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Reuse of olive mill effluents from two-phase extraction process by integrated advanced oxidation and reverse osmosis treatment

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HIGHLIGHTS

- Effective reclamation of two-phase OMW by integrated Fenton oxidation + RO membrane.
- Hydrodynamics and selectivity of the membrane accurately modelized.
- Fouling control and optimal hydrodynamics ensuring safe design and steady operation.
- Quality provided to recirculate the final effluent to the manufacture process and close the loop.
- Rending of production process environmentally friendly.

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ABSTRACT

In this work, complete reclamation of the olive mill effluents coming from a two-phase olive oil extraction process (OME-2) was studied on a pilot scale. The developed depuration procedure integrates an advanced oxidation process based on Fenton's reagent (secondary treatment) coupled with a final reverse osmosis (RO) stage (purification step). The former aims for the removal of the major concentration of refractory organic pollutants present in OME-2, whereas the latter provides efficient purification of the high salinity. Complete physicochemical composition of OME-2 after the secondary treatment was examined, including the particle size distribution, organic matter gradation and bacterial growth, in order to assess the selection of the membrane and its fouling propensity. Hydrodynamics and selectivity of the membrane were accurately modelized. Upon optimization of the hydrodynamic conditions, the RO membrane showed stable performance and fouling problems were satisfactorily overcome. Steady-state permeate flux equal to 21.1 $L\,h^{-1}\,m^{-2}$ and rejection values up to 99.1% and 98.1% of the organic pollutants and electroconductivity were respectively attained. This ensured parametric values below standard limits for reuse of the regenerated effluent, e.g. in the olives washing machines, offering the possibility of closing the loop and thus rending the production process environmentally friendly.

1. Introduction

An important growth of olive oil industry has been experienced in the recent decades due to modernization of olive oil mills in response to the increasing demand of olive oil worldwide in virtue of its nutritional, antioxidant and heart-healthy as well as cosmetic properties. Mediterranean basin countries are the main olive oil producers, highlighting Spain, Italy, Greece, Portugal, Syria and the Northern African countries where this industry is one of the main engines of the economy (Fig. 1). What is more, this industrial sector is spreading rapidly to other regions of the world, such as Australia, the USA and China, which present a significant production potential.

Currently, two main liquid effluents are generated in an olive oil mill during olive oil production. The first effluent is formed during the olives washing procedure, called olives washing wastewater (OWW). The other one comes directly from the olive oil extraction process and is named olive mill wastewater (OMW), which is composed of the humidity of the fruit along with process-added water. These effluents are commonly referred to as olive mill effluents (OME).

In ancient olive oil mills, which operated with presses or roller mills in batch mode, between 0.4 and 0.6 m^3 of OMW were yielded per ton of processed olives. This system is no longer in use, and at the present time olive oil factories work in continuous mode by employing horizontal centrifuges – also called 'decanters' – for

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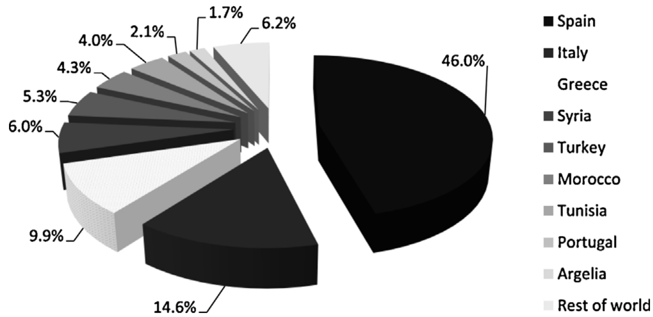

Fig. 1. Olive oil sector worldwide (International Olive Oil Council, IOOC 2011).

solid–liquid separation. As a result of this change in technology, nowadays olive oil mills lead daily to 10–15 m^3 of OMW together with 1 m^3 day^{-1} of OWW on average.

The two-phase continuous decanting system is currently the main olive oil production procedure used in many countries, such as Spain. Nevertheless, the three-phase continuous extraction process is still surviving in other countries since the capital investment to undertake the technological switch represents a major handicap for the small plants owners.

OME are among the heaviest-polluted existing industrial effluents, as much as a hundred times higher than domestic sewage. These wastewaters are known by their seasonality and toxic character due to the presence of aromatic compounds and a wide range of other organic pollutants which are not suitable to be biologically managed. OMW is one of the most polluted effluents with very high organic matter load comprising sugars, tannins, polyphenols, polyalcohols, pectins and lipids [1]. As reported by several authors, more than 30 phenolic compounds have been detected in OME, which together with long-chain fatty acids present high toxicity to microorganisms, plants and soil [2,3]. For these reasons, OME pose a serious environmental threat for an increasing number of regions, leading to problems in relation to odor nuisance, soil contamination, underground leakage and water body pollution.

