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Sequential treatment of diluted olive pomace leachate by digestion in a pilot scale UASB reactor and BDD electrochemical oxidation

Athanasia Katsoni[a], *Dionissios Mantzavinos*[b], *Evan Diamadopoulos*[a,*]

[a] *Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Greece*

[b] *Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, GR-26504 Patras, Greece*

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ABSTRACT

The efficiency of the anaerobic treatment of olive pomace leachate (OPL) at mesophilic conditions was investigated. Daily and cumulative biogas production was measured during the operational period. The maximum biogas flowrate was 65 L/d, of which 50% was methane. In addition, the applicability of electrochemical oxidation as an advanced post-treatment method for the complete removal of chemical oxygen demand (COD) from the anaerobically treated OPL was evaluated. The diluted OPL, having a pH of 6.5 and a total COD of 5 g/L, was first treated in a 600 L, pilot-scale up-flow anaerobic sludge blanket (UASB) reactor. The UASB reactor was operated for 71 days at mesophilic conditions ($32 \pm 2\,^{\circ}$C) in a temperature-controlled environment at a hydraulic retention time of 3 days, and organic loading rates (OLR) between 0.33 and 1.67 g COD/(L.d). The UASB process led to a COD removal efficiency between 35 and 70%, while the particulate matter of the wastewater was effectively removed by entrapment in the sludge blanket of the reactor. When the anaerobic reactor effluent was post-treated over a boron-doped diamond (BDD) anode at 18 A and in the presence of 0.17% NaCl as the supporting electrolyte, complete removal of COD was attained after 7 h of treatment predominantly through total oxidation reactions. During electrochemical experiments, three groups of organo-chlorinated compounds, namely trihalomethanes (THMs), haloacetonitriles (HANs) and haloketons (HKs), as well as 1,2-dichloroethane (DCA) and chloropicrin were identified as by-products of the process; these, along with the residual chlorine are thought to increase the matrix ecotoxicity to *Artemia salina*.

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* *Corresponding author*. Tel.: +30 2821037795; fax: +30 2821037852.
E-mail address: diamad@dssl.tuc.gr (E. Diamadopoulos).

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1. Introduction

Olive oil extraction, an agro-industrial activity of vital economic significance to all Mediterranean countries, is unfortunately associated with the generation of large quantities of wastewater and solid wastes, whose management, treatment and safe disposal raise serious environmental concerns.

Olive mill wastewaters (OMW) are characterized by high organic content including various classes of recalcitrant and/or toxic compounds; therefore, it is not surprising that OMW treatment has received enormous attention over the past several years and various decontamination technologies have been proposed by several research groups as summarized in a review article by Paraskeva and Diamadopoulos (2006). Conversely, the solid residue, commonly referred to as pomace, typically consists of olive pulp, stones, water and a remaining quantity of oil and is further treated by drying and solvent extraction to recover valuable oil. Raw pomace, whose annual production in the three main olive oil producing countries (i.e. Spain, Italy and Greece) is estimated at 4×10^6 tons, is treated in central extraction plants (on average, there is one such plant for every 65 olive mills) to yield oil (Mavros et al., 2008). The exhausted pomace, whose annual production is estimated at 1.6×10^6 tons, is a dry material commonly used as solid fuel although recent investigations have also reported its potential use as raw material for biogas production (Borja et al., 2005). Although the extraction process itself does not generate any wastewaters, raw pomace storage in open-air conditions prior to processing yields leachates due to both pomace weathering and its high moisture content, which is around 50% for olive pomace coming from three-phase olive mill decanters and 65% for olive pomace from two-phase decanters. As a result, OPL exists as a by-product of the olive oil extraction process.

In wastewater treatment, various biological, physical and chemical methods, as well as their combinations can be used. Amongst biological methods, anaerobic process is preferable in the case of agro-industrial effluents such as OMW and OPL, although the presence of certain classes of compounds in olive-related effluents, such as long-chain fatty acids and phenolic compounds are difficult to be degraded by microorganisms or may inhibit certain microbial groups (Gelegenis et al., 2007).

Generally, anaerobic digestion is particularly suitable for the treatment of effluents containing high concentrations of organic carbon because of the limited applicability of aerobic treatment due to the cost of aeration (Leitão et al., 2004). Anaerobic digestion generates energy in the form of biogas, while the quantity of sludge produced is significantly lower than that of aerobic processes. Furthermore, anaerobic digestion has low-energy requirements, since the only energy needed is for heating (mainly for operation at thermophilic conditions and depending on the environmental temperature for operation at mesophilic conditions), and agitation of the influent wastewater.

Among the anaerobic digesters, high-rate digesters are popularly used in sewage treatment. The up-flow anaerobic sludge blanket (UASB) reactors are by far the most robust high-rate anaerobic reactors for sewage treatment and more than 1000 such reactors have been installed worldwide. The main feature of a UASB reactor which makes it popular as a high-rate anaerobic digester worldwide (especially in tropic countries) is the availability of granular sludge, allowing it to achieve high COD removal efficiencies without the need of a support material (Weiland and Rozzi, 1991).

Furthermore, the natural turbulence caused by the rising gas bubbles which buoy the sludge, provides efficient wastewater and biomass contact. Therefore mechanical mixing is not required, thus significantly reducing the energy demand and its associated cost. Most importantly, due to the granulation/blanketing in a UASB reactor, the solids and hydraulic retention times can be manipulated independently and effectively, thus permitting the design to be based upon the degradation capacity of the biomass, resulting in the reduction of treatment times from several days to only a few days or even hours (Chong et al., 2012).

Treatment of industrial effluents by a combination of separation, biological and advanced oxidation processes is conceptually advantageous (Comninellis et al., 2008). Of the latter, boron-doped diamond (BDD) electrochemical oxidation is an environmentally acceptable technology exhibiting increased mineralization rates of the organic pollutants, as well as current efficiencies (Anglada et al., 2009). Recent studies have demonstrated the application of BDD electrochemical oxidation in the treatment of olive-related, agro-industrial effluents (Canizares et al., 2007; Chatzisymeon et al., 2009; Deligiorgis et al., 2008). However, the formation of undesirable oxidation by-products such as chlorinated organic compounds has been reported. For this reason, speciation of oxidation by-products, especially of chlorinated organics, as well as the identification of the main factors that affect their formation needs to be determined.

Despite the accumulated experience in OMW treatment, there is practically little knowledge and consequently limited research about the treatability of OPL. Mavros et al. (2008) proposed a train treatment comprising alum coagulation, activated carbon adsorption and electrochemical oxidation over BDD electrodes to treat OPL yielding a low-COD (i.e. about 150 mg/L), colorless and solids-free, yet ecotoxic effluent.

This study aims at treating OPL combining anaerobic digestion in a pilot scale UASB reactor and an emerging advanced oxidation technology, the BDD electrochemical oxidation, as the final step to mineralize the remaining organic fraction from the anaerobic reactor. In addition to evaluating the performance of the treatment scheme in terms of organic matter and color removal, biogas production, ecotoxicity and the major organochlorinated by-products were also monitored.

2. Materials and methods

2.1. *Olive pomace leachate*

Olive pomace leachate was taken from the evaporation pond of the AVEA Oil Cooperatives plant in Chania, W. Crete, Greece. The plant operates over a period of 5 months (November to March) treating 30,000 tons of pomace annually for the extraction of pomace oil. Pomace consists of around