Separation and Purification Technology 179 (2017) 161–174

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Review

# A focus on advanced physico-chemical processes for olive mill wastewater treatment

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A R T I C L E  I N F O

*Article history:*
Received 20 October 2016
Received in revised form 8 December 2016
Accepted 1 February 2017
Available online 4 February 2017

*Keywords:*
Olive mill wastewater
Advanced oxidation processes
Wastewater reclamation
Wastewater reuse

A B S T R A C T

Advanced chemical remediation strategies (advanced oxidation processes, AOPs) have turned out as a feasible solution for the treatment of bio-refractory effluents, as in the case of olive mill wastewater (OMW). In this review paper, a focus on the relevant state-of-the art on advanced physico-chemical processes - including ozonation, wet oxidation, Fenton's reagent, photocatalysis, coagulation-flocculation, as well as electrochemical, solar-driven and hybrid processes - for the treatment of OMW is presented. In particular, the extent of recalcitrant organic pollutants abatement efficiency and the grade of mineralization achieved by the various treatments available up to today is addressed. Special attention is given to the different configurations and treatment line sequences, some important effect parameters and novel materials for implementation at real industrial scale. The latter includes the latest advances and applications for OMW treatment with biopolymers for coagulation-flocculation, ferromagnetic nanocatalyst for ease of recovery and multiple long-term use, low-cost catalysts, doped nanocatalysts for enhanced sunlight activation, zeolite-based catalysts, mixed and doped electrodes, among others. Solutions reported for the management of the secondary sludge by-produced in some treatment processes are also discussed. Moreover, a glance at the specific energy consumption and associated costs comparison of the different processes proposed is also given.



**Contents**



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http://dx.doi.org/10.1016/j.seppur.2017.02.004

## 1. Introduction

The production of olive oil is not only one of the main industrial activities in the Mediterranean Basin, yet it is also increasing in other countries e.g. France, Serbia and Montenegro, Macedonia, Cyprus, Turkey, Israel, Jordan, the USA, Australia, the Middle East, and specially in China, where given the right edaphoclimatic conditions for the growth of olive trees in some of its regions it has strongly emerged as an agro-food industry, being expected to develop a considerable production potential in the near future (International Olive Oil Council, IOOC, 2013–2014). On another hand, the considerable expansion of this industrial sector in the last decades has brought as a side-effect a significant increase of the amounts of olive mill effluents (OME) generated. The treatment of these wastewaters is therefore a task of global concern that should be addressed urgently.

A modern olive oil mill of average size by-produces several cubic meters resulting from the proper centrifugation process (OMW), as well as wastewater generated during the washing of the olive fruits (OWW) and also from olive oil washing process (OOW). This represents a huge amount of highly polluted wastewaters and of potable water consumption per year, up to several millions cubic meters [1–6].

A series of hazards of these effluents related to the contamination of soil, hindrance of plants growth, leaks to the underground aquifers, pollution of water bodies, inhibition of autopurification processes, as well as phytotoxic impacts to aquatic fauna and to ecological equilibria and strong odor nuisance have been reported so far [7–11].

It has been observed that conventional physico-chemical processes and common biological treatments such as those based on active sludge do not provide a high effectiveness for the abatement of the organic load of OMW [2,12–14]. The typical physico-chemical characteristics of these effluents mainly the acidic pH, high salinity reflected by high electric conductivity, low alkalinity and low nitrogen content, and above all its lipidic and phenolic fractions, organic long chain fatty acids, tannins and organohalogenated contaminants, make this wastewater potentially recalcitrant for anaerobic treatments [15–17]. Also, the physico-chemical composition of OMW is much variable depending on the extraction process, edaphoclimatic and cultivation features, as well as the type, quality and maturity of the processed olives [1,4–6,8,10]. The high organic matter load of these effluents may be notwithstanding a valuable energetic source to obtain methane and hydrogen-rich biogas by means of anaerobiosis, through solutions like co-digestion of OMW with other substrates, as agro-livestock, or previously dephenolized [16,18–20].

