Journal of Hazardous Materials 164 (2009) 120–125

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# A comparison between Conductive-Diamond Electrochemical Oxidation and other Advanced Oxidation Processes for the treatment of synthetic melanoidins

P. Cañizares[a], M. Hernández-Ortega[b], M.A. Rodrigo[a,*], C.E. Barrera-Díaz[b], G. Roa-Morales[b], C. Sáez[a]

[a] Department of Chemical Engineering, Facultad de Ciencias Químicas, Universidad de Castilla La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain
[b] Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón intersección Paseo Tollocan S/N, C.P. 50120 Toluca, Estado de México, Mexico

ARTICLE INFO

*Article history:*
Received 8 July 2008
Received in revised form 29 July 2008
Accepted 30 July 2008
Available online 6 August 2008

*Keywords:*
Melanoidin
Conductive-diamond
Electrolyses
Fenton
Ozonation

ABSTRACT

In this study, three technologies classified as Advanced Oxidation Processes (Conductive-Diamond Electrochemical Oxidation (CDEO), ozonation and Fenton oxidation) have been compared to treat wastes produced in fermentation processes, and characterized by a significant color and a high organic load. Results of CDEO seem to strongly depend on the addition of an electrolyte salt, not only to decrease the energy cost but also to improve efficiency. The addition of sodium chloride as supporting electrolyte improves the removal percentages of organic load, indicating the important role of mediated oxidation processes carried out by the electrogenerated oxidants (hypochlorite). Fenton oxidation and ozonation seem to be less efficient, and mainly Fenton oxidation favors the accumulation of refractory compounds. The differences observed can be explained in terms of the contribution of hydroxyl radicals and other specific oxidation mechanisms involved in each technology.

## 1. Introduction

The melanoidins are brown nitrogenous polymers and co-polymers, usually contained in the effluents of the fermentation processes that use molasses as carbon source, such as those generated in ethanol production, bakery yeast processing, and brewery industry. They are generated through the Maillard reaction between amino and carbonyl groups contained in organic substances, and they are closely related to humic substances [1,2], as they show very similar chemical properties (both are highly dispersed colloids negatively charged due to the dissociation of carboxylic and hydroxylic groups) [3].

Conventional treatments for these wastes are expensive. Thus, due to the composition of these wastes, their biological oxidation is usually not very effective, and frequently the addition of a readily assimilated carbon source and/or nutrients is recommended to increase the efficiency. Likewise, conventional physicochemical treatments have shown to lead to high removal percentages of color and organic matter, although they require very large amounts of reagents. In both cases, the outstanding COD after the treatment is still very high [4].

These facts make advanced oxidation technologies as possible candidates for the treatment of these wastes. In recent years, Advanced Oxidation Processes (AOP) have emerged as potentially powerful methods that are capable of transforming the pollutants into harmless substances. Their oxidation mechanisms rely on the generation of very reactive free radicals, such as the hydroxyl radical ($OH^{\bullet}$). When these radicals are generated, they react rapidly, and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules [5,6]. In this context, the treatment of the melanoidins using AOP has not been extensively studied, although there are some significant works reporting the results of their ozonation [7,8], Fenton [9] and electro-Fenton oxidations [6].

In this study, three AOP are going to be compared: Conductive-Diamond Electrochemical Oxidation (CDEO), Fenton oxidation and Ozonation. CDEO has become a very promising technology for the electrochemical treatment of wastewaters polluted with organic compounds [5,10–16]. It was used successfully to treat many types of model synthetic and actual wastes and it was always found to be able to achieve the complete mineralization of the wastes and a very high efficiency [12,16,17], only limited by mass transfer. This technology combines the production of large amounts of hydroxyl radicals with the direct electrooxidation of the pollutants on the surface of the conductive-diamond [13,14,17] and also with mediated oxidation by other oxidants electrogenerated on

---

[*] Corresponding author. Tel.: +34 926902204100x3411; fax: +34 926295318.
*E-mail address:* manuel.rodrigo@uclm.es (M.A. Rodrigo).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.07.134

the surface from the oxidation of electrolyte salts [18]. The Fenton oxidative process has also reported promising results in cleaning up wastewater polluted with various organic pollutants. Oxidation with Fenton's reagent is accomplished with a mixture of ferrous ions and hydrogen peroxide, and it takes advantage of the reactivity of the free hydroxyl radicals produced in acidic solution by the catalytic decomposition of hydrogen peroxide [19,20] and of the coagulation produced by the ferric hydroxide precipitates. In addition, the process is simple and non-expensive, taking place at room temperature and pressure. The chemicals are readily available at moderate cost and there is no need of any special equipment [19–21]. Finally, ozone is a powerful oxidant ($E^0$: 2.07 vs NHE), particularly attractive for wastewater treatment because it can destroy most hazardous organic contaminants without producing additional wastes from its reduction [5,22]. In an aqueous system, either direct ozone or indirect free radical oxidation (including hydroxyl radical) can occur. The hydroxyl radicals are catalyzed by hydroxide ions, and it has higher oxidation potential as compared to ozone itself [23].

