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Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design

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ABSTRACT

The electrochemical treatment of an effluent from edible olive processing over boron-doped diamond electrodes was investigated. The effect of operating conditions, such as initial organic loading (from 1340 to 5370 mg/L chemical oxygen demand (COD)), reaction time (from 30 to 120 min), current intensity (from 5 to 14 A), initial pH (from 3 to 7) and the use of 500 mg/L H_2O_2 as an additional oxidant, on treatment efficiency was assessed implementing a factorial experimental design. Of the five parameters tested, the first three had a considerable effect on COD and total phenols removal, while the other two were statistically insignificant. In most cases, high levels of phenols degradation and decolorization were achieved followed by moderate mineralization. The analysis was repeated at more intense conditions, i.e., initial COD up to 10,000 mg/L, reaction times up to 240 min and current up to 30 A; at this level, the effect of treatment time and applied current was far more important than the starting COD concentration. Treatment for 14 h at optimal conditions (30 A and an initial loading of about 10,000 mg/L) led to 73% COD removal with a zero-order kinetic constant of 8.5 mg/(L min) and an energy consumption efficiency of 16.3 g COD/(m^3 A h).

1. Introduction

Wastewater generated from olive processing comes from either olive milling for oil extraction or edible olives manufacturing. Both agro-industrial activities, which are of particular economic importance to Mediterranean countries like Spain, Italy and Greece, result in effluents that are characterized by high organic content, seasonal generation and the presence of classes of pollutants such as polyphenols that may exhibit antimicrobial, ecotoxic and phytotoxic properties (Kyriacou et al., 2005; Aggelis et al., 2001). The treatment of olive mill wastewaters (OMW) has received enormous attention over the past several years and various decontamination technologies based on biological (aerobic and anaerobic), advanced oxidation, chemical and separation processes have been proposed by several research groups as summarized in recent review publications (Paraskeva and Diamadopoulos, 2006; Mantzavinos and Kalogerakis, 2005). Conversely, relatively fewer studies have been dealing with wastewaters from table olive processing wastewater (TOPW).

Table olive processing occurs through a series of steps, namely initial olive cleaning, debittering, washing, fermentation and packing; all these steps generate waste streams which, alongside the wash waters from tanks, machinery, etc., result in TOPW quantities of about 3.9–7.5 and 0.9–1.9 m^3 per ton of green and black olives, respectively

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(Kopsidas, 1992). The composition of TOPW is similar to that of OMW although the organic strength of the latter is far greater than that of the former. TOPW may have chemical oxygen demand (COD), biochemical oxygen demand) and suspended solids contents up to about 18, 6.6 and 0.4 g/L respectively (Kopsidas, 1992), while typical respective values for OMW are 170, 110 and 9 g/L (Paraskeva and Diamadopoulos, 2006). Unlike OMW, TOPW also contain high concentrations of sodium chloride and sodium hydroxide which are used for olive debittering and fermentation.

The treatability of TOPW by biological means was investigated in several previous studies under aerobic (Kyriacou et al., 2005; Aggelis et al., 2001; Beltran-Heredia et al., 2000a, b; Brenes et al., 2000) and anaerobic (Aggelis et al., 2001) conditions. Depending on the operating conditions in question, aerobic treatment was capable of reducing the COD content by as much as about 70–90% and this was accompanied by low-to-moderate degradation of phenols and other aromatics. Conversely, anaerobic treatment led to partial (i.e. about 50%) COD removal accompanied by a 12% phenolic reduction. In an attempt to improve the biodegradability of TOPW, several studies have dealt with the use of advanced oxidation processes as a suitable pretreatment method to reduce the effluent's COD and phenolic contents. Given the high alkalinity of table olive processing effluents, ozonation appears to be an attractive treatment option since ozone can react rapidly with polyphenols through a combination of direct attack and hydroxyl-radical-induced reactions. This has been demonstrated in several studies where ozone pretreatment was capable of removing most of the phenolic compounds present in TOPW and subsequently enhancing biodegradability (Benitez et al., 2002, 2001a; Beltran-Heredia et al., 2000c; Rivas et al., 2000; Beltran et al., 1999). Coupling ozonation with UV irradiation (with or without H_2O_2) has also been studied (Benitez et al., 2002, 2001a; Beltran et al., 1999) and found capable of improving the efficiency of single ozonation; this was attributed to increased occurrence of hydroxyl radical reactions. Besides ozonation, Fenton and photo-Fenton oxidation (Rivas et al., 2003; Benitez et al., 2001b) as well as wet air oxidation (Rivas et al., 2001) have also been employed to treat TOPW and, in all cases, preoxidized effluents were more readily biodegradable than the original effluent.

