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Recovery of antioxidants from olive mill wastewaters: A viable solution that promotes their overall sustainable management

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ABSTRACT

Olive mill wastewaters (OMW) are rich in water-soluble polyphenolic compounds that show remarkable antioxidant properties. In this work, the recovery yield of compounds, such as hydroxytyrosol and tyrosol, as well as total phenols (TPh) from real OMW was investigated. Antioxidants were recovered by means of liquid–liquid solvent extraction. For this purpose, a laboratory-scale pilot unit was established and the effect of various organic solvents, namely ethyl acetate, diethyl ether and a mixture of chloroform/isopropyl alcohol, on process efficiency was investigated. It was found that the performance of the three extraction systems decreased in the order: ethyl acetate > chloroform/isopropanol > diethyl ether, in terms of their antioxidant recovery yield. It was estimated that treatment of 1 m^3 OMW with ethyl acetate could provide 0.247 kg hydroxytyrosol, 0.062 kg tyrosol and 3.44 kg of TPh. Furthermore, the environmental footprint of the whole liquid–liquid extraction system was estimated by means of the life cycle assessment (LCA) methodology to provide the best available and most sustainable extraction technique. From an environmental perspective, it was found that ethyl acetate and diethyl ether had similar environmental impacts. Specifically, for the production of 1 g hydroxytyrosol, tyrosol or TPh, 13.3, 53.1 or 0.949 kg CO_2 equivalent would be released to the atmosphere, respectively. On the other hand, the chloroform/isopropyl alcohol mixture had detrimental effects onto ecosystems, human health and fossil fuels resources. In total, ethyl acetate yields low environmental impacts and high antioxidant recovery yield and thus it can be considered as the best solution, both from the environmental and technical point of view. Three alternative scenarios to improve the recovery performance and boost the sustainability of the ethyl acetate extraction system were also investigated and their total environmental impacts were estimated. It was found that with small process modifications the environmental impacts could be reduced by 29%, thus achieving a more sustainable antioxidants recovery process.

1. Introduction

Nowadays, there are growing concerns about a variety of environmental issues that accompany OMW and its effective treatment. OMW is a by-product of olive oil production and is characterized by seasonal large volumes and high organic loads (Chatzisymeon et al., 2009a; Gotsi et al., 2005). However, if properly managed, it is an inexpensive and convenient source of natural antioxidants, mainly due to its high polyphenolic content (Niaounakis and Halvadakis, 2006). Polyphenols are water soluble organic compounds and, therefore, they are found in abundance in OMW (Obied et al., 2005). So far, more than forty phenols have been identified in OMW with hydroxytyrosol being the main natural polyphenolic compound due to its high bio-antioxidant capacity (Tsimidou et al., 1992). In general, all polyphenolic compounds exhibit potential antioxidant properties; the way they act is through elimination of free radicals in cells, thus providing protection against oxidative stress in biomolecules like proteins, lipids and DNA (Boskou, 2006). Moreover, as natural substances their high potential antioxidant properties are reflected in their high market price, and their great demand in the cosmetic, pharmaceutical and food industry. Among them, hydroxytyrosol is in abundance in OMW and it is considered to be the most active antioxidant (Gordon et al., 2001). On the other hand, if polyphenols are left without any further treatment into the

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OMW, they are gradually oxidized and/or polymerized rendering OMW highly toxic and recalcitrant (Chatzisymeon et al., 2009b; Celano et al., 2008; Martirani et al., 1996). Hence, the recovery of the polyphenolic content of OMW not only provides economic benefits but it also makes OMW less toxic and easier to treat, thus promoting the overall sustainability of the OMW management (Federici et al., 2009).

Until now, several methods for polyphenols recovery have been suggested, including solvent extraction (Bertin et al., 2011; De Leonardis et al., 2007; Grizis et al., 2003; Lesage-Meessen et al., 2001), adsorption onto resins (Scoma et al., 2011; Agalias et al., 2007), supercritical fluid extraction (Lafka et al., 2011), selective concentration by ultrafiltration (Galanakis et al., 2010; Lin and Juang, 2009) and integrated membrane systems (El-Abbassi et al., 2011; Garcia-Castello et al., 2010; El-Abbassi et al., 2009). Moreover, interesting alternative processes include the use of microparticles (Puoci et al., 2012) and biofilters (Ena et al., 2012), cloud point extraction (Gortzi et al., 2008) and ultrasound-assisted extraction (Klen and Vodopivec, 2011). Among them, liquid–liquid solvent extraction is an easy to operate technique thus, it could be applied even in small, family-owned olive oil mills that exist in most Mediterranean countries, including Greece. The concept has been very recently demonstrated by Sannino et al. (2013) who proposed liquid–liquid extraction using ethyl acetate followed by chromatographic fractionation for the production, at small-scale, of high grade, purified hydroxytyrosol. Furthermore, many researchers found that the most promising solvents for liquid–liquid extraction were diethyl ether, ethyl acetate and a mixture of chloroform with isopropyl alcohol (De Leonardis, 2007; Grizis et al., 2003; Lesage-Meessen et al., 2001). Due to the different polar properties of the target phenolic compounds typically found in OMW, such as hydroxytyrosol which is the main constituent in OMW exhibiting amphiphilic properties, different solvent systems were chosen to assess their selectivity to extract the target compounds.