In recent works, the performance of these three technologies has been compared with very different types of wastes including synthetic wastes polluted with dyes, aliphatic compounds, aromatic compounds and actual wastes coming from fine chemicals, olive-oils, ink-manufacturing industries, etc. [5,18,19]. In all these works, it was found that CDEO overcomes the other two AOP. The present work is focused on the study of the performance of these AOP processes in the treatment of a synthetic melanoidin waste as a model of waste polluted with a complex pollutant. It will be tried to confirm if the CDEO is in this case a better technology compared to Fenton and Ozonation as it was found in those previous works for other type of pollutants. To do this, both the efficiencies of the processes and the extension of the treatments (mineralization) are studied.

## 2. Experimental

### 2.1. Preparation of synthetic melanoidin

Synthetic melanoidin was prepared by mixing glucose and glycine in equimolar concentration (1 M) in the presence of sodium bicarbonate (0.5 M). The mixture was heated for 7 h at 95 °C. Milli-Q water was used for dilutions.

### 2.2. Analytical procedure

The carbon concentration was monitored using a Shimadzu TOC-5050 analyser. Chemical Oxygen Demand (COD) was determined using a HACH DR2000 analyser. UV–vis spectra were obtained using a Shimadzu 1603 spectrophotometer and quartz cells.

### 2.3. Conductive-diamond electrochemical oxidation

CDEO assays were carried out in a single-compartment electrochemical flow-cell working under a batch operation mode [24]. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 $cm^2$ and an electrode gap of 9 mm. The wastewater was stored in a glass tank (0.6 $dm^3$) and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 2.5 $dm^3\ min^{-1}$). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point. The experimental setup also contained a cyclone for gas–liquid separation, and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide. Boron-doped diamond films were provided by CSEM (Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si (100) wafers (0.1 Ω cm, Siltronix). The electrolysis was carried out the in lack of additional electrolyte (except for carbonates) and in the presence of NaCl (ranging from 17.5 to 85 mM). The pH of the sample was not controlled during the treatment.

### 2.4. Ozonation

Ozonation experiments were carried out by continuously feeding an ozone–oxygen gas stream in a mixed semi-bach bubble reactor (continuous for gas and batch for liquid). The experimental setup consists of an ozone generator (Ambizon, Model GMF-10, Sistemas y Equipos de Ozonización S.L., Madrid, Spain) and a jacketed cylindrical reactor (2.5 $dm^3$) equipped with a porous gas distribution plate and baffles to increase the ozone absorption capacity. The ozone–oxygen mixture gas stream was sparged with a constant flow rate of 0.5 $dm^3\ min^{-1}$ (flow controller Cole Parmer, model #32907-39) and the average production of ozone was around 1 g $h^{-1}$. The volume of wastewater treated was 2 $dm^3$. The pH was maintained in a set point close to 12 ± 0.1 to favor the generation of hydroxyl radicals. A jacket reactor coupled with a controlled thermostatic bath (Tectron, model 3473200 Selecta, Madrid, Spain) was used to maintain the temperature at the desired set point (25 °C).

### 2.5. Fenton process

Fenton oxidation assays were carried out in lab-scale thermostated mixed batch reactors. The experimental setup consists of a multistirrer device (Ikamag RO 5 power, IKA-WERKE GmbH & Co. KG, Staufen, Alemania) with fifteen mixing sites coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain). Pyrex flasks (250 $cm^3$) hermetically sealed and equipped with magnetic stirrers were used as reactors. They were submerged in the thermostatic bath. In every assay, the reactors were filled with 100 $cm^3$ of wastewater. Then, the iron dose was added (as $FeSO_4{\cdot}7H_2O$) and the pH was adjusted to 3 ± 0.1 with sodium hydroxide or sulphuric acid to favor the generation of hydroxyl radicals. Hydrogen peroxide was measured according to Eisenberg [25]. The COD value was corrected with the value of hydrogen peroxide to obtain the COD value associated to the organic pollutants contained in the wastes. Several sets of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results.

### 2.6. Determination of the Oxygen-Equivalent Chemical-Oxidation Capacity (OCC)

To compare the performance of different AOP it is desirable one parameter which quantifies in arbitrary units the oxidants added to the waste. In this work, it is proposed to use the Oxygen-Equivalent Chemical-Oxidation Capacity (OCC) that is defined as the kilogram of $O_2$ that are equivalent to the quantity of oxidant reagents used in each AOP to treat 1 $m^3$ of wastewater. The OCC has the same purpose that the frequently used Chemical Oxygen Demand which quantifies the kilogram of oxygen required to oxidize chemically any given reduced species present in a wastewater (although the actual chemical oxidation essay is carried out with permanganate or dichromate). The main difference between them is that the COD is used to determine the concentration of organic substrate contained in the waste and the OCC is proposed to quantify the amount of oxidant supplied in the oxidation process. This parameter is related to the different oxidants used in the three Advanced