



New approaches on heterogeneous electro-Fenton treatment of winery wastewater



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ABSTRACT

A new approach on heterogeneous electro-Fenton of winery wastewater was investigated. The high organic load and the dependence on the wine industry period makes necessary to find an appropriate treatment able to efficiently reduce the environmental risk of this waste. For this purpose, the electro-Fenton process was improved by searching different catalyst supports (manganese alginate gel beads (Mn-AB); iron alginate gel beads (Fe-AB) and iron loaded activated carbon (Fe-AC)) and evaluating the applied potential difference effect. Fe-AC attained a fast decolorization and high degradation results at 15 V. To further understand the main degradation mechanisms on this new catalyst, the contribution of the HO[•] generated in solution and on the anode surface was analyzed. In addition, the positive effect of nickel foam on an extra input of H₂O₂ production through the generation of [•]O₂⁻ and its effect on the treatment were proved.

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1. Introduction

The disposal of wastes from industrial and domestic sources is becoming a serious problem throughout the world. Winemaking is one of the industries whose wastes are classified as hazardous to the environment. A huge number of liters of winery wastewater (WW), that are characterized by a low pH value, high organic content, presence of color and unpleasant odors are originated every-year, which constitutes both environmental and aesthetic problems [1,2]. The industrial production of wine follows different steps such as: vintage, racking, or bottling; that produce different volumes of wastewater with different characteristics and seasonal variability [3]. Color on wines is due to the presence of phenols, in the case of red wines it is mainly due to the flavonoid group [4]. Soluble sugars (fructose and glucose), organic acids (tartaric, lactic and acetic), alcohols (glycerol and ethanol) and high-molecular-weight compounds, such as polyphenols, tannins and lignin are the main organic compounds on WW [5]. Furthermore, the addition of sulfur dioxide (SO₂) is widely used for its antioxidant and preservative properties, which hinders the efficiency of traditional degradation treatments [6].

Due to the complexity of WW, principally the high chemical oxygen demand (COD) values that vary from 500 to 45000 mg/L [3], their treatment increases the cost of wine production. Thus, the identification of effective and low cost degradation processes has increased the attention of researches worldwide [7,8].

Advanced oxidation processes (AOPs) are degradation treatments that involve the generation of highly reactive radical species that are known for their ability to mineralize a wide range of organic compounds. Among them, the electro-Fenton treatment has attracted particular attention in the research community [9–11]. In this process the degradation of organic matter is produced by direct oxidation and transfer of one electron and through indirect electrochemical oxidation from hydroxyl radicals (HO[•]), a nonspecific and highly oxidative radical that is responsible of high degradation values [12–14]. The generation of HO[•] from the electro-Fenton process corresponds with Eq. 1 (electrochemical generation on the electrode surface), Eq. 2 (activated carbon catalyst of HO[•]) and Eq. 3 (transition metal catalyst of H₂O₂) from Table 1. The electro-Fenton process has the advantage of the *in situ* production of H₂O₂ (Eq. 4), avoiding potential risks arisen from transportation, storage and handling; besides, catalysts, usually iron or other transition metals, are continuously recycled due to the redox reactions (Eq. (6)) [15].

The iron catalyst activity can be substituted by other transition metals (such as Mn, Cd, Co, Cr, Cu, Mn, Ni, and Zn) [16]. Fernández de Dios et al. [17] demonstrated the feasibility of Mn alginate gel

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Table 1

Main reactions taking place in the heterogeneous electro-Fenton configuration developed in this work.

Eq.	Description	Reaction	Result
1	Anionic oxidation	$EM^1 + H_2O \rightarrow EM(HO^\bullet) + H^+ + e^-$	HO [•] generation
2	AC catalyst of HO [•]	$AC(e_{cb}^-) + O_2 \rightarrow AC(O_2^\bullet)$ $AC(h_{vb}^+) + H_2O \rightarrow AC(2HO^\bullet) + H^+$ $AC(O_2^\bullet) + H^+ \rightarrow AC(2HO^\bullet)$	
3	Metal ² catalyst of HO [•]	$H_2O_2 + Metal^{(n)+} \rightarrow HO^\bullet + OH^- + Metal^{(n+1)+}$	
4	Oxygen reduction	$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2$	H ₂ O ₂ generation
5	1) Superoxide generation 2) Superoxide reduction	$Ni + 2O_2 \rightarrow Ni^{2+} + 2 \cdot O_2^-$ $\cdot O_2^- + e^- + 2H^+ \rightarrow H_2O_2$	
6	Metal reduction	$Metal^{n+} + e^- \rightarrow Metal^{(n+1)+}$	
7	HO [•] reactive action	$R + HO^\bullet \rightarrow CO_2 + H_2O$	Catalyst recycling
8	Reactions of Metal in excess	$Metal^{(n+1)+} + HO^\bullet \rightarrow Metal^{n+} + OH^-$	Degradation of organic compound
9		$H_2O_2 + Metal^{n+} \rightarrow Metal^{(n+1)+} + HO_2^\bullet + H_2O$	HO [•] consumption H ₂ O ₂ consumption

¹ EM is electrode surface.² Metal is a transition metal (Fe, Mn or Ni).

beads as catalysts for HO[•] production from H₂O₂ and their effective behaviour in continuous and batch processes for the treatment of recalcitrant organic pollutants.

