



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

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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.

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1. Introduction

The melanoidins are brown nitrogenous polymers and copolymers, 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].

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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•). 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

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 cm² and an electrode gap of 9 mm. The wastewater was stored in a glass tank (0.6 dm³) and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 2.5 dm³ 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 in the 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-batch 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 dm³) 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 dm³ 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 dm³. 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 cm³) 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 cm³ of wastewater. Then, the iron dose was added (as FeSO₄·7H₂O) 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 O₂ that are equivalent to the quantity of oxidant reagents used in each AOP to treat 1 m³ 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

Oxidation Processes studied in this work according to Eqs. (1)–(3).

$$\text{OCC}(\text{kg O}_2\text{m}^{-3}) = 0.298 \cdot Q(\text{kA h m}^{-3}) \quad (1)$$

$$\text{OCC}(\text{kg O}_2\text{m}^{-3}) = 1.000 \cdot [\text{O}_3](\text{kg O}_3 \text{ m}^{-3}) \quad (2)$$

$$\text{OCC}(\text{kg O}_2\text{m}^{-3}) = 0.471 \cdot [\text{H}_2\text{O}_2](\text{kg H}_2\text{O}_2 \text{ m}^{-3}) \quad (3)$$

These equations are obtained from stoichiometrical calculations, taking into account the number of electrons exchanged in the reduction of the different oxidants (in the case of ozone and hydrogen peroxide) and also the Faraday number in the case of CDEO.

3. Results and discussion

3.1. Effect of the salt concentration on the electrochemical oxidation of melanoidin wastes

The conductivity of the raw melanoidin wastewaters is usually very small ($<480 \mu\text{S cm}^{-1}$) and this appears as one important drawback for the use of CDEO as a treatment technology because it would lead to large cell potentials and hence, to significant ohmic losses of energy. Usually, an economic solution to this problem is the addition of an electrolyte (typically a sodium chloride or sulphate salt) to the waste. Taking this into account, it was decided to study the effect of the concentration of electrolyte in the performance of the electrochemical treatment before comparing this technology with the other two AOP.

Thus, Fig. 1 compares the results obtained in the electrolysis with concentrations of NaCl solutions ranging from 0 to 86 mM. As it can be observed, the electrolysis without addition of NaCl leads to the accumulation of refractory compounds (it remains around 20% of initial COD) while electrolyses with NaCl electrolyte obtain the complete removal of COD. In literature [26], it is proposed that chloride can be oxidized to hypochlorite on the anodic surface. Hypochlorite is a powerful oxidant that can play an important role in the oxidation process (mediated-oxidation). On the other hand, it is also important to remark the significant decrease in the cell potential with increasing sodium chloride concentrations and the different changes in the pH during the time course of the reaction. The first was expected, but it has to be noted that the more significant decrease in the cell potential is obtained with small concentrations of NaCl and that the use of concentrations five times higher improves the value of the cell potential only slightly. Likewise, it should be noted that there is not any improving effect in the COD removal on increasing the salt concentrations. Hence, the addition of the salt is necessary to the process, but the use of high concentrations is not cost-effective. Regarding the pH changes, it has to be noted that the pH of the waste (previous to the electrochemical process) decreases with the addition of the salt. Likewise the changes of the pH during the process are quite different in the treatment of the wastes with and without NaCl electrolyte. Besides the acidification caused by anodic water oxidation and the alkalization caused by cathodic water reduction, the changes in the structure of the polymers and the buffer effect caused by the carbonates compounds could help to explain the changes observed in the pH profile.

