Journal of Hazardous Materials 285 (2015) 69–76

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Purification of olive mill wastewater phenols through membrane filtration and resin adsorption/desorption

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HIGHLIGHTS

- A fraction (from membrane filtration) of olive mill wastewater was further treated.
- Resin adsorption/desorption was used for the separation of phenols–carbohydrates.
- Batch and kinetic experiments were carried out for the optimization of the process.
- After the removal of carbohydrates, phenols were condensated to high concentration.
- 74% of the initial amount of hydroxytyrosol was condensated to 0.054% of the volume.

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
21 November 2014
Accepted 27 November 2014
Available online 28 November 2014

Keywords:
Olive mill wastewater
Phenols
Hydroxytyrosol
Resin adsorption
Membrane filtration

ABSTRACT

Olive tree cultivation has a long history in the Mediterranean countries, and even today consists an important cultural, economic, and environmental aspect of the area. The production of olive oil through 3-phase extraction systems, leads to the co-production of large quantities of olive mill wastewater (OMW), with toxic compounds that inhibit its biodegradation. Membrane filtration has been used for the exploitation of this byproduct, through the isolation of valuable phenolic compounds. In the current work, a fraction of the waste occurring from a membrane process was used. More specifically the reverse osmosis concentrate, after a nanofiltration, containing the low-molecular-weight compounds, was further treated with resin adsorption/desorption. The non ionic XAD4, XAD16, and XAD7HP resins were implemented, for the recovery of phenols and their separation from carbohydrates. The recovered phenolic compounds were concentrated through vacuum evaporation reaching a final concentration of 378 g/L in gallic acid equivalents containing 84.8 g/L hydroxytyrosol.

1. Introduction

Olive tree cultivation is an important aspect of Mediterranean countries' landscape economy and society since ancient times. Some of the oldest samples of fossilized olive tree leafs have been discovered at caldera of Santorini, dating back to 50,000–60,000 years [1]. The main product of olive tree cultivation is olive oil which is rich in phenolic compounds and thus very beneficial for human health [2–4]. During olive oil production via the 3-phase method, large quantities of wastewater are co-produced. This waste, characterized by its heavy organic load which is not easily biodegradable and contains toxic constituents (e.g., phenols), is usually disposed to aqueous receptors or the soil [5] either directly (untreated) or inadequately treated. Although the phenolic compounds inhibiting OMW's biodegradation are toxic at high concentrations, especially for microorganisms, if properly isolated and at the appropriate concentration they have beneficial effects on human health, possessing strong antioxidant properties [3]. Moreover, the difficulty in naturally occurring phenol isolation leads to increased value, making their purification very appealing. Considering that this liquid stream contains compounds with high-added value (such as phenolics), if successfully isolated and purified in high concentrations,

Abbreviations: OMW, olive mill wastewater; MF, microfiltration; UF, ultrafiltration; NF, nanofiltration; RO, reverse osmosis; OD, osmotic distillation; MBMR, multiphase biocatalytic membrane reactor; COD, chemical oxygen demand; TS, total solids; TSS, total suspended solids; Ph, phenols; Ch, carbohydrates; DAD, diode array detection; MWCO, molecular weight cut-off; rv, resin volume; HT, hydroxytyrosol.

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http://dx.doi.org/10.1016/j.jhazmat.2014.11.038
0304-3894/

it can be considered a byproduct of the oil extraction process posing a challenge for the isolation of these valuable constituents.

Membrane filtration is a relatively new separation technology. Membranes have been implemented for the purification of olive mill wastewater (OMW) by many researchers, some of whom are trying to isolate and purify the phenolic compounds contained. Russo [6], tested a membrane system consisting of microfiltration (MF)/ultrafiltration (UF) and reverse osmosis (RO) where the low-molecular-weight phenols were concentrated in the RO step and also proposed the addition of a nanofiltration (NF) step before RO, where phenols could be concentrated instead. The final product had a concentration of free low-molecular-weight phenols at 0.5 g/L with 80% being hydroxytyrosol. Garcia-Castello, et al. [7] proposed a system consisting of MF, NF, and Osmotic Distillation (OD)/Vacuum Membrane Distillation. The low-molecular-weight phenols were concentrated to 0.5 g/L in the OD step with 56% being hydroxytyrosol. Conidi, et al. [8] combined a MF and UF system followed by a multiphase biocatalytic membrane reactor (MBMR) system for the conversion and separation of oleuropein to oleuropein-aglycon. The conversion achieved in the MBMR step was 45.7% for a feed concentration of 545 mg/L oleuropein. El-Abbassi, et al. [9], proposed the use of membrane distillation for the concentration of all compounds contained in the waste, including phenols and the removal of clear water. Cassano, et al. [10], tested the effect of UF membranes used for the separation of phenols from OMW and proposed an integrated membrane system, consisting of two sequential UF steps and finally a NF membrane for the concentration of OMW phenols with a final concentration of 960 mg/L [10,11]. In previous works of the authors [5,12] the combination of UF- NF/RO was examined resulting to a final phenol concentration of 10 g/L. Membrane filtration can also be used for the treatment of the liquid waste streams that occur during the two phase extraction of olive oil, mainly consisting of the olive fruits and olive oil washing waters [13,14].

