Journal of Environmental Management 162 (2015) 46–52

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Use of solar distillation for olive mill wastewater drying and recovery of polyphenolic compounds

Sotirios Sklavos, Georgia Gatidou, Athanasios S. Stasinakis*, Dias Haralambopoulos

Department of Environment, University of the Aegean, University Hill, Mytilene 81 100, Greece

A R T I C L E I N F O

Article history:
Received 17 April 2015
Received in revised form
23 June 2015
Accepted 14 July 2015
Available online xxx

Keywords:
Olive mill wastewater
Treatment
Recovery
Valorisation
Antioxidants

A B S T R A C T

Olive mill wastewater (OMW) is characterized by its high organic load and the presence of phenolic compounds. For first time, a solar distillator was used to investigate the simultaneous solar drying of OMW and the recovery of phenolic compounds with antioxidant properties in the distillate. Two experiments were conducted and the role of thermal insulation on the performance of the distiller was studied. The use of insulation resulted to higher temperatures in the distillator (up to 84.3 °C and 78.5 °C at the air and sludge, respectively), shorter period for OMW dewatering (14 days), while it increased the performance of distillator by 26.1%. Chemical characterization of the distillate showed that pH and COD concentration gradually decreased during the experiments, whereas an opposite trend was noticed for conductivity and total phenols concentration. Almost 4% of the total phenols found initially in OMW were transferred to the distillate when an insulated solar distillator was used. Gas chromatographic analysis of collected distillates confirmed the presence of tyrosol in all samples; whereas hydroxytyrosol was found only in fresh collected distillate samples. Further experiments should be conducted to optimize the process and quantify the concentrations of recovered phenolic compounds.

1. Introduction

Olive mill wastewater (OMW) is a major by-product of olive oil production industry. More than 10 million m^3 OMW are produced per year in the Mediterrarean climate region; while the seasonality of olive oil production and the characteristics of wastewater (Chemical Oxygen Demand, COD > 80 g L^{-1}, Total Suspended Solids, TSS > 20 g L^{-1}, pH 4–5, phenolic compounds 1.5–10 g L^{-1}) make its management difficult and costly (Niaounakis and Halvadakis, 2006).

So far, several physicochemical and biological methods have been tested for OMW treatment (Niaounakis and Halvadakis, 2006; Paraskeva and Diamadopoulos, 2006; Stasinakis et al., 2008; Ochando-Pulido et al., 2013; Rahmanian et al., 2014). The application of physicochemical processes in full-scale systems is problematic as none of these methods alone and with reasonable cost can decrease sufficiently the toxicity and organic load of OMW (Paraskeva and Diamadopoulos, 2006). Moreover, the application of biological processes usually requires chemical pretreatment or/and significant dilution of OMW (Niaounakis and Halvadakis, 2006; Nesseris and Stasinakis, 2012). So far, very few studies have successfully used undiluted raw OMW during anaerobic digestion (Sampaio et al., 2011; Gonçalves et al., 2012). On the other hand, the drying of OMW in open evaporation ponds with retention time of several months is a common, low-cost practice in rural areas of the Mediterranean (Jarboui et al., 2010). However, this method requires large areas and causes significant nuisance due to the emitted odors and the possible contamination of aquifers. To enhance OMW drying avoiding the aforementioned effects, in a preliminary study, Potoglou et al. (2004) used a solar distillator and obtained a solid residual with 15% humidity after 9 days retention time.

Beyond the aforementioned difficulties on OMW management, this type of wastewater seems to have significant economical interest. Specifically, so far, more than 50 different phenolic compounds have been identified in OMW (Obied et al., 2007a; Rahmanian et al., 2014). These compounds are water soluble, thus it is expected to be found at much higher concentrations in OMW comparing to olive oil (Rodis et al., 2002). Moreover a great number of scientific articles have proved their bioactive properties, including antioxidant, antiflammatory, neuroprotective, antiaging and antiatherogenic effects (Obied et al., 2007b; Cárdeno et al., 2013). Due to their ability to modulate cell death, they have also

* Corresponding author.
E-mail address: astas@env.aegean.gr (A.S. Stasinakis).

http://dx.doi.org/10.1016/j.jenvman.2015.07.034
0301-4797/

been proposed as chemopreventive and therapeutic agents (Giovannini and Masella, 2012). Among them, hydroxytyrosol and tyrosol seem to be the most abundant phenolic compounds in OMW either from two-phase or three-phase olive mills, being detected at concentrations as high as 898 mg L^{-1} and 388 mg L^{-1}, respectively (Bertin et al., 2011). It is worth mentioning that hydroxytyrosol and tyrosol are amongst the compounds approved by the European Food Safety Authority for their ability to protect low density lipoproteins (LDL) particles from oxidative damage (EFSA, 2011).

Due to the above, food industries, cosmetics and drugs have shown considerable interest in the recovery of phenolic compounds contained in OMW. During the last years, several articles have been published, suggesting methods for the recovery of these compounds from OMW. The applied methods include adsorption onto resins and other sorbent materials, solvent extraction, supercritical fluid extraction, selective concentration by ultrafiltration and other membrane systems (Galanakis et al., 2010; El-Abbassi et al., 2011; Scoma et al., 2011; Ena et al., 2012; Kalogerakis et al., 2013; Rahmanian et al., 2014; Zagklis et al., 2015). The main weaknesses of these methods that hamper their implementation in full-scale are the requirement for OMW pretreatment in order to reduce significantly solids concentration, as well as their high cost either due to the use of chemicals for pre-concentration and/or extraction of target compounds or due to the significant energy requirements.

