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Electrochemical mineralization of anaerobically digested olive mill wastewater

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ABSTRACT

A novel approach was developed for the energetic valorisation and treatment of olive mill wastewater (OMW), combining anaerobic digestion and electrochemical oxidation. The electrochemical treatment was proposed as the final step to mineralize the remaining OMW fraction from the anaerobic reactor. The electrooxidation of anaerobically digested OMW was investigated over dimensionally stable anodes (DSAs). RuO_2 based anode was significantly more efficient than IrO_2-type DSA, mainly for the COD removal. IrO_2 based anode promoted a selective oxidation of phenols and colour removal. For instance, after an electrolysis charge of 10.4×10^4 C L^{-1}, COD removals of 14 and 99%, phenols removals of 91 and 100% and colour removals of 85 and 100% were obtained for IrO_2 and RuO_2 DSAs-type, respectively. The electrochemical post-treatment was effectively performed without using a supporting electrolyte and in the presence of the solids that remained from the anaerobic process. The achievement of the required effluent quality for sewer systems disposal depends on the operating conditions of the anaerobic process. Consequently, special care must be taken with the chloride and nitrogen levels that may surpass the legal discharge limits. The electrochemical oxidation over RuO_2 based DSA is an appropriate second-step treatment for OMW disposal, after the recovery of its energetic potential.

1. Introduction

Effluents from olive oil production are persistently discarded into the rivers and water streams. The polluting content of olive mill wastewater (OMW) is incompatible with the domestic or even industrial wastewater treatment plants capacity. The scientific research on the treatment and valorisation of OMW started more than 50 years ago (Niaounakis and Havaldakis, 2006). However, few attempts have been done to scale-up the process (Michailides et al., 2011).

Biological treatment of polluted water is one of the most economical processes if the wastewater does not contain toxic and/or recalcitrant pollutants. If it does, one interesting alternative is to use a coupled process: partial oxidation-biological treatment (Kapalka et al., 2010a). The oxidation processes are commonly used as pretreatments to decrease the toxicity and increase the biodegradability of the wastewater (Khoufi et al., 2006; Patoni et al., 2010). However, the pretreatments concomitantly degrade organics that could be easily converted to methane by anaerobiosis, decreasing the energetic potential of the effluent. If the biological treatment can be applied directly, the oxidation process as a post-treatment is more economically feasible. Few studies have been reported about integrated processes combining

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anaerobic digestion with electrochemical oxidation. The electrochemical oxidation of anaerobically digested synthetic vegetable wastewaters (Panizza and Cerisola, 2004), dairy manure (Ihara et al., 2006) and leachate (Wang et al., 2001) were successfully applied. This process sequence has never been applied to OMW mineralization.

The electrochemical degradation of raw OMW has been performed over different anode materials, Ti/RuO_2 (Un et al., 2008), Ti/IrO_2 (Chatzisymeon et al., 2009), Ti/TiRuO_2 (Panizza and Cerisola, 2006), Ti/Pt (Israilides et al., 1997; Kotta et al., 2007) and Ti/Ta/Pt/Ir (Gotsi et al., 2005; Giannis et al., 2007) anodes. The most recent and remarkable results in terms of complete mineralization were obtained over Ti/RuO_2 (Un et al., 2008) and Ti/TiRuO_2 (Panizza and Cerisola, 2006). Un et al. (2008) performed the electrooxidation of raw OMW (41 kg COD m^{-3}) and they almost achieved the complete conversion of COD (99.6%), phenols, turbidity (99.85%) and oil and grease (99.54%). Panizza and Cerisola (2006) completely eliminated the COD content and achieved the decolourization of the effluent. Nevertheless, most of these studies were performed with electrolyte addition (NaCl) and with the soluble fraction of the effluent. Kotta et al. (2007) studied the effect of the presence of solids during the electrochemical oxidation of olive mill effluent over Ti/Pt anodes and concluded that the OMW solids may partially impede the electrooxidation process. Consequently, they proposed a pre-conditioning step before electrolysis to separate the solid fraction. Furthermore, Israilides et al. (1997) concluded that the electrolytic method for the total oxidation of OMW is possible but not economically feasible. Bioenergy recovery from raw olive mill wastewater (OMW) was accomplished by anaerobic digestion as a first-step treatment (Gonçalves et al., 2012a,b). Nevertheless, a post-treatment is required to degrade recalcitrant compounds and, consequently, attain the discharge limit values. After the anaerobic treatment of OMW, the main issues are related to the remaining organic matter (COD), recalcitrant phenolic compounds (40–50%) and effluent dark-brown colour.

