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Polyphenolic characterization of olive mill wastewaters, coming from Italian and Greek olive cultivars, after membrane technology

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ABSTRACT

The aim of this work was to recover and identify the phenolic compounds from olive mill wastewater (OMWW) samples belonging to two Italian (*Cellina* and *Coratina*) and three Greek (*Asprolia*, *Lianolia* and *Koroneiki*) olive cultivars. The OMWWs were processed using membrane technologies to obtain three fractions: microfiltrate (MF), ultrafiltrate (UF) and nanofiltrate (NF). These steps allowed purifying the OMWWs in order to achieve fractions with different profile and concentrations of polyphenols. In particular, the amount of polyphenols ranged from 2456 μg/mL to 5284 μg/mL in MF; from 1404 μg/mL to 3065 μg/mL in UF and from 373 μg/mL to 1583 μg/mL in NF. Among the cultivars analyzed *Coratina* followed by *Lianolia* showed the highest amount of verbascoside (VB) (308 μg/mL in *Coratina* versus 145 μg/mL in *Lianolia*, respectively) in UF fractions.
Furthermore, UF fractions that showed adequate purification degree and polyphenol enrichments, were used for the identification of the phenolic compounds by liquid chromatography/diode array detection/electrospray ion trap tandem mass spectrometry (LC/DAD/ESI–MS^n) analysis. Twenty three compounds, belonging to the following classes of constituents: secoiridoids and their derivatives, phenyl alcohols, phenolic acid and derivatives, and flavonoids, were identified in almost all the UF fractions of the different cultivars. Finally, differences were observed among the cultivars regarding the presence of elenolic acid derivatives, hydroxytyrosol glucoside, and β-hydroxyverbascoside diastereoisomers. The results obtained showed that OMWW can be considered as raw material for the isolation of valuable bioactive compounds able to be used in food, cosmetic and pharmaceutical industry.

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1. Introduction

Olive mill wastewaters (OMWWs) are seasonally generated effluents in the olive oil extraction industry operating in three-phase mode. This agro-industrial waste is produced in huge amounts (6–7 million tons/year) and it is characterized by a strong undesirable smell, an intense brown to dark color, a pH between 3 and 6 and a highly diverse organic pollutant load (Ginos, Manios, & Mantzavinos, 2006). OMWW, a complex medium containing polyphenols of different molecular masses, is produced in Mediterranean countries. This waste is claimed to be one of the most polluting effluents among those produced by the agro-food industries because of its high polluting load and high toxicity to plants, bacteria, and aquatic organisms, owing to its contents (14–15%) of organic substances and phenols (up to 10 g/L). These latter compounds, characterized by high specific chemical oxygen demand (COD) and resistance to biodegradation, are responsible for its black color, depending on their state of degradation and the olives they come from (Capasso, Cristinzio, Evidente, & Scognamiglio, 1992).

For a long time, OMWW has been regarded as hazardous waste with negative impact on the environment and an economic burden on the olive oil industry. Their phytotoxicity is mainly attributed to the high phenolic content (0.5–24 g/L), that, on the other hand, are antioxidant compounds with potential health-benefits (Obied et al., 2005a). In light of these findings, the OMWWs are recognized as a potential low-cost starting material rich in bioactive compounds, that can be extracted and applied as natural antioxidants for the food and pharmaceutical industries.

A typical phenolic substance identified in olive fruit is oleuropein, a secoiridoid glucoside that is absent in OMWW due to enzymatic hydrolysis during olive oil extraction, resulting in the formation of side products such as hydroxytyrosol and elenolic acid. Other phenolics identified in OMWW are verbascoside, tyrosol, catechol, 4-methylcatechol, p-hydroxybenzoic acid, vanillic acid, syringic acid, and gallic acid (Capasso et al., 1992; Visioli et al., 1999).

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The most abundant biophenols occurring in OMWW are hydroxytyrosol followed by tyrosol. In particular, hydroxytyrosol is the most potent antioxidant phenolic compound occurring in olive oil (Nissiotis & Tasioula-Margari, 2002), and numerous studies have focused on its many other health-beneficial effects (Obied, Allen, Bedgood, Prenzler, Robards, et al., 2005a) among them in inhibition of low-density lipoprotein oxidation (EFSA, 2011). Moreover, the good solubility of hydroxytyrosol in oil and aqueous media and its high bioavailability allow its useful application in multi-component foods, encouraging prospects in commercialization of it in functional foods and natural cosmetics (Bouzid et al., 2005). However, the phenolic composition of OMWW varies strongly between studies, as it is characterized by a significant complexity (Bianco et al., 2003; Obied, Allen, Bedgood, Prenzler, & Robards, 2005b; Obied, Bedgood, Prenzler, & Robards, 2007) and many compounds are recently identified (Cardoso, Falcão, Peres, & Domingues, 2011). Indeed, hydroxytyrosol acyclodihydroelenolate and p-coumaroyl-6′-secologanoside (comselogoside) were recently identified in OMWW and were examined for their antioxidant and antiproliferative activities (Obied, Karuso, Prenzler, & Robards, 2007; Obied, Prenzler, Konczak, Rehman, & Robards, 2009).

Traditionally, to isolate and recover polyphenols from matrix such as OMWW, liquid–liquid extraction is employed. This method utilized a large amount of solvent that has a negative impact for both health and environment. Membrane separation has become a promising technology with several advantages: low power consumption, water-reuse and by-products recovery, stabilization of effluent, absence of organic solvents. Some studies are already carried on, and the OMWW may be treated efficiently by using microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and/or reverse osmosis (RO), to obtain a permeate fraction which can be discharged in aquatic systems according to national or EU regulations or to be used for irrigation (Paraskeva, Papadakis, Tsarouchi, Kanellopoulou, & Koutsoukos, 2007).

