

## Olive mill wastewater conversion into a stream for agricultural application: anaerobic and electrochemical processes

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### ABSTRACT

Anaerobic digestion and the electrochemical oxidation were used to valorise the effluent of the olive oil production (olive mill wastewater, OMW). Anaerobiosis was realized in an anaerobic hybrid reactor, operating at a low hydraulic retention time of about 6 days and digesting the raw OMW, without any previous substrate alterations. Electrochemical process worked with a dimensionally stable anode (DSA), without adding further support electrolytes, at low potential values and at moderate dilution factor of the substrate.

Comparatively, anaerobic digestion provides the conversion of the greatest fraction of the organic matter content (about 81-82 % of COD, chemical oxygen demand) into a gas energy carrier (biogas) but it does not perform the OMW colour removal. On the other hand, the electrochemical approach is energy demanding but it removes completely the colour and phenols content. The fact that this process reduces the influent COD in 70 % and it represents a loss of the energy potential, reinforces the idea that the electrochemical oxidation can be advantageously associated with the anaerobic digestion as a second step of OMW agricultural valorisation.

**Keywords:** OMW, anaerobic digestion, electrochemical degradation, wastewater remediation, DSA.

### INTRODUCTION

Olive Mill Wastewater (OMW) is the olive oil extraction liquid waste and represents a serious environmental problem in Mediterranean countries. This is mainly due to its high load of phenolic matter and lipid content and to the inexistence of a technically feasible, economically viable, and socially acceptable management solution (Marques, 2001).

Biological treatments, like anaerobic digestion, is an advantage and a viable option concerning OMW. However, the operation under low hydraulic retention time (HRT) results into a low phenol and a null colour removal efficiencies (Marques, 2001; Sampaio et al. 2011).

Advanced oxidation processes (AOPs) are an appealing option for barely biodegradable wastewaters treatment. Typically AOPs involve the generation and use of highly reactive hydroxyl free radicals ( $\cdot\text{OH}$ ) as a strong oxidant ( $E^0$  2.80 V vs. SHE, Standard Hydrogen Electrode) to destroy compounds that are hardly oxidized by conventional methods. The non selective nature in their mode of attack and the ability to operate at normal temperature and pressure, allow an effective oxidation of almost all substrates without restriction to specific classes or groups of compounds, as compared to other oxidants, like oxygen, ozone and chlorine (Oller et al., 2011; Comninellis and Chen, 2009).

Among the existing AOPs, the electrochemical methods have many appealing features. There is no need to use chemicals. In fact, only electrical energy is consumed for the mineralization of organic pollutants. Additionally, the possibility of oxidize organic material over

dimensionally stable anodes (DSA, usually a titanium base metal covered by a thin layer of a metal oxide or non-stoichiometric metal oxides, MO<sub>x</sub>) is another relevant advantage (Comninellis and Chen, 2009).

OMW electrochemical treatment under DSA anodes had been subject of several studies but dealing with highly diluted OMW samples (Papastefanakis et al., 2010; Chatzisyneon et al., 2009) and/or addition of supporting electrolytes (Kotta et al., 2007; Gotsi et al., 2005; Panizza and Cerisola, 2006).

Those experimental conditions allow the use of high electric potential/current intensities, which result in unnecessary energy consumptions on secondary reactions, such as extensive oxygen evolution, being only a small part of the evolved O<sub>2</sub> use fully consumed in the mineralization process. Moreover, the lowering of the ohmic drop through the use of supporting electrolytes, may give rise (if NaCl is employed) to the formation of organochlorine compounds with high toxicity (Gotsi et al., 2005) and to a highly conductive effluent.

The objective of the present work is to develop an approach to OMW valorization in order to overcome the limitation of the anaerobic digestion to remove colour. Advantages and drawbacks of the two processes - anaerobic digestion and the electrochemical oxidation - will be addressed.

## MATERIAL AND METHODS

The OMW used in this study was collected during the campaign of 2010 in an olive oil production plant located in Rio Maior (Portugal), equipped with a three-phase extraction process. The unit is characterized by an average olive oil production capacity of 42 m<sup>3</sup> year<sup>-1</sup>.

The chemical oxygen demand (COD) was evaluated by using commercial Merck Tests. Colour measurements were assessed by determining the optical absorbance at 390 nm, using a Hitachi U-2000 Spectrophotometer and total phenolic compounds (TPh) were expressed as caffeic acid equivalents, via a modified Folin-Ciocalteu method (Singleton and Rossi, 1965). The anaerobic hybrid reactor operation is described elsewhere (Sampaio et al., 2011; Gonçalves et al., 2012a).

