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Remediation of a winery wastewater combining aerobic biological oxidation and electrochemical advanced oxidation processes

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ABSTRACT

Apart from a high biodegradable fraction consisting of organic acids, sugars and alcohols, winery wastewaters exhibit a recalcitrant fraction containing high-molecular-weight compounds as polyphenols, tannins and lignins. In this context, a winery wastewater was firstly subjected to a biological oxidation to mineralize the biodegradable fraction and afterwards an electrochemical advanced oxidation process (EAOP) was applied in order to mineralize the refractory molecules or transform them into simpler ones that can be further biodegraded. The biological oxidation led to above 97% removals of dissolved organic carbon (DOC), chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD_5), but was inefficient on the degradation of a bioresistant fraction corresponding to 130 mg L^{-1} of DOC, 380 mg O_2 L^{-1} of COD and 8.2 mg caffeic acid equivalent L^{-1} of total dissolved polyphenols. Various EAOPs such as anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2), electro-Fenton (EF), UVA photoelectro-Fenton (PEF) and solar PEF (SPEF) were then applied to the recalcitrant effluent fraction using a 2.2 L lab-scale flow plant containing an electrochemical cell equipped with a boron-doped diamond (BDD) anode and a carbon-PTFE air-diffusion cathode and coupled to a photoreactor with compound parabolic collectors (CPCs). The influence of initial Fe^{2+} concentration and current density on the PEF process was evaluated. The relative oxidative ability of EAOPs increased in the order AO-H_2O_2 < EF < PEF ≤ SPEF. The SPEF process using an initial Fe^{2+} concentration of 35 mg L^{-1}, current density of 25 mA cm^{-2}, pH of 2.8 and 25 °C reached removals of 86% on DOC and 68% on COD after 240 min, regarding the biologically treated effluent, along with energy consumptions of 45 kWh (kg DOC)$^{-1}$ and 5.1 kWh m^{-3}. After this coupled treatment, color, odor, COD, BOD_5, NH_4^+, NO_3^- and SO_4^{2-} parameters complied with the legislation targets and, in addition, a total dissolved polyphenols content of 0.35 mg caffeic acid equivalent L^{-1} was found. Respirometry tests revealed low biodegradability enhancement along the SPEF process.

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1. Introduction

Winery wastewaters are generated by the different activities carried out during processing and cleaning operations in wineries. The production of this kind of effluent is seasonal, which leads to significant variations in volume and organic load produced throughout the year, according to the type of wine (red, white, rosé, sparkling, etc.), the phase of production (grape harvesting, crushing, fermentation, aging, filtration, bottling, etc.), the processing operations and the cleaning practices. Typically, winery wastewaters are characterized by pH values from 2.5 to 6.0 and chemical oxygen demand (COD) values of 0.8–70 g L^{-1} (Petruccioli et al., 2002; Silva et al., 2011; Ioannou and Fatta-Kassinos, 2013; Orescanin et al., 2013; Souza et al., 2013). The major constituents of such effluents are organic contaminants like organic acids (tartaric, lactic and acetic), sugars (glucose and fructose) and alcohols (ethanol and glycerol) and also recalcitrant high-molecular weight compounds like polyphenols, tannins and lignins (Chapman et al., 2001). The release of winery wastewaters into natural aquatic environments without adequate treatment can cause negative effects on the oxygen balance, bad odors and decrease of natural photoactivity due to color and turbidity.

