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Life cycle assessment of advanced oxidation processes for olive mill wastewater treatment

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ABSTRACT

The efficient management of biorecalcitrant agro-industrial effluents, such as olive mill wastewater (OMW), is a matter of concern along all Mediterranean countries. However, the applicability of any treatment technique is strongly related, apart from its mineralization and detoxification efficiency, to its joint environmental impacts. In this work, the life cycle assessment methodology was utilized to estimate the environmental footprint of three advanced oxidation processes (AOPs), namely UV heterogeneous photocatalysis (UV/TiO_2), wet air oxidation (WAO) and electrochemical oxidation (EO) over boron-doped diamond electrodes, for OMW treatment. It was observed that both EO and WAO can be competitive processes in terms of COD, TPh and color removal. EO was found to be a more environmentally friendly technique as it yields lower total environmental impacts, including CO_2 emissions to atmosphere. The environmental impacts of all three AOPs show that human health is primarily affected followed by impacts onto resources depletion. All in all, it was found that the environmental sustainability of AOPs is strongly related to their energy requirements and that their total environmental impacts decline according to the following order: UV/TiO_2 > WAO > EO.

1. Introduction

The foodstuff processing industry based on olive oil extraction constitutes a large part of agro-industrial activities and is an economically important activity for many Mediterranean regions. However, this process results in seasonal large quantities of biorecalcitrant wastewaters, that come from the vegetation water and the soft tissues of the olive fruits mixed with the water used in the different stages of oil production. All these wastewaters together with the industry wash-waters, make up the so-called olive mill wastewaters (OMW). The main environmental impacts of OMW derive from its high organic (COD values range between 45 and 170 g/L) and polyphenolic content (0.5–24 g/L) that result in high ecotoxicity and strong antibacterial action (Chatzisymeon et al., 2009a; 2009b). The presence of these biorecalcitrant organic compounds together with the seasonal production of large OMW quantities (about $4 \cdot 10^5$ m^3/y in Greece) constitute the major obstacles in the efficient effluent management.

Up to now, the majority of agro-industrial effluents such as OMW were discharged to evaporation ponds where they are left to evaporate naturally with the most hazardous of all being the seepage of organic pollutants into groundwater (Avraamides and Fatta, 2008; Komnitsas et al., 2011; Salomone and Ioppolo, 2012). The direct discharge of OMW to evaporation ponds was prohibited by Greek legislation. Olive mills operation is regulated by the new Laws 3982/11 and 4014/11 that establish a classification of olive mills according to their capacity and their environmental impacts and define the environmental commitments of each activity (Hellenic Republic, 2011a; 2011b). These are further specified by the Joint Ministerial Decision 15/4187/266 (Hellenic Republic, 2012) where it is made clear to olive mill operators that OMW has to undergo pre-treatment in order to reach an organic load of about 1 g/L COD, thus it can be safely discharged to evaporation ponds or be reused after further treatment. Hence, researchers have been focused on the investigation of new treatment strategies that would efficiently treat OMW and safely discharge it to the environment.

A great variety of physical, chemical, thermal and biological processes, as well as several combinations of them, have been investigated for OMW treatment aiming at removing the organic matter from the liquid phase in order to make it acceptable for discharge into the environment. Among them, advanced oxidation processes (AOPs) have been extensively studied regarding their efficiency to treat OMW, while it is generally accepted that a process train comprising aerobic/anaerobic biological and advanced oxidation processes may be the only viable option to

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treat OMW (Mantzavinos and Kalogerakis, 2005). Generally, research efforts have been mainly directed toward the investigation of the operating conditions of AOPs that affect OMW mineralization and/or detoxification (Chatzisymeon et al., 2009c; Mert et al., 2010), while there are few studies comparing several processes, including AOPs, from the economical point of view (Cañizares et al., 2009). However, when designing or planning a new technology its environmental impacts should be taken into account, which have not yet been identified for OMW treatment. Therefore, a comparison of AOPs environmental impacts for agro-industrial effluents treatment is a highly important subject that is still pending.

Regarding wastewater treatment, AOPs have been primarily proposed as a pre- or post-treatment step to destruct the most bio-recalcitrant organic substances before or after further biological or physicochemical treatment (Chatzisymeon et al., 2009b). Comninellis et al. (2008) declared that the higher the polluting load and the extent of pollution removal needed, the harsher the treatment conditions to be applied are. In this view, OMW treatment performance can be enhanced only by coupling several of the above processes including AOPs.