In addition, it is also important to remark the time-course of the cell potential. As it can be observed in part c of Fig. 1, in the case of the wastes with NaCl, the cell potential is maintained almost constant during the electrolysis, indicating that the formation of non-conductive layers on the surface of the electrodes and the electrodes corrosion do not occur [5]. Conversely, in the case of the treatment of wastes without NaCl, it decreases significantly during the process. This observation can be easily explained taking

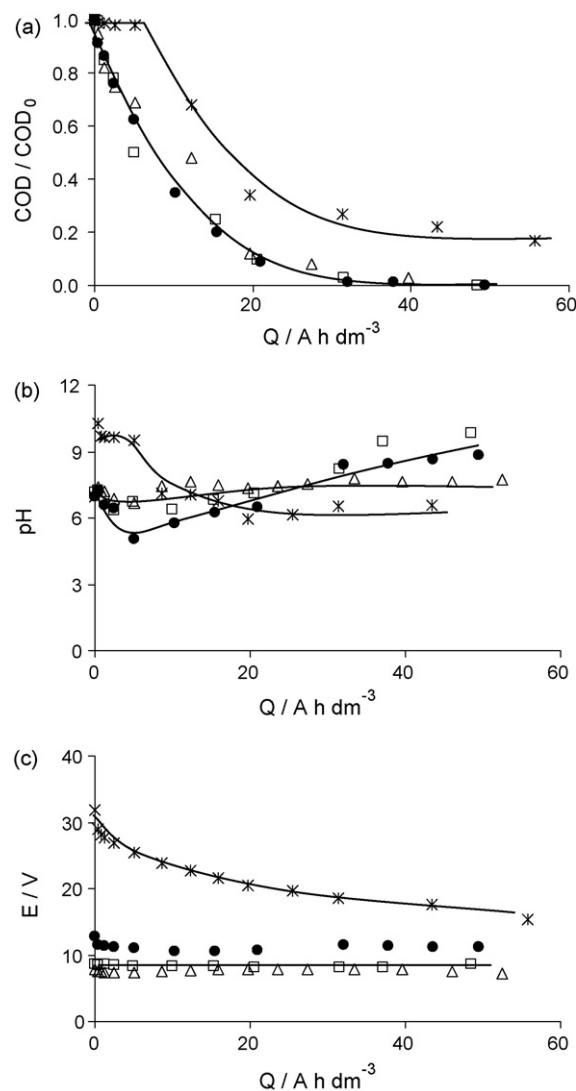


Fig. 1. Changes in the COD (a), pH (b) and cell potential (c) during electrolyses of synthetic melanoidins with different supporting electrolyte concentrations. (Δ) 86.0 mM NaCl solution, (\square) 35.0 mM NaCl solution, (\bullet) 17.5 mM of NaCl solution, (\times) without supporting electrolyte. Operation conditions. current density: 300 A m^{-2} ; T : 25°C ; natural pH.

into account the formation of ionic species during the treatment (mainly carboxylic acids) which increases the waste conductivity and hence, decreases the cell potential.

3.2. Technical feasibility of the Advanced Oxidation Processes

Figs. 2–4 show the changes of the COD, TOC and UV-vis spectra during the treatment of a melanoidin waste with the three different AOP technologies studied in this work. As it can be observed, very different results are obtained, despite hydroxyl radicals are assumed to be the main oxidants in the three technologies.

In the case of CDEO, the complete removal of the COD and TOC is obtained. In addition, during the oxidation process, COD and TOC profiles are overlapped. This fact can be indicative of the absence of intermediates and hence of an apparently quasi-direct oxidation of organic compounds into carbon dioxide. Part b of the figure confirms this assumption, since the reaction progress does not lead to the formation of new peaks in the UV-vis spectra. Hence, once the CDEO starts the oxidation of a pollutant molecule, it remains up to the formation of carbon dioxide. This has to be explained

