Journal of Environmental Chemical Engineering 4 (2016) 373–384

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Selective isolation of valuable biophenols from olive mill wastewater

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ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form 4 November 2015
Accepted 8 November 2015
Available online 14 November 2015

Keywords:
Olive mill wastewater
Biophenol
Sorption

ABSTRACT

A number of experimental procedures using acidification, sedimentation and membrane filtration process of natural olive mill wastewater (OMW) have been conducted. Valuable biophenols were isolated from multi-compound model and natural OMW under different conditions. Selective uptake of hydroxytyrosol, tyrosol, caffeic acid, oleuropein and luteolin was investigated onto 16 commercial sorbents. AFs resins demonstrated the highest selectivity towards hydroxytyrosol and tyrosol and thus, the extraction of these compounds was evaluated and optimized. Molecularly imprinted polymers (MIPs) were also used to recover the biophenols from OMW. MIPs seem to constitute a promising technology with regard to the recovery of biophenols from OMW. The loading of both hydroxytyrosol and tyrosol was much higher onto AFs resins, while the desorbed ratios were much higher from the MIP. The results demonstrate a possibility to gain individual biophenols and/or particular phenolic subclasses from OMW by combining an effective pretreatment with the different appropriate sorbents in series.

1. Introduction

Olive oil industry produces two main by-products that are an aqueous liquid known as olive mill wastewater (OMW) and a solid waste (pomace) from traditional and three-phase systems or a semisolid waste from two-phase systems [1,2]. Three-phase extraction systems, which are still widely used in olive oil mills, involve the addition of large amounts of water (up to 50 L/100 kg olive paste) resulting in an annual worldwide production of more than 30 million m^3 of OMW. While two-phase systems involve a reduction of OMW volumes but an increased concentration in organic matter [2]. Owing to its seasonality and resistance to degradation, OMW is a major problem facing the development of a sustainable olive oil industry, as it has broad spectrum toxicity and antimicrobial activity leading to the consequent difficult biological degradation, which is essentially due to its phenolic fraction that has high hydrophilicity. However, isolated biologically active phenolics (biophenols) are considered as antioxidants and free radical scavengers [1,2]. OMW has been considered for long time as a problematic wastewater [3]. This has changed to recognize OMW as a potential low-cost material rich in biophenols that can be extracted and applied as natural antioxidants for food and pharmaceutical industries [4–12]. OMW extract may be also useful in cosmetics as anti-aging and anti-wrinkle products [13]. OMW could be considered as an alternative source of natural biophenols [14,15].

OMW is characterized by intensive violet-dark brown up to black color, strong specific olive oil smell and high degree of organic pollution wherein COD is 40–220 g/L and BOD_5 35–110 g/L, TOC 25–45 g/L, pH between 4 and 6, high content of polyphenols (0.5–24 g/L), lipids 0.3-23 g/L, sugar portion of up to 60% of the dry substance, total solids 5.5–17.6% [16], suspended solids (4–17% on average) [17], mineral matter (5–14 g/L), high content of potassium (4 g/L) [16] and high conductivity (11 mS/cm) [18].

The occurrence of specific biophenols in OMW depends on the fruit e.g. cultivar and maturity, irrigation and climatic conditions particularly during olive ripening, growing location (soil), storage time in addition to the processing technique [13,17,19–24]. The amount of antioxidants in olive oil is 1–2% of that available in the fruit. The rest is lost with the wastewater (53%) and the pomace (45%) depending on the extraction system [25].

The phenolic composition of OMW is very different from that of olive fruit [26]. While olives are very rich in secoiridoid glucosides, OMW shows a high concentration of secoiridoid derivates, such as hydroxytyrosol (Fig. 1) [19,23,27,28]. OMW phenolic fraction is characterized by a great complexity [29] and includes a number of simple phenols, flavonoids and secoiridoids.

Treatment of OMW by integrated membrane processing (MF/UF, NF and/or RO) allows the recovery of concentrates rich in different phenolics and other water soluble compounds [3,7,9,30–32]. However, selective separation of the phenolics by this technology alone is still so far not feasible [33].

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http://dx.doi.org/10.1016/j.jece.2015.11.010
2213-3437/