Fig. 1 shows the evolution of research articles on winery wastewaters treatment from 1995 to 2013. The proposals for the treatment of this kind of effluent were introduced in 1995 but the interest of the scientific community on this topic rose only since 2005. Nevertheless, only 88 publications along all years have been carried out. The major focus was on biological treatments (e.g. Petruccioli et al., 2002; López-Palau et al., 2009; Ganesh et al., 2010; Silva et al., 2011) since the high biodegradability of this kind of effluents can often justifies this choice. However, such treatments may not be able to degrade the bioresistant fraction of these wastewaters and hence alternative treatment strategies have been investigated. Among them, the application of advanced oxidation processes (AOPs) as a single stage treatment acquired significance. The main applied AOPs have been (i) ozone and ozone based processes (O_3, O_3/UV, O_3/UV/H_2O_2) (Lucas et al., 2010); (ii) catalysis with titanium dioxide (TiO_2) and combined with H_2O_2 (TiO_2/H_2O_2) and $S_2O_8^{2-}$ (TiO_2/$S_2O_8^{2-}$) (Lucas et al., 2009a); and (iii) Fenton's reaction based processes like photo-Fenton (Fe^{2+}/H_2O_2/UV) (Mosteo et al., 2006), solar photo-Fenton (Fe^{2+}/H_2O_2/UV–Vis) (Lucas et al., 2009a) and ferrioxalate-assisted solar photo-Fenton (Monteagudo et al., 2012). In contrast, the combination of biological oxidation and AOPs was not extensively studied, only in 8 published research articles (Sigge et al., 2005; Mosteo et al., 2007, 2008; Anastasiou et al., 2009; Lucas et al., 2009b; Ioannou et al., 2013; Ioannou and Fatta-Kassinos, 2013; Souza et al., 2013). The AOPs have been used both as pretreatment and post-treatment steps, although the recommended treatment strategy for high biodegradable wastewaters, like winery effluents, may combine (i) a biological pretreatment to remove the biodegradable compounds; (ii) a further AOP to convert the bioresistant molecules into simpler ones that are able to be further biodegraded; and (iii) a final biological polishing step (Oller et al., 2011). This integrated system may lead to the total mineralization of organics along with the minimization of the total treatment cost. Regarding the electrochemical processes, few studies have been performed, including only electrocoagulation and electrochemical oxidation methods (Kirzhner et al., 2008; Kara et al., 2013; Orescanin et al., 2013). To the best of our knowledge, no reports on electrochemical AOPs (EAOPs), alone or in combination with other processes, were disclosed. In fact, the application of EAOPs based on Fenton's reaction chemistry to the treatment of real wastewaters is reduced and mainly refers to electro-Fenton (EF) technology (Wang et al., 2010; Zhu et al., 2011; Da Pozzo and Petrucci, 2013).

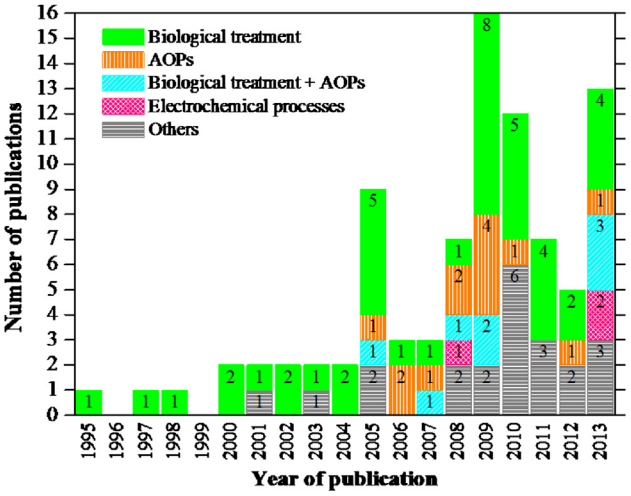

Fig. 1 – Research articles on winery wastewater remediation per year arranged by treatment process. Source: http://www.scopus.com/, December 2013, search for "winery wastewater treatment" with further manual refinement to exclude misclassified articles and distribute them by treatment process.

EAOPs with H_2O_2 electrogeneration may reduce the cost related to H_2O_2 consumption, which is the main cost factor regarding consumables for traditional AOPs based on Fenton's reaction (Malato et al., 2009). In these EAOPs, H_2O_2 is directly electrogenerated at the cathode of the electrochemical cell from the two-electron reduction of injected O_2 via Eq. (1) (Brillas et al., 2009):

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

Good efficiencies for H_2O_2 generation from Eq. (1) have been described for various carbonaceous cathodes, with highlighting on carbon felts (Oturan et al., 2011; Mhemdi et al., 2013) and carbon-PTFE gas (O_2 or air) diffusion electrodes (Brillas et al., 2003; Moreira et al., 2013; Garcia-Segura et al., 2014).

In the EAOPs, •OH adsorbed at the anode (M) surface, denoted M(•OH), are formed as intermediate of O_2 evolution from water oxidation through Eq. (2) (Brillas et al., 2008):

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \quad (2)$$

When a one-compartment cell is utilized, the simplest EAOP is the anodic oxidation with electrogenerated H_2O_2 (AO-