Electrochemical technologies such as electrooxidation, electrocoagulation and electroflotation have been widely used in water and wastewater treatment and several applications have been recently reviewed by Chen (2004). Over the past two decades, electrooxidation has been widely investigated for wastewater treatment over electrodes made of several different materials such as graphite, Pt, TiO_2, SnO_2, IrO_2, RuO_2, PbO_2 and several Ti-based alloys. In recent years, a new type of electrode material, namely boron-doped diamond (BDD) has received growing attention for pollutants oxidation since it exhibits significant chemical and electrochemical stability, good conductivity as well as it achieves increased rates of effluent mineralization with very high current efficiencies (Canizares et al., 2007; Chen et al., 2005). Although the electrochemical oxidation over BDD electrodes of several classes of organic pollutants has been studied extensively (Chen et al., 2005; Chen, 2004), process application for agro-industrial effluent treatment is limited; only recently has the electrooxidation of OMW over BDD anodes been reported (Canizares et al., 2007, 2006). Nevertheless and to the best of our knowledge, the electrochemical treatment of TOPW over BDD electrodes or, indeed, any other anodic materials has not been investigated yet.

The aim of this work was to study the electrochemical oxidation of TOPW over a BDD anode regarding the effect of various operating conditions such as current intensity, initial concentration, effluent pH, contact time and the addition of hydrogen peroxide on the conversion of COD, phenols, aromatics and color. A factorial design methodology was adopted to determine the statistical significance of each parameter as well as optimal treatment conditions.

2. Materials and methods

2.1. TOPW

The effluent used in this study was taken from a table olive-manufacturing plant located in the region of Chania, Western Crete, Greece. The process through which the effluent was generated comprises mixing 130–140 kg of black olives of the Kalamai variety, 10 kg of sodium chloride, 0.24 kg of calcium chloride and 1 kg of lactic acid in 90–100 kg of water. The original effluent's major properties are as follows: COD = 60,000 mg/L, total phenols (TP) = 5200 mg/L, conductivity = 111.5 mS/cm and pH = 4.5. The effluent has a dark brown–black color and contains a substantial fraction of aromatic compounds. In all cases, the original effluent was diluted with water to achieve the desirable initial concentration and then fed to the electrolytic cell. For those samples where the starting concentration was less than about 5500 mg/L COD, the effluent's pH was neutral.

2.2. Electrochemical degradation experiments

Experiments were conducted in a DiaCell® (type 100) single-compartment electrolytic flow-cell manufactured by Adamant Technologies (Switzerland). Two circular electrodes of 0.1 m diameter made of BDD on silicon were used as the anode and cathode; each electrode area was 70 cm^2 and the distance between them 0.01 m.

In a typical run, the diluted effluent was batch loaded in a vessel and continuously recirculated in the cell through a peristaltic pump operating at a maximum flow rate of 0.02 m^3/min. In all cases, the working volume was 10 L. A spiral coil immersed in the liquid and connected to tap water supply was used to remove the heat liberated from the reaction. All experiments were conducted at ambient temperature; nonetheless, temperature was found to increase slowly with treatment time with the extent of temperature rise being dependent of the operating conditions employed. However, temperature never exceeded 34 °C at the end of each experiment which, in most cases, lasted for 120 min. For those experiments where the diluted effluent's ambient pH (which was 7 at initial concentrations of less than about 5500 mg/L COD) was adjusted to acidic conditions, the appropriate amount of 98% w/w H_2SO_4 was added. In those cases where hydrogen peroxide was used as an extra oxidant, the appropriate amount of a 35% w/w solution was added to achieve a 500 mg/L H_2O_2 initial