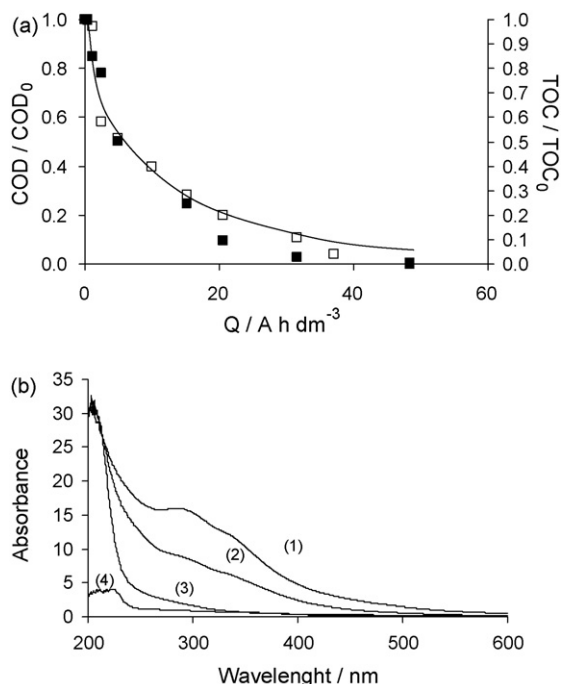


Fig. 2. (a) Changes in the removal of COD (■) and TOC (□) with the specific electrical charge during electrolyses of synthetic melanoidins. (b) Changes in the ultraviolet spectrum during electrolyses of synthetic melanoidins. (1) 0 Ah dm⁻³, (2) 2.5 Ah dm⁻³, (3) 15 Ah dm⁻³ and (4) 48 Ah dm⁻³. Operation conditions. Current density: 300 A m⁻²; T: 25 °C. Waste composition. Sodium chloride 35 mM dm⁻³; natural pH.

taking into account that oxidation is developed mainly on the nearness of the electrode surface where very large amounts of hydroxyl radicals (and hypochlorite) are formed. The selectivity of these radicals is very small and they attack indiscriminately all the inter-

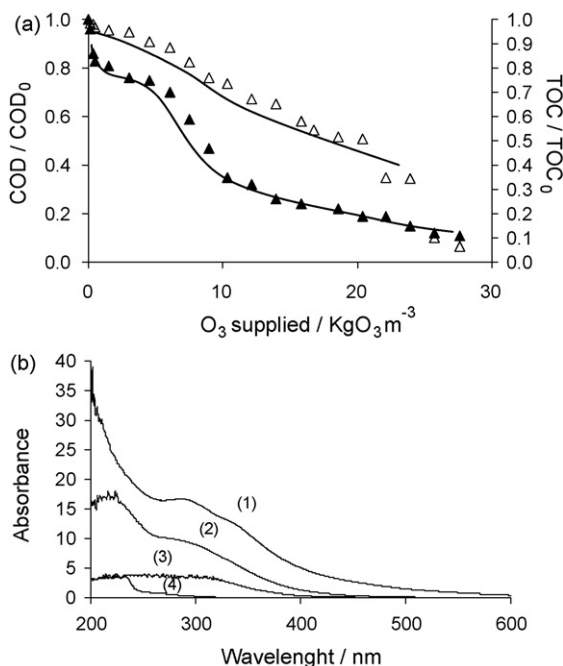


Fig. 3. (a) Changes in the COD (▲) and TOC (△) with the ozone supplied during ozonation of synthetic melanoidins. (b) Changes in the ultraviolet spectrum during ozonation of synthetic melanoidins. (1) 0 kg O₃ m⁻³, (2) 1.5 kg O₃ m⁻³, (3) 6 kg O₃ m⁻³ and (4) 27 kg O₃ m⁻³. Operation conditions. Ozone production: 1 g h⁻¹; T: 25 °C. pH 12.