In this work, the applicability of electrochemical oxidation as the second and final treatment of OMW was studied for the first time. The performance of RuO_2 and IrO_2 based DSAs was compared by cyclic voltammetry and bulk electrolysis. The experiments were carried out with alkaline samples from the anaerobic reactors comprising 1–10 g COD L^{-1}, depending to the digester operational conditions. The presence of solids and the requirement of a supporting electrolyte were evaluated. Additionally, two distinct effluents from different anaerobic reactors operating at the harshest conditions were tested and compared at the best defined electrochemical conditions.

2. Material and methods

2.1. *Effluents characterization*

OMW1 and OMW2 were obtained from two different olive oil mills in Amarante and Rio Maior (Portugal), respectively. Both olive mills have a three-phase olive oil extraction process. The effluents designated as AD1a and AD1b were obtained from an anaerobic digester treating diluted OMW1 at concentrations of 48 and 10 g COD L^{-1}, respectively (Gonçalves et al., 2012a). The effluent designated as AD2 was obtained from an anaerobic reactor treating OMW2 complemented with 17% v/v of piggery effluent, corresponding to an influent COD concentration of 40.7 g COD L^{-1} (Gonçalves et al., 2012b). The effluents were stored at −20 °C until being used. The effluents were characterized and the mean values obtained are summarized in Table 1.

2.2. *Cyclic voltammetry*

The electrochemical measurements were performed in a conventional three electrodes/two compartments cell. Platinum (area = 7.85E−3 cm^2) and iridium oxide (IrO_2) or ruthenium oxide (RuO_2) type dimensionally stable anodes supplied by De Nora Tech, Inc. (geometric area = 0.5 cm^2) were employed as working electrodes, being its potential controlled against the saturated calomel electrode (SCE) by an EG&G Princeton Applied Research potentiostat model 273. A large area platinum sheet was used as counter electrode. The experiments have been carried out at room temperature (20 ± 2 °C) in the presence and absence of raw and anaerobically digested OMW with 0.1 M KNO_3 as supporting electrolyte. The samples were centrifuged before the experiments. The electrooxidation studies were performed by cyclic voltammetry in the potential range of $-0.8 < E < 1.6$ V vs. SCE at 100 mV s^{-1} scan rate.

2.3. *Bulk electrolysis*

The electrochemical oxidation of anaerobically digested OMW was performed at room temperature and atmospheric pressure. Potentiostatic experiments were performed in a glass

Table 1 – Effluents characterization.

Parameter	OMW1	AD1a	AD1b	OMW2	AD2
pH	4.7 ± 0.1	8.6 ± 0.2	8.9 ± 0.17	5.1 ± 0.1	8.0 ± 0.2
Conductivity (mS cm^{-1})	6.9 ± 0.1	7.9 ± 0.6	5.0 ± 0.1	10.6 ± 0.1	11.6 ± 0.9
COD_{total} (g L^{-1})	130.1 ± 7.4	7.3 ± 0.5	1.5 ± 0.1	44.5 ± 1.1	8.1 ± 0.2
$COD_{soluble}$ (g L^{-1})	69.4 ± 1.4	5.6 ± 0.5	1.1 ± 0.1	38.0 ± 0.4	6.7 ± 0.2
TP (gallic acid, g L^{-1})	4.3 ± 0.4	0.7 ± 0.1	0.1 ± 0.0	3.3 ± 0.2	1.5 ± 0.0
Colour (Abs; dil. 1:20)	1.12 ± 0.08	0.72 ± 0.02	0.17 ± 0.01	1.46 ± 0.08	1.27 ± 0.18

Average value ± error 95% confidence.
OMW1 and OMW2 – Raw OMW; AD1a and AD1b – anaerobically digested OMW1; AD2 – anaerobically digested OMW2.