At this point, it is of great significance to mention that the sustainability of the aforementioned polyphenols recovery techniques has never been studied before. Besides, the environmental footprint of any process can reveal important information regarding the scaling-up of the process and enhance its overall sustainability by introducing alternative “green” scenarios.

Life cycle assessment (LCA) is the concept of analyzing and quantifying the environmental impacts of any given product, process, service or activity throughout its lifespan (Tsoutsos et al., 2010). It is also known as cradle-to-grave assessment due to the fact that one has to take into account all the stages of a product’s or service life, which start from the extraction of resource inputs and ends to the eventual disposal of the product or its waste (ISO 14040, 2006). The main benefit of LCA is its capability to link the environmental loads of any product, process, service or activity with its mass and energy flows (Kniel et al., 1996).

The aim of this work was to investigate the recovery yield of various polyphenolic compounds such as hydroxytyrosol and tyrosol, as well as TPh from real OMW by means of solvent extraction. This information was then employed to estimate the environmental footprint of the process by means of LCA and to provide the best available and sustainable extraction technique. For this purpose, a laboratory-scale pilot unit was setup and the type of the organic solvent was investigated.

2. Materials and methods

2.1. Materials

Ethyl acetate ($C_4H_8O_2$), diethyl ether ($C_4H_{10}O$), chloroform ($CHCl_3$) and isopropyl alcohol (C_3H_8O) were purchased from Merck (analytical grade) and used as extraction solvents. Chloroform and isopropyl alcohol were mixed at a 7:3 (v/v) ratio according to the work of Grizis et al. (2003).

Hydroxytyrosol ($C_8H_{10}O_3$, ≥90%), tyrosol ($C_8H_{10}O_2$, ≥95%) and oleuropein ($C_{25}H_{32}O_{13}$, ≥98%) were purchased from Extrasynthese Chemicals Company. Caffeic (≥98%) and gallic (≥98%) acids were purchased from Sigma Aldrich Company.

A model solution containing 250 mg/L oleuropein, 1000 mg/L tyrosol, 250 mg/L gallic acid, 250 mg/L caffeic acid and 270 mg/L hydroxytyrosol in ultrapure water was prepared to evaluate the ability of liquid–liquid extraction to recover them. It should be noted that the mixture of phenolic compounds was stirred vigorously for one day to ensure complete dissolution. The pH of the synthetic solution was fixed to 5 adding NaOH to match that of the actual OMW. The degree of recovery of the phenolic compounds from the model solution was calculated measuring their concentration at the initial solution and immediately after the liquid–liquid extraction had been completed. The discrepancy between these two values divided by the initial concentration results in the recovery yield of each compound.

The actual effluent was provided by a three-phase, olive oil mill located in Chania, Western Crete, Greece. Its main physicochemical characteristics were as follows: pH = 5, initial soluble COD = 98.6 g/L, total solids = 70.5 g/L, conductivity = 9.25 mS/cm and TPh = 6 g/L, while its color was black-brown.

2.2. Sample pretreatment

Due to the effluent’s high content of solids, the samples were first filtered through mess gauge filters and then centrifuged at 3000 rpm for 20 min to remove most of the solid particles. Afterwards, the supernatant fats and the solid precipitates were removed, and the remaining aqueous phase was subjected to further filtration by means of a 0.45 μm filter. Following this pretreatment, its main properties were: pH = 4.8, initial COD = 90 g/L, total solids = 0.5 g/L, conductivity = 9.5 mS/cm and TPh = 5 g/L.

It should be noted here that filtration is unlikely to be employed as a preconditioning stage for solids removal in actual applications; on the contrary, coagulation-flocculation using inexpensive materials (i.e. ferrous ions) would be a reasonable pretreatment method prior to extraction as has been demonstrated in a recent study of our group (Papaphilippou et al., 2013). Moreover, sample pretreatment is not a trivial procedure since it can influence the efficiency of extraction.

2.3. Recovery procedure

Sample pretreatment was followed by liquid–liquid extraction to efficiently separate the target polyphenols from the OMW. A laboratory-scale pilot unit was setup in order to perform experiments in batch mode operation. The solvent to OMW ratio was always constant at 2:1 v/v (100:50 in mL). Moreover, it is important to note that all runs were carried out at ambient temperature (ca 27 °C) in order to avoid enzymatic degradation and oxidation of polyphenols.

At first, the OMW and the appropriate solvent were loaded in an Erlenmeyer flask with 250 mL headspace, which was then tightly sealed and continuously stirred magnetically for 30 min at 120 rpm. During this step, the polyphenolic compounds were extracted from the aqueous phase (i.e. OMW) to the organic liquid phase (i.e. solvent). Afterwards, this OMW-organic solvent mixture was left to settle in a separate funnel for 30 min. After settling, the two liquid phases were separated and the organic phase was recovered. Recovery was followed by evaporation of the organic liquid phase to dryness. Evaporation took place at 40 °C in a bathwater under