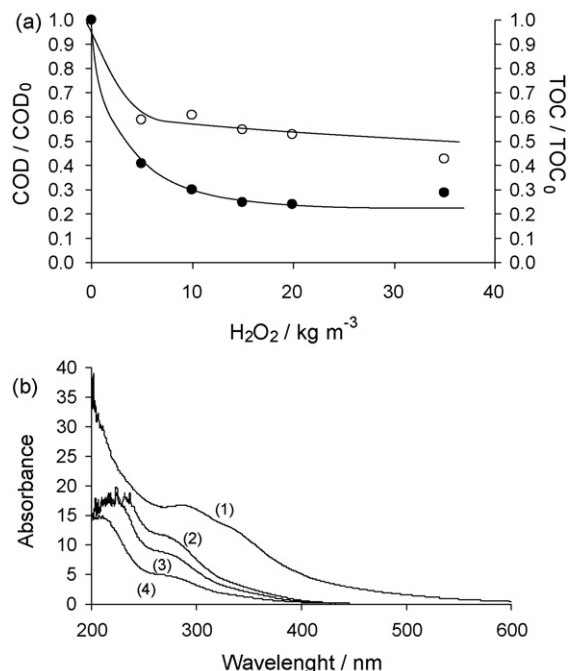


Fig. 4. (a) Changes in the COD (●) and TOC (○) with the hydrogen peroxide added during the Fenton oxidation of synthetic melanoidins. (b) Changes in the ultraviolet spectrum during the Fenton oxidation of synthetic melanoidins. (1) 0 kg H₂O₂ m⁻³, (2) 5 kg H₂O₂ m⁻³, (3) 15 kg H₂O₂ m⁻³ and (4) 35 kg H₂O₂ m⁻³. Operation conditions. pH 3; T: 25 °C; Fe²⁺: 1000 mg dm⁻³.

mediates formed. The organic intermediates that are refractory to the oxidation with hydroxyl radicals are successfully oxidized by hypochlorite (as it was shown in Fig. 1) and this makes CDEO to be a very powerful treatment technology.

Ozonation is also a very effective technology to treat these wastes. As it can be observed, it achieves very significant removals of COD and TOC (>80% and >70%, respectively) and the almost complete disappearance of the color, but there are two important differences in CDEO: changes in TOC and COD are not overlapped (the changes in the COD are faster than those of the TOC), and there is an important change in the shape of the UV-vis spectra. Both observations indicate the formation of large amounts of intermediates, and so the existence of softer oxidation conditions. In addition, there is a certain accumulation of ozonation-refractory compounds at the end of the treatment. This accumulation has been observed in the treatment of many types of pollutants, and it is associated to the formation of some types of carboxylic acids whose oxidation by hydroxyl radicals is very slow. These differences may be indicative of the weaker activity of hydroxyl radicals over these pollutants and, as it was pointed out below, they can also be indicative of the existence of an other important oxidation mechanism in CDEO and ozonation (such as hypochlorite oxidation and direct-oxidation in CDEO and molecular ozone oxidation in ozonation) [5].

Fenton process obtains the worse results in terms of mineralization and color removal. As it can be observed, this technique is not able to achieve the complete mineralization of the waste, and a high TOC remains at the end of the treatment (>40%). These high concentrations of refractory carbon also appear in the Fenton oxidation of other kind of aqueous wastes [19,21] and they also seem to be characteristic of this oxidation technology. The comparison of the TOC and COD profiles (curves not overlapped) and the UV spectra (new peaks) indicates that there is an important production of intermediates. The differences observed between this AOP and the previous ones can be explained in terms of the presumed mechanisms involved in the oxidation process. In this case, hydroxyl