The goal and scope of this work is to utilize the life cycle assessment (LCA) methodology in order to assess the environmental footprint of several AOPs in bench-scale, under Greek conditions, to identify their advantages and disadvantages in terms of their environmental impacts, compare them and provide feedback on the most sustainable process for future scaling-up of the OMW treatment facilities. For this purpose, three advantageous, regarding organics degradation efficiency, AOPs, for wastewater treatment, namely UV heterogenous photocatalysis (UV/TiO_2), wet air oxidation (WAO) and electrochemical oxidation (EO) over boron-doped diamond electrodes, were studied. However, the environmental footprint of each of these techniques has to be taken into account to get a thorough picture of the whole problem. Up to now and to the authors' best knowledge, there is no published research dealing with this subject. Moreover, these techniques were compared in terms of organics degradation efficiency and energy requirements in order to assess their overall performance from both an environmental and technical point of view.

2. Materials and methods

2.1. Description of the studied wastewater

The OMW was once collected by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. The effluent was subjected to filtration to remove most of its total solids and it was then kept at 4 °C, to ensure that its physicochemical characteristics will not be lessened or weathered. The effluent had a strong malodor of degraded olive oil, a dark black–brown color and its main properties prior to and after filtration are given in Table 1.

It has to be noted that OMW sample was diluted with distilled water to achieve the appropriate initial COD value as shown in Table 2.

Table 1
Properties of OMW used in this study.

Physicochemical characteristics	OMW before filtration	OMW after filtration
COD, g/L	47	40
Total phenols (TPh), g/L	8.1	3.5
Total solids, g/L	50.3	0.6
pH	4.6	4.4
Conductivity, mS/cm	17	18

2.2. Experimental runs

This work is based on previously published experimental studies used to derive optimal operating parameters for three (3) common AOP systems, namely photocatalytic (UV/TiO_2), electrochemical and wet air oxidation. The main parts and characteristics of these systems are given at Table 2. More details regarding the experimental set-ups, their operating mode and conditions of the oxidation processes are given in Chatzisymeon et al. (2009a, 2009b and 2009c). To meet these operating standards (i.e. initial COD), AOPs should be utilized as part of a treatment battery incorporating various physicochemical and biological processes as can schematically be illustrated in Fig. 1.

Keeping in mind the potential use of these processes in train treatment schemes (Fig. 1), it was decided to investigate whether the bench-scale experimental data obtained from our previous publications (a summary of which is shown in Table 2) can be used to scale-up the process and further perform an LCA at larger scale. Therefore, a pre-design cost estimation of the three AOPs was performed for a prospective industrial AOP treatment plant for OMW treatment. Generally, direct scaling-up from laboratory to industrial scale bears serious calculating inaccuracies. Hence, performance of the AOPs technologies should take place at pilot-scale first, before any further larger-scale application. However, the proposed pre-designing cost methodology can be a useful tool for researchers to get an indicative view of treatment expenses when scaling-up such processes.

2.3. Impact assessment methodology

The software package SimaPro 7.3.3 (PRe Consultants, 2012) was used in this work and the mandatory (selection of impact categories, category indicators and characterization models, classification, and characterization) and optional (normalization, grouping, and weighting) elements of the life cycle impact assessment (LCIA) according to ISO 14040 were utilized (ISO 14040, 2006; Tsoutsos et al., 2010; Foteinis et al., 2011). Furthermore, two impact assessment methods were used and these are IPCC 2007 version 1.02 and ReCiPe version 1.06. The first one compares processes based on CO_2 emissions equivalent (CO_2-eq), used to measure Global Warming Potential (GWP), which is a standard indicator of environmental relevance. The ReCiPe framework, which encompasses GWP indicator, is the most recent impact assessment method that exhibits certain advantages comparing to other approaches, such as Eco-Indicator 99. The primary advantage is that ReCiPe comprises a broadest set of midpoint impact categories, including several environmental issues, one of them being GWP, to assess sustainability (Goedkoop et al., 2009). Analytically, the ReCiPe method can transform the life cycle inventory (LCI) results into a limited number of indicator scores that are expressed per environmental impact category and also as an aggregated single score. Furthermore the results were simulated using the three different perspectives, namely individualist (I), hierarchist (H) and egalitarian (E). The latter was finally chosen to evaluate the results, since it takes into account the long term, precautionary environmental impacts, which better corresponds to the scope of this study.

2.3.1. System boundaries

First of all, the system boundaries for each AOP were determined (Fig. 2). In this study, OMW generation and its transportation to the laboratory were not included inside the boundaries, since AOPs can be applied as an onsite treatment nearby the olive mill. Finally, since this work refers to experiments that were carried out in laboratory-scale, land use was not taken into account. The main system flows of this work were: (i) the energy inputs (electricity