The main objective of this study was to investigate the use of solar distillation for simultaneous OMW drying and recovery of selected phenolic compounds. For this reason, a lab-scale solar distillation unit was used in the absence (Experiment A) and presence of thermal insulation (Experiment B). The temperatures of ambient air, vapor inside the distillator and retentate (sludge) as well as the solar radiation were constantly monitored during different experiments. The quantitative and qualitative characteristics of the distillate were studied, while the presence of tyrosol and hydroxytyrosol in the distillate was investigated using GC–MS techniques. Building on the work of Potoglou et al. (2004), this is the first study where solar distillation systematically has been used for simultaneous OMW drying and phenolic compounds recovery.

2. Materials and methods

2.1. OMW and reagents

OMW was collected by a three-phase, olive oil mill located in Lesvos Island, Greece and stored at 4 °C until the start of the experiments. The characteristics of OMW used during the experiments are presented in Table S1.

Analytical standards of hydroxytyrosol [2-(3,4-dihydroxyphenyl)ethanol, $C_8H_{10}O_3$, ≥98%] and tyrosol [2-(4-hydroxyphenyl) ethanol, $C_8H_{10}O_2$, >99.5%] were purchased from Extrasynthese (France) and Sigma–Aldrich (U.S.A.), respectively. Bis(trimethylsilyl) trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS) solution, used for silylation, were purchased by Supelco (USA). Oasis HLB cartridges (500 mg/6 cc) were supplied by Waters (U.S.A.), while Folin-Ciocalteu's phenol reagent was purchased from Merck (Germany).

2.2. Solar distillator

The solar distillator used in both experimental periods consisted of the liquid basin where the OMW was placed, the glass cover where vapors condensed and the supporting structure (Fig. 1, Fig. S1). Excepting the glass cover, the entire apparatus was made of galvanized steel sheets, with a thickness of 2 mm and an iron frame.

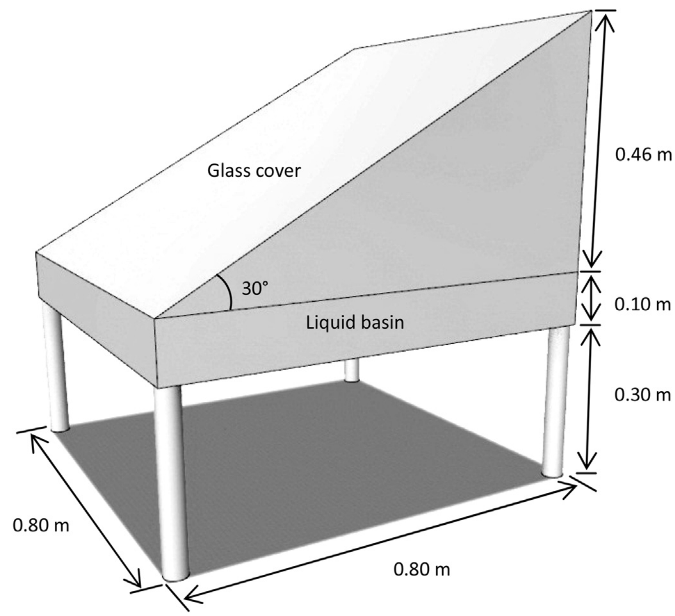

Fig. 1. Three dimensional representation of the laboratory solar distillator used in this study.

The glass cover was 3 mm thick and had an inclination of 30°, facing directly south at latitude of 38° north.

During Experiment B, all four sides and the floor of the solar distillator were covered with panels of extruded polystyrene foam (thickness: 70 mm) to improve thermal efficiency (Fig. S1b). This material is widely used for improving the thermal insulation of buildings. According to the manufacturer (Fibran, 2014), its thermal conductivity after 25 years is 0.034 W m^{-1} K^{-1}, while Papadopoulos (2005) reported that this value varies between 0.025 and 0.035 W m^{-1} K^{-1}.

2.3. Experimental design

At the beginning of each experiment, 13 L of OMW were placed in the solar distillator. Experiment A was conducted between 24th of September and 10th of October 2013 (duration: 16 days), whilst the Experiment B was performed from the 14th to the 28th of October 2013 (duration: 14 days). Apart from periods of precipitation, the solar distillator was uncovered for 12 h every day (8:00–20:00). Measurements of temperature (ambient air, air inside the distillator, and sludge inside the distillator) and solar radiation were recorded on a 24 h basis during both experimental phases. Temperatures were measured using T-type (copper-constantan) thermocouples at 6 s intervals and were averaged every minute with a Campbell Scientific CR10X data logger. Incident solar radiation was measured with a CM11 Kipp & Zonen pyranometer which had identical tilt and the same orientation with the glass cover of the solar distillator. This variable was measured, averaged and recorded in the same way as the aforementioned temperature measurements. At the end of each 24 h period, the distillate was collected in a dark glass bottle, measured in a volumetric cylinder and stored at 4 °C. Soon after collection, distillate samples were analyzed for pH, electrical conductivity, COD and total phenols. Distillate samples that were collected in Days 13, 15 (Experiment A) and Days 10, 12 (Experiment B) were also analyzed for the existence of hydroxytyrosol and tyrosol. Regarding OMW sludge samples, during the first experiment, these samples were collected from the liquid basin at the end of Days 4, 11 and 16.