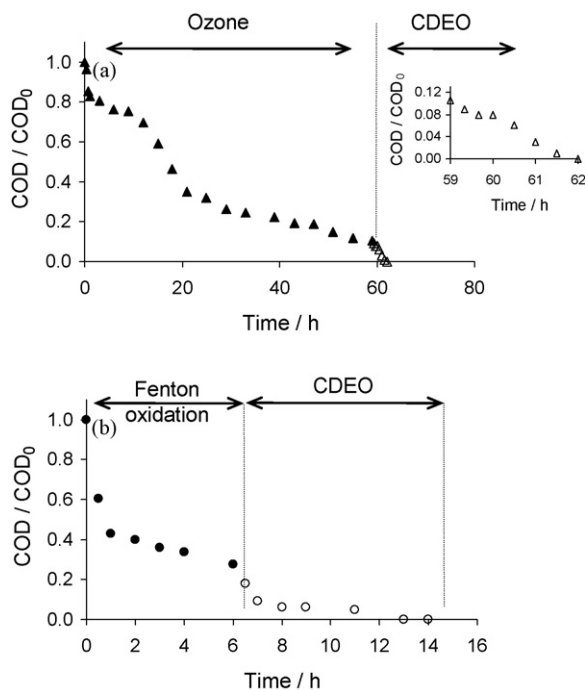


Fig. 5. (a) Combined ozonation (▲) and CDEO (△) applied to the oxidation of synthetic melanoidins. (b) Combined Fenton oxidation (●) and CDEO (○) applied to the oxidation of synthetic melanoidins. Operation conditions. CDEO: natural pH; T : 25 °C; j : 300 A cm⁻². Ozonation production: 1 g h⁻¹, T : 25 °C; pH 12, T : 25 °C Fenton process: pH 3; T : 25 °C; Fe²⁺: 667 mg dm⁻³.

radical is assumed to be the lone oxidant. As it can be observed, at the beginning of the process, the efficiency is very high. However, after a given dose of hydrogen peroxide, the efficiency decreases. This fact could be indicative of a fast oxidation of raw compounds to intermediate compounds (mainly carboxylic acids) that cannot be further oxidized by hydroxyl radicals [5].

To verify the role of the different mechanisms involved in the electro-oxidation of organic compounds with BDD electrodes, a last combined oxidation essay was carried out. Fig. 5 shows the COD profile with the amount of oxidant supplied during the combined Ozonation-CDEO (Fig. 5a) and Fenton-CDEO (Fig. 5b) of the synthetic melanoidins. As it can be observed, both processes (the ozonation and the Fenton oxidation) are not able to achieve the complete removal of the waste and a residual effluent containing refractory organics is obtained. From this point, the CDEO of this refractory effluent was carried out. The results show that the complete mineralization of the waste is obtained and no refractory compounds remain at the end of the process in both cases. Hence, the combined oxidation conditions of the CDEO (direct oxidation, hydroxyl radicals and hypochlorite) can successfully remove all the intermediates formed in the other to AOP. At this point, it is important to remember that CDEO also leads to the accumulation of refractory compounds when chloride is not present. In those conditions, only hydroxyl radicals and direct electrolytic oxidation can occur because no hypochlorite can be produced.

3.3. Effectiveness of three Advanced Oxidation Processes

To compare the effectiveness of the three technologies, results of the oxidations were represented versus the Oxygen-Equivalent Chemical-Oxidation Capacity [27]. This parameter informs about the chemical efficiency of the oxidants used in each process and quantifies the oxidants added to the waste with the same arbitrary units (kg O₂ per m³ of wastewater). Fig. 6(a) shows the changes in

the COD removal with the quantity of oxidant added in the three AOPs studied. As it can be observed, for very small doses of oxidants (OCC < 1 kg O₂ m⁻³), the efficiencies of three AOP are similar. This indicates that hydroxyl radicals formed from each oxidation system can attack the raw pollutant with the same efficiency. From this point, the efficiency of the ozonation becomes worse (maybe because of a more difficult oxidation of the intermediates) but that of the Fenton and CDEO remains the same, up to an OCC of about 5 kg O₂ m⁻³, which corresponds to the point at which the Fenton process reaches the maximum removal of COD. From this point, the addition of oxidant in the Fenton process is useless. However, the addition of oxidants in the ozonation and, especially in the CDEO, is still important. In case of ozonation, there is a second high-efficiency zone in the curve prior to the accumulation of refractory compounds. In case of CDEO the treatment is completed for OCC under 10 kg O₂ m⁻³.

