Pareja, M.P. & Ramos Cormenzana, A. The biological purification of waste products from olive oil extraction, *Bioresource Technology*, **43**,215-219, 1993.

[44] García García, P., Fernández, A.G., Chakman, A., Lemonier, J.P., Overende, R.P. & Chornet, E. Aplicación de la tecnología jet-reactor a la oxidación húmeda de las aguas residuales de las industrias derivadas del olivo, *Grasas y Aceites*, **41**, 158-162, 1990.

[45] Israilides, C.J., Vlyssides, A.G., Mourafeti, V.N. & Karvouni, G. Olive oil wastewater treatment with the use of an electrolysis system, *Bioresource Technology*, **61**, 163-170, 1997.

[46] Sayadi, S. & Ellouz, R. Screening of white rot fungi for the treatment of olive mill wastewaters, *J. Chem. Tech. Biotechnology*, **57**, 141-146, 1993.

[47] Project Improlive (FAIR CT96-1420) – Final Report – Annex A2, in www.nf-2000.org/publications/f1420fin.pdf

[48] Davies L., Valorização da água ruça como fertilizante orgânico por recurso a polímeros superabsorventes, MSc Thesis, Instituto Superior Técnico, Universidade Técnica de Lisboa, 2002