Adsorption on selective resins has also been investigated for the removal of phenols from aqueous solutions, either through molecular adsorption or ion exchange mechanisms. Moreover, ion exchange resins can be used as a pretreatment for the removal of ions, decreasing the concentration polarization phenomenon in membrane filtration and facilitating higher filtration fluxes [15]. Caetano, et al. [16] tested the removal of phenol through ion exchange mechanism on polymeric resins followed by desorption with methanol/water mixtures. Zhu et al. [17] tested the adsorption of phenol on *N*-butylimidazolium functionalized strongly basic anion exchange resin with the results showing that at acidic pH the dominant mechanism was molecular adsorption were as at alkaline pH phenol was removed through an ion exchange mechanism. XAD4, XAD7, and XAD16 are nonionic polymeric resins, widely used for this purpose. Juang, et al. [18] studied the adsorption of phenol and 4-chlorophenol on XAD4, XAD7, and XAD16, while Scordino, et al. [19], examined their efficiency, among other resins, for the adsorption of hesperidin with efficiency around 90% for XAD16. Bertin, et al. [20], examined the direct adsorption of OMW phenols on XAD7 and XAD16 resins followed by desorption with different solvents. The results were very encouraging, exhibiting high adsorption percentages, with 95% of the adsorbed phenols being desorbed with acidified ethanol. Apart from polymeric resins, several naturally occurring materials and industrial by-products have been tested for the adsorption of phenols, offering a cheap alternative to the expensive synthetic materials commonly used [21].

The aim of the present work was the development of an innovative integrated process for phenols recovery from 3-phase OMW comprising of a combination of purification steps based on the molecular weight of the phenolic compounds contained in the waste, through in line membrane filtration of OMW with UF–NF–RO and their further separation based on their polarity with adsorption/desorption on resins. The proposed process, through synergy of properly selected complimentary methods resulted in high concentration of phenols in the final obtained product.

2. Materials and methods

The OMW, used in the present study, was obtained from a 3-phase olive mill during January of 2013 in the region of Patras, Greece. This particular OMW sample was relatively poor in phenolics (2.64 g/L) probably because it was collected near the end of the harvesting season and the olives were ripe [22]. The membrane filtration experiments were carried out immediately after sample collection. The RO concentrate as well as all intermediate samples during membrane processing were kept at −25 °C. Total chemical oxygen demand (COD) was measured according to method 5220 D, total solids (TS) according to method 2540 B and total suspended solids (TSS) according to method 2540 D of *Standard Methods* [23]. Phenols (Ph) were measured with the Folin–Ciocalteu method [24], using gallic acid as standard at 760 nm, and carbohydrates (Ch) were measured with L-tryptophan reagent and glucose as standard at 525 nm [25]. The HPLC – diode array detection (DAD) model Agilent 1200 series system was used for the determination of free low-molecular-weight phenolic compounds. The analytical column used was Luna C18(2) 100A (250 mm × 4.6 mm, i.d., 5 μm particle size) with security guard cartridge C18 (4 mm × 3 mm) by Phenomenex. The separation of polyphenols was achieved by gradient elution according to [26]. A four-step linear solvent gradient was applied starting from 10% CH_3CN (gradient grade for liquid chromatography, ≥99.9%, Merck) and 90% H_2O (adjusted to pH 3.2 by 85% H_3PO_4) up to 100% MeOH. Initially the eluent was 10% CH_3CN and 90% H_2O (pH 3.2) maintained for 15 min. To purge the column, the concentration of acetonitrile was increased twice. Therefore, the acetonitrile percentage was raised to 30% in 10 min for 20 min (30:70% CH_3CN:H_2O, respectively) and increased again up to 40% CH3CN (40:60% CH_3CN:H_2O, respectively) in 10 min maintained for 5 min. Finally, the methanol (gradient grade for liquid chromatography, ≥99.9%, Merck) percentage was increased to 100% in 10 min for 30 min. The run-time analysis was 100 min with a flow rate of 1 mL/min at constant temperature of 35 °C. Prior to HPLC analysis, the eluent (H_2O, 18.2 MΩ cm) was acidified to pH 3.2 and the experimental samples to pH 2 with 85% and 10% H_3PO_4, respectively, and filtered (through 0.45 μm glass microfiber and 0.2 μm nylon filters, Whatman, respectively). The chromatograms were acquired at 254, 280, and 360 nm. Standards of polyphenolic compounds of p-coumaric acid, gallic acid, tyrosol, and cinnamic acid as well as caffeic acid, vanillic acid, oleuropein, and hydroxytyrosol were purchased from Merck and Sigma–Aldrich, respectively. The only phenolic compounds detected in appreciable amounts in our samples, as identified by comparison of their retention time and spectra with those obtained from the corresponding standards, were gallic acid, hydroxytyrosol and tyrosol. The concentration measurement for each identified compound was performed using a five-point regression curve (with an average of $r2 = 0.9954$) obtained using the available standards. It must be mentioned that the phenol determination performed is not unequivocal since mass spectroscopy was not performed.

The resins used were supplied by Sigma–Aldrich. Three resins were tested, Amberlite XAD4 (matrix: styrene–divinylbenzene, 20–60 mesh, 1.02 g/L density, 40 Å mean pore size, CAS: 37380-42-0) XAD16N (matrix: styrene–divinylbenzene, 20–60 mesh, 200 Å mean pore size, CAS: 37380-42-0) and XAD7HP (matrix: acrylic, 20–60 mesh, 1.14 mL/g pore volume, CAS: 37380-43-1) which have been reported to yield good adsorption results for phenols [18–20]. Prior to every experiment, the resin was firstly soaked in acetone for 8 h under magnetic stirring and then dried at room temperature. This step ensured the removal of any monomers trapped in the resin