Olive Mill Wastewater Transformation From Pollutant To Sun Protection Paste CORFU 2022 Conference

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Olive mill wastewater (OMWW) is one of the by-products of olive oil production process. It is produced world wide in excess of 3 x 10^7 m^3 every year. OMWW is claimed to be one of the most polluting effluent with negative impact, to soil and aquatic environments, due to its compositions of polyphenols (up to 30 g/l), biological oxygen demand (BOD) and chemical oxygen demand (COD) levels that may be as high as 100 and 200 g/l, respectively and low pH (4.2-5.2) (Mekki, 2007). This is why a number of physical, physico-chemical and even biological strategies have been proposed for the treatment of OMWW (Ochando-Pulido, 2017, Elkacmi, 2019). Besides being costly, these techniques cause biodegradation or destruction of the phenolic fraction of OMWW, thus resulting in a loss of valuable, functionally active, exploitable and green compounds. For long time, OMWW has been regarded as a hazardous waste with an economic burden on the olive oil industry. However in the last decade, this view has changed and OMWW is now being recognized as a potential low-cost starting material rich in natural antioxidants, antibacterial, antiviral, and antifungal compounds (Azaizeh, 2012; Obied, 2005). Polyphenols and phenolic glycosides in OMWW (Fig 1) are potentially sunscreen compounds, effective for protecting the skin from the solar UV radiation (290 nm - 400 nm, UVB and UVA rays), indicated by its promising values of the Sun Protection Factor (SPF) and critical wavelength (CW > 370 nm, reflection of a broad spectrum). Commercially available sunscreens are mainly a mixture of synthetic chemicals, some of which have been removed from the list of the FDA-approved substances due to side effects (Kyu, 2017). Our research focuses on the transformation of OMWW from pollutant to an organic alternative for the preparation of a natural sunscreen product.

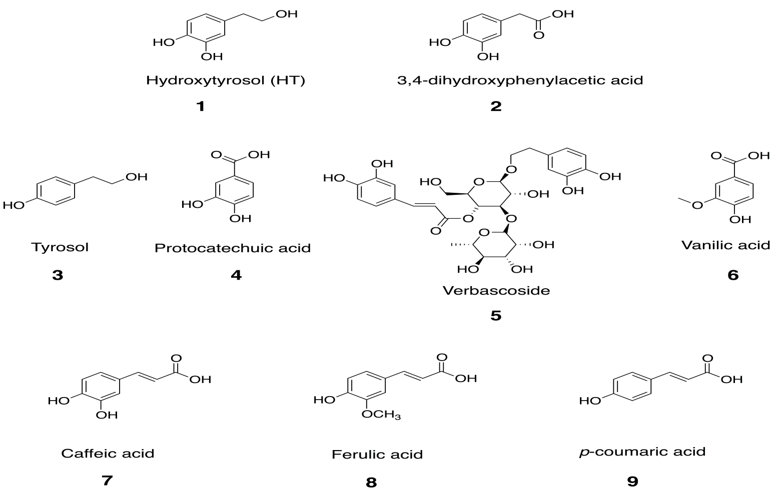


Fig 1: Structures of some bioactive phenols and phenolic glycosides in OMWW.

The objective of the proposed study was to produce, optimize and characterize an organic extract from OMWW in order to obtain a prototype product composed of natural materials with high activity to protect the skin from UV rays.

Fractionation Guided Assay (FGA) (Azaizeh, 2012) was used to study the chemical content of the most promising polyphenol in the so called Antisolvent fraction, a fraction that was obtained from treated OMWW. This method utilizes the polar properties of the various polyphenols, by using different solvents with increasing polarity for the extraction process, solvents like chloroform ($CHCl_3$) and Ethylacetate (EtOAc). Special resins were used to isolate and absorb phenols and glycosides from the Antisolvent. Extraction of the substances that were adsorbed to the resins was carried out using alcohols and water. In this study, we follow the *in vitro* method of Mansur (Mansur, 1986), to determine the absorption characteristics (SPF) of the phenolic fractions utilizing

UV spectrophotometry, and COLIPA (The European Cosmetic, Toiletry and Perfumery Association), to determine *in vitro* measures of UVA wavelength or the Critical Wavelength (CW).