The anodic oxidation of the OMW was performed in a conventional three electrodes/one compartment glass cell, comprising a stainless steel cathode and a RuO<sub>2</sub> type DSA electrode (geometric area = 5.74 cm<sup>2</sup>), kindly supplied by De Nora Tech, Inc. The experiments were conducted using a DC power supply (PeakTech 6010 D), being the anode potential held at 1.8 V against the saturated calomel electrode (SCE), following with the voltammetric data for the OMW organic matter oxidation retrieved previously (Gonçalves et al., 2008; Gonçalves et al., 2012b). OMW was initially centrifuged, then diluted (original COD<sub>T</sub> of 55.28 kg m<sup>-3</sup>) and kept at 4°C until use. Relevant properties of the initial solution are summarized in Table 1. All experiments were carried out at room temperature. The electrolytic process operated under low electric potential values, low dilution factors and without addition of supporting electrolyte.

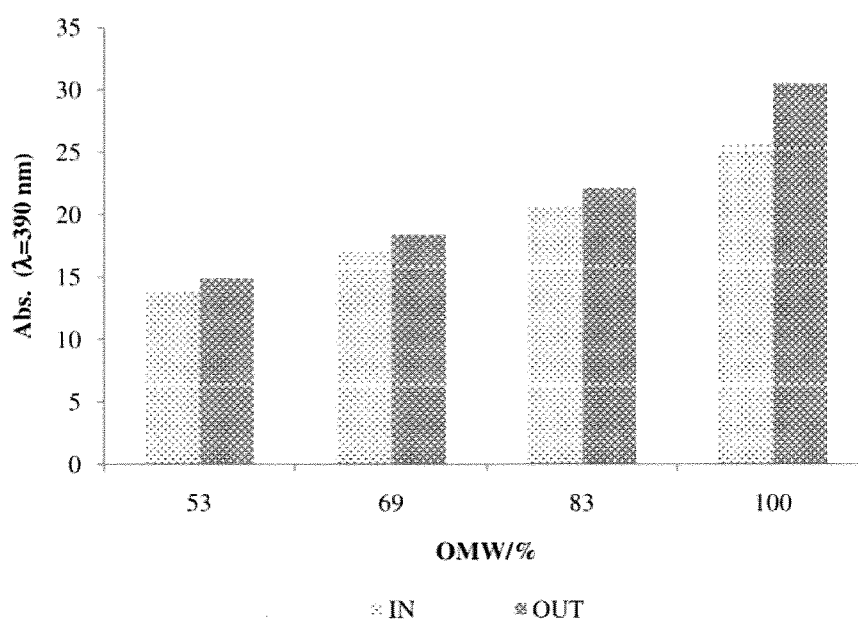
**Table 1** Substrate initial characteristics

$V_i$ ( $10^{-6} \text{ m}^3$ )	$\text{COD}_i$ ( $\text{kg}/\text{m}^3$ )	$\text{Colour}_i$	$\text{TPh}_i$ ( $\text{kg}/\text{m}^3$ )
50	6.38	5.000	<b>0.408</b>

$V_i$  – substrate initial volume;  $\text{COD}_i$  – initial chemical oxygen demand,  $\text{TPh}_i$  – initial total phenols

## RESULTS AND DISCUSSION

In Figure 1 is shown that during the anaerobic processing of OMW (at several concentrations), at 37 °C with about 6 days hydraulic retention time, an increase of the anaerobic outlet liquid flow colour intensity was observed. The absorbance values changed from 13.9 – 25.7 (influent) to 14.9 – 30.5 (outlet).



**Fig. 1.** Hybrid digester data: Colour assayed by the measurement of the absorbance at 390 nm; IN- influent; OUT-effluent; OMW as % (v/v).

The main responsible for the dark colour of OMW is the presence of high molecular weight phenolic compounds, as documented in several studies (Marques, 2001; Sayadi et al., 2000; Dareioti et al., 2009). Due to the high dimension of the polymerized phenolic compounds, they hardly penetrate the cell membrane (Healy and Young, 1979), preventing their degradation. That the colour increase after the anaerobic step is a known occurrence already mentioned by Marques (2001). It can be due to a polymerization (Sayadi et al., 2000) or dissolution of polymerized phenolic compounds. In this last case, the acid is transformed into the highly soluble saline form (phenoxide ion: Reaction 1) (Brown et al., 2011) that results from the pH implementation during anaerobic process (Sampaio et al., 2011).



Despite the energy consumption instead of energy production, the electrochemical approach offers an efficient route to decontaminate OMW with simultaneous reduction of the colour intensity. In this work the degradation of the effluent was carried out over  $\text{RuO}_2$  based

dimensionally stable anodes by anodic oxidation in potentiostatic mode at low applied electrode potential without addition of any supporting electrolyte. As illustrated in Figure 2, the experimental time of the trials was quite long (up to 800 hours), when compared with other reported works on the OMW electro chemical treatment (Papastefanakis et al. 2010; Kotta et al., 2007; Gotsi et al., 2005; Israilides et al., 1997). This is due to the fact that, in the present work, all the adverse conditions of high initial COD, low applied potential and absence of supporting electrolyte are assembled. The low ratio DSA geometric area/OMW volume also contributed to this result.