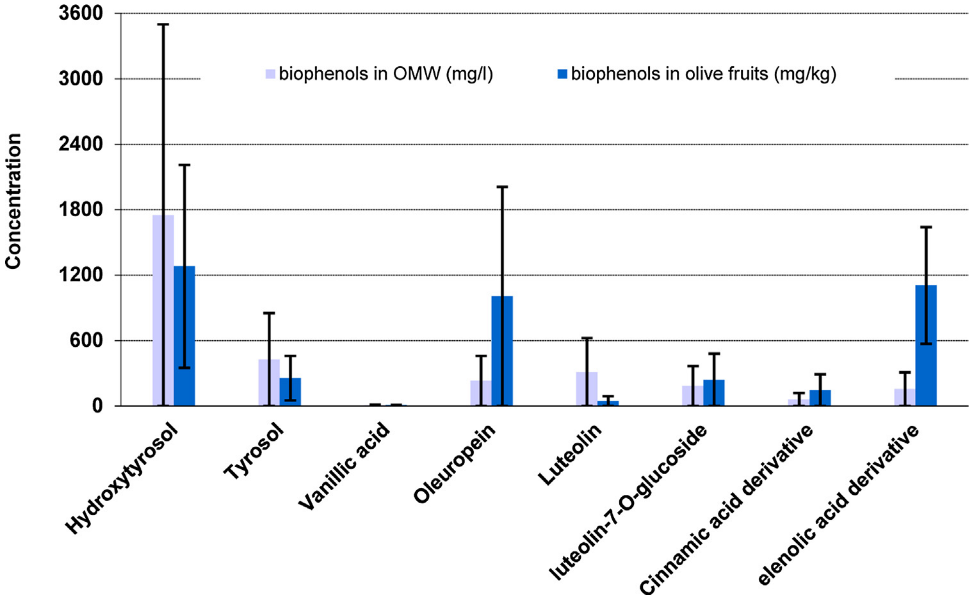

Fig. 1. Reported concentrations of biophenols in OMW and olive fruits [19,23,27,28].

Adsorption technology is one of the most commonly applied processes for the recovery of polyphenols from plant extracts and is gaining increasing importance in food industry [34]. The application of synthetic resins has several advantages such as relatively low operation costs, simple handling, its long service lives resulting of regeneration and reuse ability [35]. Compared with alternative technologies, adsorption is attractive for its relative simplicity of design, operation and scale up, its potential selectivity to toxic substances. Besides, adsorption avoids toxic solvents and minimizes the transformation of the target substances [36]. Among the disadvantages of adsorption technology are the limited overall purification efficiency [16], the loss of capacity observed after the first regeneration and solvent regeneration which has to be developed and/or adapted. However, there are several alternatives available for regeneration including chemical, steam and microwave regeneration [37] as well as sonication [38].

A method for gathering hydroxytyrosol by means of a two-step chromatographic treatment was suggested [39]. Likewise, an aqueous fraction of hydroxytyrosol from an aqueous phenolic extract was recovered [40]. Researchers used Amberlite XAD or Duolite to obtain extracts rich in antioxidants while in some patents applied Amberlite XAD was followed by Sephadex LH-20 or Amberlite XAD/Lewatit EP [41]. Recovery of phenolics from OMW by resins was also investigated in other studies [12,33,42–45].

Molecular imprinting is a promising technique for the preparation of synthetic polymers with predetermined selectivity for a desired target compound (template) [46]. This technology involves the formation, in the solution, of the template with appropriate functional monomers [47]. An MIP prepared with one template molecule will also show selectivity for other target molecules with a similar three-dimensional arrangement of interacting functional groups [48]. In this context, two MIPs were prepared, using caffeic acid and *p*-hydroxybenzoic acid as templates, and applied to isolate polyphenols from OMW [49]. The later was not selective in aqueous environment as in acetonitrile while the former retained a high percentage of several acids like gallic, *p*-coumaric and protocatechuic acids.

In the present investigation selective uptake of biophenols from model and natural olive mill wastewater under different conditions has been evaluated and improved. Acidification, sedimentation and membrane filtration of OMW were carried out. The adsorptivity towards the biophenols was investigated onto 32 different MIPs and NIPs (non-imprinted control polymers) present in an ExploraSep C–plate as well as on 16 commercial sorbents. To the best of the author's knowledge, the ExploraSep plate and eleven of the sorbents have been applied for the first time in this field. This study can be considered as an attempt for a low cost developed strategy to gain valuable phenolic compounds that belong to different subclasses from natural OMW.

2. Materials and methods

2.1. Chemicals

Hydroxytyrosol ≥90%, oleuropein ≥80%, tyrosol ≥98%, caffeic acid = 99% and luteolin = 97% were purchased from Extrasynthese-Genay, France and the German companies Roth, Merck, Fluka and ABCR, respectively. Methanol, acetone and acetonitrile ≥99.9% were purchased from Merck, Germany. Deionised water was used in all experimental and analytical works. The adsorbents Amberlite XAD-4, XAD-7HP, XAD-761, XAD-16 nonionic and FPX-66 were provided by Rohm and Hass, Germany; PVPP (Polyvinylpolypyrrolidone-crosslinked form of PVP) was purchased from Fluka, Germany; Lewatit AF5, AF6, AF7, MonoPlus-M800, VP OC-1064-MDPH, VP OC-1600, MonoPlus-SP 112 and K6387 were provided by Lanxess Deutschland GmbH, Germany and powdered activated carbon CAL-I from Calgon Carbon by Chemviron Carbon, Germany; granulated activated carbon was purchased from Merck, Germany. The properties of the adsorbents are given in Table 1. AF6 and AF7 have a similar matrix to AF5 but larger specific surface areas.

2.2. Model wastewater

Five phenolic standards belonging to different subclasses were dissolved in 100% methanol to prepare a stock solution stored at −30 °C as follows: 100 mg hydroxytyrosol (a simple phenol); 60 mg oleuropein (a secoiridoid); 50 mg tyrosol (a simple phenol); 20 mg luteolin (a flavonoid); 20 mg caffeic acid (a cinnamic acid) in 200 ml flask. Standard solutions of 50 mg/l hydroxytyrosol; 30 mg/l oleuropein; 25 mg/l tyrosol; 10 mg/l luteolin; 10 mg/l caffeic acid in deionized water with the original pH value of approximately