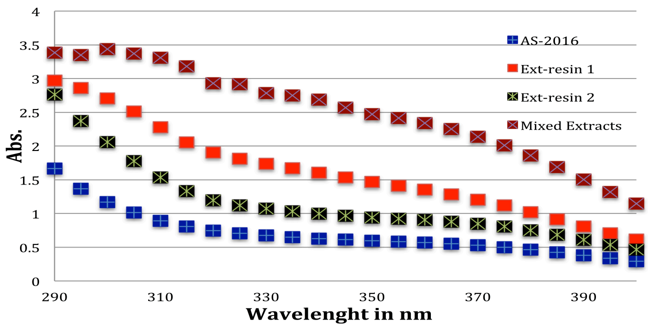
Results:

- ❖ Fractionation Guided Assay (FGA) yielded $CHCl_3$ Ext. and EtOAc 3^{rd} Ext. fractions with improved values of SPF but CW values were dropped (Table 1).
- ❖ The mixed fraction obtained from the adsorbent resins process (Mixed Ext 1+2) showed a very high SPF > 30 and CW >380 compared to SPF of the original Antisolvent fraction (Fig 2 & Table 1). In our calculations we found that each liter of OMWW can get 10 grams of natural material with high activity to protect the skin from the sun's rays.

Table 1: pH, SPF and CW values of the fractions obtained from FGA method and Resin's extracts.

Sample 800 ppm	pH± 3std	SPF± 3std	CW± 3std
Antisolvent	5.28± 0.15	11.27± 0.70	378± 1.15
Chloroform Ext. from FGA	ND	11.51±1.32	347±2.56
EtOAc 3^{rd} Ext. from FGA	ND	24.87±2.87	350±3.25
Ext-resin 1	4.41± 0.18	26.83± 2.30	377± 0.57
Ext-resin 2	4.28± 0.06	18.78± 0.51	377± 1.10
Mixed Ext 1+2 from	4.3± 0.09	31.21± 2.32	382± 1.50

Fig 2: UV absorption of resin's extracts 1, 2 and mixed in comparison to Antisolvent



Conclusions:

- ❖ Polyphenols in OMWW are responsible for the SPF values and active against UVB radiation, while phenolic glycosides in OMWW are active against UVA radiation and responsible for the CW values.
- ❖ The fractions obtained from FGA process are active against UVB rays only and they could no longer be considered as broad spectrum.
- ❖ Adsorbent resins were a breakthrough in this research because they could selectively adsorb phenols and phenolic glycosides from Antisolvent fraction, with impressive values (SPF > 30 and CW > 380).

References:

- Azaizeh, H., Halahleh, F., Najami, N., Brunner, D., Faulstich, M., and Tafesh, A. **2012**. Antioxidant activity of phenolic fractions in olive mill wastewater. *Food Chemistry* 134:2226-2234.
- Elkacmi, R., Bennajah, M., Advanced oxidation technologies for the treatment and detoxification of olive mill wastewater: a general review. **2019**. *Journal of Water Reuse and Desalination*. 463-505.
- Kyu-Bong, K., Young-Woo, K., Seong-Kwang, L., Tae-Hyun R., Du-Yeon, B., Seul-Min, C., Duck-Soo L., Byung-Mu L. **2017**. (2017) Risk assessment of zinc oxide, a cosmetic ingredient used as a UV filter of sunscreens. *Journal of Toxicology and Environmental Health, Part B* 20:3, pages 155-182.
- Mansur, J. S.; Breder, M. N. R.; Mansur, M. C. A.; Azulay, R. D. **1986**. Determinação do fator de proteção solar por espectrofotometria. *An. Bras. Dermatol.,* Rio de Janeiro, v. 61, p. 121-124.
- Mekki, A., Dhouib, A., Sayadi, S. **2007**. Polyphenols dynamics and phytotoxicity in a soil amended by olive mill wastewaters. *Journal of Environmental Management*. Volume 84, Issue 2, pages 134-140.
- Obied, H.K., Allen, M.S., Bedgood, D.R., Prenzler, P.D., Robards, K., Stockmann, R. **2005**: Bioactivity and analysis of bio-phenols recovered from olive mill waste. *J. Agric. Food Chem.* 53, 823–837.
- Ochando-Pulido, M., Pimentel-Moral, S., Verardo, V., Martinez-Ferez, A., A focus on advanced physico-chemical processes for olive mill wastewater treatment, *Sep. Purif. Technol*. 179 (2017) 161.

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