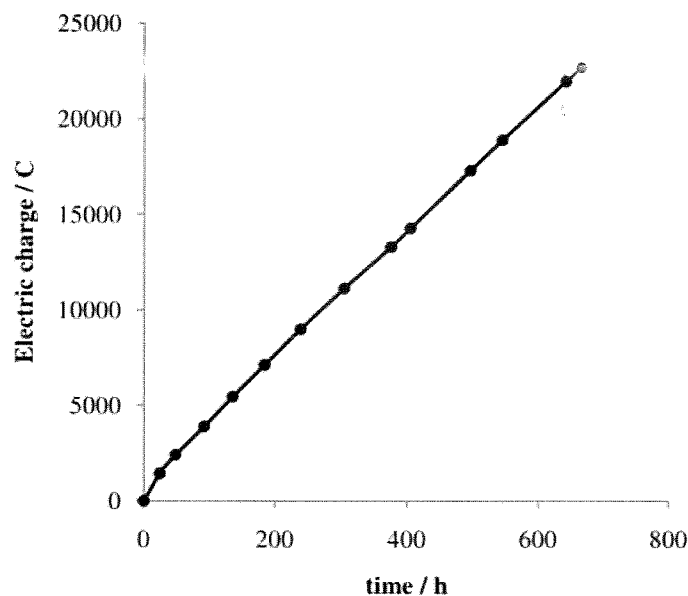


Fig. 2 Consumption of electric charge during an electrolysis trial

During the electrolysis experiments some critical solution parameters were measured, namely the colour intensity, total phenol concentration and chemical oxygen demand. The obtained results are depicted in Figure 3. Under our experimental conditions, a charge flow of about 13 kC reduces both the colour and total phenols to negligible values and removes about 70% of the organic matter measured as COD.

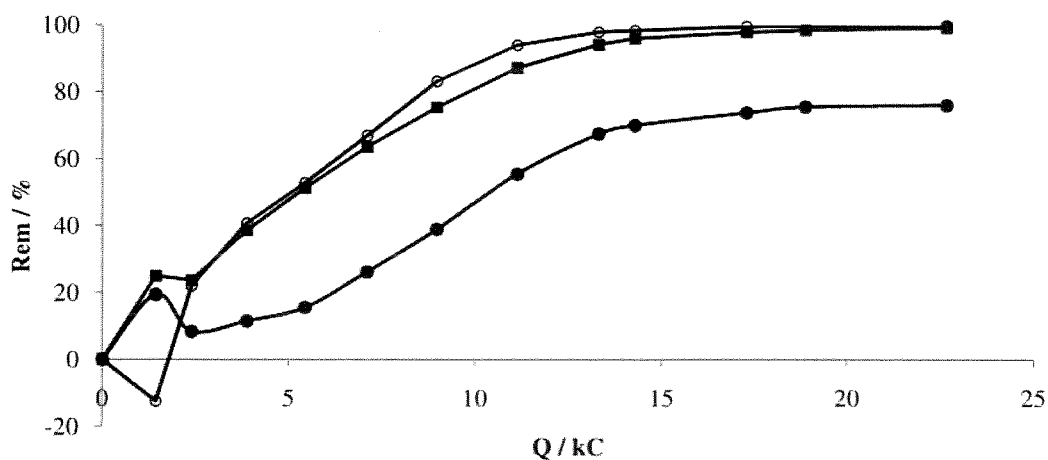


Fig. 3 Colour (open circles), TPh (solid squares) and COD (solid circles) removal performance, in percentage, as function of the passed electric charge

At the beginning of the experiment it was noticed a thin film formation on the DSA surface, originating anomalous values of the monitored solution parameters. This is a known phenomenon that commonly happens when the electrooxidation takes place at a fixed anodic potential before the oxygen evolution and is accentuated when substrates rich in aromatic compounds such as phenols are present (Chatzisyneon et al., 2009; Comninellis and Chen, 2009).

Compared to the colour and phenolic matter removals, the COD elimination efficiency was quite low. This behaviour is due to the "active" nature of RuO<sub>2</sub> based DSA that typically allows only a partial oxidation of the organic material (Comninellis and Chen, 2009).

Indeed, the mechanism involved in the mineralization of organic matter by an active anode such as the RuO<sub>2</sub>, comprises the double bonds and aromaticity disruption by direct oxidation but not the total mineralization of the substrate to CO<sub>2</sub> and water. Since the double bonds are responsible for the visible light absorption, the efficiency in the colour removal is very high.

## 1. CONCLUSIONS

The electrochemical processing of OMW through the anodic oxidation of the effluent on RuO<sub>2</sub> based DSA electrodes has been proven a suitable methodology for a successful effluent remediation. Such operation can be achieved without addition of supporting electrolyte to the effluent and operating at low potential values. Under these conditions, nearly complete colour and phenols removals were achieved and a reduction of 70% of the chemical oxygen demand was attained. The electrochemical approach must then be considered as an important stage to treat the effluent prior or after the anaerobic digestion step. Being used as a pre-treatment of OMW, it can act over the recalcitrant compounds to anaerobic digestion, without compromising too much the energetic potential. If it employed as a post-treatment, it will remove the effluent colour and the phenols that were not processed in the anaerobic digestion stage and provides the energy recovery contained in the raw OMW.

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