A membrane process for the selective fractionation and total recovery of polyphenols, water and organic substances from OMWW was also proposed by Russo (2007). It was based on the preliminary MF of the OMWW, followed by two UF steps realized with 6 kDa and 1 kDa membranes, respectively, and a final RO treatment. The RO retentate, containing enriched and purified low molecular weight polyphenols, was proposed for food, pharmaceutical or cosmetic industries, while MF and UF retentates can be used as fertilizers or in the production of biogas in anaerobic reactors (Garcia-Castello, Cassano, Criscuoli, Conidi, & Orioli, 2010).

The current investigation aimed at identifying the phenolic compounds in the OMWW samples belonging to different Italian and Greek olive cultivars. The OMWWs were processed using membrane technologies in order to investigate the impact of different cultivar in the phenolic profile of the fractions. The fractions were quantified regarding the main polyphenols present by HPLC analysis and were deeper studied, using LC/DAD/ESI–MS^n analysis, in order to elucidate the identity of phenolic components that could also be a characteristic of each OMWW coming from different olive variety.

2. Material and methods

2.1. Chemicals

Extraction and chromatography solvents, methanol (MeOH), acetonitrile (MeCN), glacial acetic acid (AcOH), and ethanol (EtOH), were of certified high-performance liquid chromatography (HPLC) grade, and pure standard of hydroxytyrosol (HT), tyrosol (Tyr), caffeic acid (CAA), coumaric acid (CUA), verbascoside (VB), isoverbascoside (IsoVB), were obtained from PhytoLab GmbH & Co. KG (Vestenbergsgreuth, Germany). Folin–Ciocalteu reagent was purchased from Sigma-Aldrich (Milano, Italy).

2.2. OMWW samples

All the OMWWs utilized in this study raised from mills that used a three-phase system. Five fresh OMWW samples (~30 L), among them two Italian cultivars: *Cellina* and *Coratina* obtained respectively from: Cooperativa Agricola Nuova Generazione Srl (Martano, Lecce, Italy) and Oleificio Di Molfetta (Bisceglie, Bari, Italy) from Apulia region mills and three Greek cultivars, *Koroneiki*, *Lianolia* and *Asprolia* (all organic), collected from Greek mills.

Italian samples were processed within 4 days after olive oil production, Greek samples were collected and shipped 2 days later, so were processed within 7 days after olive oil production. Acetic acid was added to pH 5, in the samples, to avoid phenolic compounds oxidation.

The raw material was firstly sieved through a test sieve with 425 μm as porosity. This process allows the removal of large particles and colloids from the OMWW before the microfiltration process. With this procedure, all traces of oil, leaves, seeds, which could then cause problems of clogging of the membranes, are eliminated.

2.3. Filtration units (MF, UF and NF)

The raw OMWWs coming from the five different cultivars were processed with a laboratory-scale system (Permeare s.r.l., Milano, Italy) present in the laboratory of ISPA-CNR of Bari. This system, that utilizes a continuous parallel flow, is consisting of two different units: Pilot Plant N022/N256C and N021/N256C (Figs. 1 and 2).

The first (Fig. 1), filled by external tank, performed microfiltration (MF) process with continuous recirculation of the sample and by using a ceramic membranes, PERMAPORE EOV 1046, with cut-off of about ~100,000 Da (membrane porosity 0.1 μm). The volume which can be processed daily will be limited by the substances contained in the fluid. In general, it is possible to treat from 200 up to 2000 L per day. This unit can support transmembrane pressure (differences between the inlet pressure and outlet pressure) up to 6 bars, at 25 °C.

The Pilot Plant N021/N256C unit (Fig. 2) is composed of the following sections: process tank (5–10 L), high pressure pump, pressure vessel for membrane housing. The unit can support operating pressure up to 75 bar and operating temperatures that ranges between 5 °C as minimum and 60 °C as maximum. Cooling device is supplied for eventually cooling the solution in order to maintain an acceptable temperature during process. Furthermore, the maximum size of eventual suspended solids in the feed solution should be less than 3 μm. Pressure vessel for membrane is composed of three AISI316 stainless steel parts: testate, end cup and body for membrane housing with 5 cm of diameter and 30.5 cm of length.

This unit performed ultrafiltration (UF) and nanofiltration (NF) processes, utilizing polymeric membranes at different porosities. For UF, was employed a polyethersulfone membrane, PERMAPORE DGU 1812 BS EM with cut-off of 5000 Da, instead for NF, the filtration was performed using a polyamide membrane, PERMAPORE AEN 1812 BS with cut-off of 200 Da. After utilization, the membranes were washed with alkaline detergent following the manufacture instructions because the OMWW can provoke the membrane clogging during the process. All the membrane utilized act as a molecular sieve without any chemical interactions with the matrix. In addition, the ceramic membrane was utilized for MF because they are chemically stable and mechanically and biologically inert. In addition, they are available only as limited range of porosity and, for this reason, mainly utilized for microfiltration.

2.4. Determination of total phenolic content

The total phenolic content of the OMWW and fractions was determined using a modified Folin–Ciocalteu spectrophotometric method 100 μL of properly diluted samples, calibration solutions or blank were pipetted into separate test tubes and 100 μL of F–C reagent were added to each. The mixture was mixed well and was allowed to equilibrate.

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