The immobilisation of catalyst facilitates its reuse [17–19] and the development of continuous processes avoiding its continuous addition on the inflow and its loose on the outflow [18].

Several studies have focussed on metal sorption or entrapment in different matrixes for their use in Fenton, electro-Fenton, photo-Fenton or similar processes. The metal can be immobilised in organic structures such as hydrogels [12,13,17,20] that have a good performance, though these structures are fragile for long treatment times. On the other hand, inorganic structures for metal immobilisation have also attained successful results [19,21,22]. Nonetheless, few studies deal with supports that efficiently capture the metal catalyst and that provide catalytic properties themselves. Activated carbon (AC) is characterised by its great absorption capacity [23], therefore it can be used as Fe support; furthermore its behaviour as heterogeneous catalyst on the generation of HO[•] from dissolved oxygen in water was already proved (Eq. (2)) [24].

In addition to this, the selection of proper electrodes that increase the effectiveness of this process is a limiting factor that should be considered. Several authors demonstrated that Boron-Doped Diamond (BDD) electrode, improves the efficiency when used as anode [25–27]. Cathode material should optimise the generation of H₂O₂ among other reduction reactions [28]. Foam materials have higher reaction surface, thus the use of nickel foam as cathode can improve the production of HO[•]; furthermore the presence of nickel produces an additional H₂O₂ generation from the superoxide radical ($\cdot O_2^-$) (Eq. (5)) [29].

The main objective of this work is to develop a highly efficient heterogeneous electro-Fenton process by optimizing the generation of HO[•] for the degradation of a highly organic loaded effluent such as WW.

2. Materials and methods

2.1. Winery wastewater

A simulated WW was generated by dilution (1:4) of commercial red wine. This WW had an initial chemical oxygen demand (COD) of 52.8 g/L; a total organic carbon (TOC) of 13.75 g/L, a pH of 3.1 and a maximum absorbance at 513 nm.

2.2. Catalysts supports

2.2.1. Fe activated carbon

For the iron load on activated carbon (Fe-AC), adsorption assays were carried out by mixing a constant volume (0.15 L) of iron

aqueous solution at 0.017 M of Fe³⁺ (Fe₂(SO₄)₃; Sigma-Aldrich, Spain) with 3 g of Activated Carbon (AC) (Granulated n°2 QP Panreac Spain) in 0.25 L Erlenmeyer flasks. The flasks were agitated in an incubator (Thermo Forma 420) at 150 rpm and 20 °C for 2 hours. In order to analyze iron adsorption, samples were taken from the supernatant and centrifuged (Sigma 3K-18) for 10 minutes at 7000 rpm to remove solid. Atomic Absorption Spectrometry (Agilent 240FS) was used to measure the iron that remained unadsorbed in the supernatant liquid. All the adsorption studies were repeated three times and the reported values are the average of measurements.

Scanning Electron Microscopy (SEM) of Fe-AC was performed on a JEOL JSM-6700F equipped with an Energy Dispersive Microanalysis (EDS) Oxford Inca Energy 300 using an accelerating applied potential difference of 20 kV (Electron Microscopy Service, C.A.C.T.I., University of Vigo).

2.2.2. Fe and Mn alginate gel beads

A solution of sodium alginate 2.0% (w/v), purchased from Prolabo (Barcelona, Spain), was dropped through a syringe into the hardening solutions composed of 0.05 M Fe³⁺ (Fe₂SO₃; Sigma-Aldrich, Spain) to create the spherical alginate beads loaded with Fe (Fe-AB) and a solution composed of 0.2 M Mn²⁺ (MnCl₂·4H₂O; Sigma-Aldrich, Spain) to create the spherical alginate beads loaded with Mn (Mn-AB).

These formed particles were cured at 4 °C for 2 hours in the gelling solution then they were filtered off and washed repeatedly with distilled water. Finally, they were stored at 4 °C in distilled water for the electrochemical studies.

2.3. Electrochemical reactor set up

The heterogeneous electro-Fenton of WW (EF-WW) was carried out in a cylindrical glass reactor with a working volume of 0.15 L. The electric field was applied by a 1.6 mm thick nickel foam cathode (Goodfellow Cambridge Ltd United Kingdom) and a BDD anode (DIACHEM[®], Germany).

The electrodes (surface 11 cm²) were placed opposite to each other at 1 cm above the bottom of the cell and with an electrode gap of 6 cm. A constant potential drop was applied with a power supply (HP model 3662). Current intensity was monitored along the process with a multimeter (Fluke 175). Continuous saturation of air at atmospheric pressure was ensured by bubbling 1 L/min of compressed air near the cathode.

Reaction mixture contains the selected catalyst in 0.15 L of WW with electrolyte Na₂SO₄ (0.01 M). In these experiments the pH was not modified. The mass of catalyst supports was 8.7 g of Fe-AB, 14.25 g of Mn-AB and 3 g of Fe-AC with different iron uptakes.

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