WATER RESEARCH 44 (2010) 2773–2780

Available at www.sciencedirect.com

ScienceDirect

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

Pilot treatment of olive pomace leachate by vertical-flow constructed wetland and electrochemical oxidation: An efficient hybrid process

*Petros Grafias, Nikolaos P. Xekoukoulotakis, Dionissios Mantzavinos, Evan Diamadopoulos**

Department of Environmental Engineering, Technical University of Crete, GR-73100 Chania, Greece

ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form
31 January 2010
Accepted 10 February 2010
Available online 16 February 2010

Keywords:
Constructed wetland
Boron-doped diamond
Electrolysis
Pomace leachate
Process integration
Treatment

ABSTRACT

A hybrid process comprising biological degradation in a vertical-flow constructed wetland (CW) and electrochemical oxidation over boron-doped diamond electrodes to decolorize, mineralize and detoxify a leachate from olive pomace processing (OPL) was investigated. Two alternative treatment schemes were compared: According to the first treatment scheme, OPL was treated by electrochemical oxidation followed by treatment in a constructed wetland pilot unit (CW-A). The second scheme comprised of treatment in a constructed wetland followed by electrochemical treatment (CW-B). The constructed wetlands units were planted with *Phragmites australis* (reeds) and were fed intermittently at organic loadings between 5 and 15 g COD m^{-2} d^{-1} and a residence time of 3 d. Electrochemical oxidation (EO) was performed for 360 min at 20 A.

Treatment of OPL in the wetland at 15 g COD m^{-2} d^{-1} led to mean COD and color reduction of 86% and 77%, respectively; the wetland effluent with a COD of about 800 mg L^{-1} was polished electrochemically for 360 min after which the overall COD and color removal of the combined process (i.e. CW-B/EO) was around 95%, while the final effluent was not toxic against the marine bacteria *Vibrio fischeri*.

Electrochemical oxidation of the original OPL at COD values between 6250 and 14 100 mg L^{-1} led to moderate COD and color reduction (i.e. less than 40%) through zero order kinetics. When this was coupled to constructed wetland post-treatment (i.e. EO/CW-A), the overall COD and color removal was 81% and 58%, respectively. The decreased efficiency may be assigned to the increased toxicity of the electrochemically treated effluent which was only partially removed in the natural treatment system.

1. Introduction

Constructed wetlands (CW) have long proven to be efficient, low-cost and low-maintenance treatment systems for removing organic matter, nutrients and suspended solids from municipal or domestic wastewaters. In recent years, CW have also been researched for the treatment of runoff (e.g. urban, highway, airport, greenhouse), agricultural waste streams (e.g. dairy, pig farms and aquaculture wastes) and industrial effluents (Vymazal, 2009). Regarding the latter, treatment by CW is less documented since the high organic loadings and/or toxicity of industrial wastewaters may limit CW applications.

* *Corresponding author*. Tel.: +30 28210 37795; fax: +30 28210 37846.
E-mail address: diamad@dssl.tuc.gr (E. Diamadopoulos).
0043-1354/$ – see front matter
doi:10.1016/j.watres.2010.02.015

Calheiros et al. (2007) reported that treatment of tannery wastewaters in a horizontal-flow CW at organic loadings between 33.2 and 160.2 g COD m^{-2} d^{-1} could lead to 41–73% COD and 41–58% BOD_5 reduction, respectively. A CW comprising two vertical- and a horizontal-flow beds and operating at 70 g COD m^{-2} d^{-1} loading was capable of removing 90% of color and 84% of COD from a textile effluent (Bulc and Ojstrsek, 2008). In other recent studies, CW have been employed to degrade textile dyes in model aqueous solutions (Davies et al., 2009, 2008) or simulated effluents (Nilratnisakorn et al., 2009; Ong et al., 2009). The performance of a three-bed CW to treat sanitary landfill leachate was monitored over a period of 7 years showing, on average, 50–60% reduction of COD, BOD_5, ammonia nitrogen and phosphorous (Bulc, 2006). Other industrial pollutants that have been considered for CW treatment are associated with oil refineries (Aslam et al., 2007) and the petrochemical industry (Eke and Scholz, 2008), industrial parks (Chen et al., 2006), ethanol production (Sohsalam and Sirianuntapiboon, 2008) and the use of formalin (Herrera Melian et al., 2008a).

Olive oil extraction, an agro-industrial activity of vital economic significance to many Mediterranean countries, is unfortunately associated with the generation of large quantities of wastewaters 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 recent review article (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 adsorbent for heavy metals removal (Malkoc et al., 2006; Pagnanelli et al., 2005) and biogas production (Borja et al., 2005). Although the extraction process itself does not generate any wastewaters, leachates associated with raw pomace storage in open-air conditions prior to processing are likely to occur due to both pomace weathering and its high moisture content (around 50% for olive pomace coming from three-phase olive mill decanters and 65% for olive pomace from two-phase decanters).

Despite the accumulated experience in OMW treatment, information regarding the treatability of olive pomace leachate (OPL) is scarce. We recently proposed (Mavros et al., 2008) a train treatment comprising alum coagulation, activated carbon adsorption and electrochemical oxidation over boron-doped diamond (BDD) electrodes to treat OPL yielding a low-COD (i.e. about 150 mg L^{-1}), colorless and solids-free but yet ecotoxic effluent. Similarly, there is very little known on the use of CW to treat agro-industrial effluents associated with the olive industry. Bubba et al. (2004) employed a horizontal-flow CW to treat OMW that had been precipitated by lime to remove suspended solids and diluted several times with the effluent of an activate sludge plant to reduce the concentration of inhibitory/recalcitrant organics. Under these conditions, the process could remove, on average, 74% and 83% of inlet COD and polyphenols, respectively; nonetheless, the outlet COD was still quite high (i.e. between about 1 and 7.5 g L^{-1}). Coupling CW to advanced oxidation has merely been reported in the literature. Herrera Melian et al. (2008b) proposed TiO_2 photocatalysis as a precursor to CW to treat model solutions of phenol, while a similar approach was described by Arana et al. (2008) for the degradation of various commercial pesticides.

Treatment of industrial effluents by a combination of separation, biological and advanced oxidation processes is conceptually advantageous (Comninellis et al., 2008). Of the latter, 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 (Chatzisymeon et al., 2009; Deligiorgis et al., 2008; Canizares et al., 2007) have demonstrated the application of BDD electrochemical oxidation in the treatment of olive-related, agro-industrial effluents.

This study aims at developing a hybrid process for the pilot treatment of agro-industrial effluents. This is done through testing a low-cost, low-tech and easy-to-handle natural system (vertical-flow constructed wetland) and an emerging advanced oxidation technology (BDD electrochemical oxidation) for the treatment of OPL, a high-COD industrial effluent from olive oil processing. The treatment efficiency, in terms of decolorization and mineralization, of the individual processes and their combinations is evaluated as a function of various operating parameters. Furthermore, the acute toxicity of treated OPL against the marine bacteria *Vibrio fischeri* is monitored to assess whether the effluent can be disposed of in water bodies.

2. Materials and methods

2.1. Olive pomace leachate (OPL)

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 at the plant consists of around 50% water, 45% crude olive cake and 5% pomace oil. The pomace undergoes drying and solvent extraction with hexane to recover oil, while the process also generates a solid residue which is used as fuel. In general, no liquid wastes are generated as a result of oil recovery. However, during pomace storage in open-air silos, weathered pomace leaches an effluent which is collected and sent to an evaporation pond.