Legal actions have been undertaken in the last decades in the producing countries, i.e. the straight disposal of untreated OMW to the ground fields and superficial waters bodies is prohibited in Spain currently, and also in Italy, Portugal and other European countries it is just allowed the partial discharge onto certain terrains. Moreover, the direct discharge of these wastewaters to the municipal sewage collectors is prohibited too, given the high concentrations of organic refractory pollutants. Legal limits are established in order to prevent inhibition of the biological treatment processes that take place in wastewater treatment plants.

**Table 2**
Different effluents flow rates in continuous extraction mills [22].

| Effluent, L/kg | 3-phase extraction | 2-phase extraction |
|---|---|---|
| Washing of olives (OWW) | 0.06 | 0.05 |
| Horizontal centrifuge | 0.90 | 0 |
| Vertical centrifuge | 0.20 | 0.15 |
| Cleaning | 0.05 | 0.05 |
| Total | 1.21 | 0.25 |

The physico-chemical composition and average volumes of the effluents by-produced in batch and continuous olive oil mills are reported in Tables 1 and 2, respectively [1,21,22]. The two-phase system seems more ecological from the point of view that it leads to the generation of lower volumes of effluents. It has substituted the three-phase system in Spain in the last two decades, and it is now becoming implemented successively in Portugal, Greece and Italy as well. However, the three-phase system is still surviving in countries where financial scarcity has not yet permitted the switch of the technology equipment.

As it can be seen, OWW is typically composed of a high concentration of suspended solids resulted from the washing procedure of the olive fruit (peel, pulp, ground, branches and leaves debris), but presents relatively low concentration of dissolved organic matter - that depends on the frequency of the exchange of the water employed in the washing machines during the fruit cleaning procedure - usually below the standard limits for discharge on superficial suitable terrains (e.g. Guadalquivir Hydrographical Confederation in Spain, 2006–2014: TSS < 500 mg/L and COD < 1000 mg/L). On the contrary, the effluents exiting the centrifuges (OMW2 and OMW3) present a major load of dissolved organics, mostly phytotoxic compounds recalcitrant to biological degradation.

Several stand-alone and integrated processes for the treatment of OMW have already been developed but have not yet led to completely satisfactory results, including lagooning or natural evaporation and thermal concentration [2,23], composting [24–26], treatments with clay [27] and with lime [28], physico-chemical procedures such as coagulation-flocculation [29,30], electrocoagulation [31,32] and biosorption [33–35], advanced oxidation processes comprising ozonation [36–38], Fenton's reaction [8,10] and photocatalysis [39,40], electrochemical treatments [31,41,42] and hybrid processes [15,43–47].

The majority of the processes proposed up to the date for the treatment of OMW are rather cost-ineffective or inefficient, and olive oil industry in its current status, composed of little and dispersed factories, cannot bear such high costs. Within this context, chemical remediation strategies have turned out as a feasible solution for the depuration of these bio-refractory wastewaters. In this paper, a focus on the relevant state-of-the art on advanced physico-chemical processes - including ozonation, Fenton's reagent, photocatalysis, as well as electrochemical, solar-driven and hybrid processes - for the treatment of OMW will be reviewed.

**Table 1**
Characteristics of the effluents of batch and continuous olive oil extraction processes [8,10,21,30].

| Process | Effluent | COD, g/L | $BOD_5$, g/L | TSS, g/L | pH | EC, mS/cm | TPh, g/L |
|---|---|---|---|---|---|---|---|
| Olives cleaning | OWW | 0.8–2.2 | 0.3–1.5 | 8–18 | 5.5–6.6 | 2.5–3.0 | 0–0.1 |
| Batch press | OMWP | 30–130 | 90–100 | 10–12 | 4.5–5.0 | 2.0–5.0 | 1.0–2.4 |
| Three phase | OMW3 | 30–200 | 5–45 | 5–35 | 3.5–5.5 | 2.0–7.9 | 0.3–7.5 |
| Two phase | OMW2 | 4–16 | 0.8–6.0 | 2–7 | 3.5–6.0 | 1.5–2.5 | 0.1–1.0 |

COD: chemical oxygen demand; $BOD_5$: biological oxygen demand; TSS: total suspended solids; EC: electric conductivity.
TPh: total phenols; OWW: olives washing wastewater; OMWP: press OMW; OMW3: three-phase OMW; OMW2: two-phase OMW.