At the moment there is no specific European legislation regulating olive mill wastes, and standards are left to individual countries. For instance, in 1981 the Spanish Government prohibited the direct discharge of these effluents into rivers, since high pollution levels were detected in the Guadalquivir river basin. Furthermore, the pollutants load of these effluents is extremely variable depending not only on the extraction process, but also on edaphoclimatic and cultivation parameters, as well as on the type, quality and maturity of the olives [4–6]. These factors, in addition to small size and geographical dispersion of olive oil mills, make the management of OME sensibly difficult.

Biological treatment of OME is right now not applied on a large scale as it is not quite efficient, given the fact that dilutions of up to 50% of the raw effluent may be necessary due to its resistance to microbial degradation [6–10]. Hence, a plethora of other reclamation practices as well as combined treatments have already been proposed and developed, although they have not led to completely satisfactory results. Among these treatments we can highlight lagooning or natural evaporation and thermal concentration [5,11], treatments with lime and clay [12,13], composting [14–16] and physicochemical procedures such as coagulation–flocculation [17–19] and electrocoagulation [20,21].

Within this context, chemical remediation strategies – including ozonation [22], Fenton's reagent [23,24], photocatalysis [25–27] as well as electrochemical [28–30] and hybrid processes [31–34] – are required for the depuration of these bio-refractory wastewaters [4,5]. Among them, Fenton's process appears to be the most economically advantageous since it may be conducted at ambient temperature and pressure conditions, and also due its equipment simplicity and operational ease.

OME also exhibit significant saline toxicity levels, confirmed by high electroconductivity (EC) values. Inorganic compounds including chloride, sulfate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are common traits of OME [35]. Conventional physicochemical treatments cannot abate this high inorganic load, and thus advanced separation technologies are needed to attempt complete depuration of OME.

In this regard, as regulations become more stringent every year, membranes technology offers many advantages in contrast with other separation processes: no need to use chemical reagents – such as solvents – to achieve separation; lower capital and operating costs and energy consumption than many conventional separation procedures, but still ensuring high purifying capacity, selectivity and recovery rates; and also easy industrial scaling in virtue of its modular nature, ease of design and operation and low maintenance requirements [36–41].

In this work, complete reclamation of the effluents from a two-phase olive oil extraction process (OME-2) was addressed. The quality standards for reuse of the purified effluent in the olive oil production process were also checked. With this goal, a depuration procedure integrating both an advanced oxidation process based on Fenton's reagent (secondary treatment) coupled with a final reverse osmosis (RO) stage (tertiary or purification step) was studied on a pilot scale.

2. Experimental

2.1. Physicochemical analyses

OME samples were collected from several olive oil factories in the Andalusian provinces of Jaén and Granada (Spain) during winter months, taken from the olives washing machines (OWW) as well as at the outlet of the centrifuges from three-phase (OMW-3) and two-phase (OMW-2) extraction processes. Samples were then rapidly analyzed in the laboratory, whereas kept refrigerated for further research when necessary.

Analytical grade reagents and chemicals with purity over 99% were used for the analytical procedures, which were all applied in triplicate. Chemical oxygen demand (COD), total suspended solids (Tss), total phenols (TPh), total iron, electroconductivity (EC) and pH measurements were carried out in the raw wastewater and at the end of each depuration step according to standard methods [42].

For the measurement of the total iron concentration, all iron ions were reduced to iron ions (II) in a thioglycolate medium with a derivative of triazine, forming a reddish-purple complex that was determined photometrically at 565 nm (Standard German methods ISO 8466-1 and German DIN 38402 A51) [42]. EC and pH measurements were assessed with a Crison GLP31 conductivity-meter and a Crison GLP21 pH-meter, with autocorrection of temperature, whereas a Helios Gamma UV–visible spectrophotometer (Thermo Fisher Scientific) served for COD, TPh and total iron measurements. Effluent samples were diluted when necessary with MilliQ® water for their analysis, and samples of RO permeate were analyzed directly without dilution.

Ionic concentrations were analyzed in the effluent exiting the secondary treatment (OMEST-2) as well as in the permeate stream of the final membrane stage with a Dionex DX-120 ion chromatograph as described in previous works [36,37].