The OCC parameter only provides information about the chemical efficiency of the oxidants involved in the treatment with these AOPs, but it does not give any additional information about the real cost of the treatment, as the price of the oxidants used can vary. However, to compare operating cost of ozonation and electrochemical technology is not difficult, as both oxidizing agents can be generated in situ and the cost can be compared in terms of energy consumption. Nevertheless, to include in this comparison the operating cost of the Fenton oxidation is very difficult because the cost of the raw materials (hydrogen peroxide and iron), sludge treatment and reagents used to change the pH can vary a lot. Moreover, they depend on the country, the year and many other parameters that should not be included in a scientific work [5]. Taking this into account, Fig. 6(b) shows the energy consumption requirements in

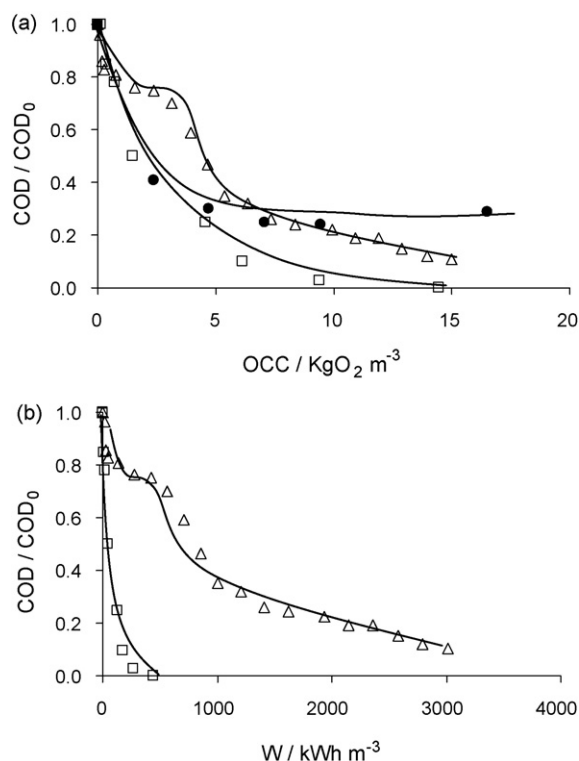


Fig. 6. (a) Changes in the COD/COD₀ ratio with the OCC during the oxidation of synthetic melanoidins: (□) CDEO, (△) Ozonation and (●) Fenton Oxidation. (b) Changes in the COD/COD₀ ratio with the power consumptions (W) required by CDEO (□) and Ozonation (△) as a function of the COD removal in the oxidation of synthetic melanoidins. Operation conditions. CDEO: current density: 300 A m⁻²; Ozonation: ozone production: 1 g h⁻¹, T : 25 °C; pH 12, T : 25 °C; natural pH. Fenton oxidation pH 3; T : 25 °C; Fe²⁺: 500 mg dm⁻³.

the treatment of the synthetic melanoidins by CDEO and Ozonation as a function of the COD. It is observed that the energy requirements are significantly lower for CDEO. This observation was previously reported in literature for other types of wastes [28].

4. Conclusions

Although the conductive-diamond electrochemical oxidation, the Fenton Process and the Ozonation are classified as Advanced Oxidation Processes and consequently, hydroxyl radicals are assumed to be involved in the three oxidation technologies, the treatment of fermentation-industries effluents with the three technologies leads to very different results. Results of CDEO depend strongly on the addition of an electrolyte salt, not only to decrease the energy cost but also to improve efficiency. The addition of salts seems to favor the removal percentage of the organic content of the wastes. This means that mediated oxidation processes by electrogenerated oxidants are essential to obtain a high efficiency treatment. Ozonation at alkaline conditions seems to be able to reduce significantly the organic content but with a low efficiency. Fenton oxidation is very efficient during the first stages, but it leads to an important accumulation of refractory compounds. The similar efficiencies obtained during the initial stages by the three technologies show that the hydroxyl radicals produced are good oxidants for complex molecules. However, the formation of simpler molecules (probably carboxylic acids) that are refractory to these radicals, needs to be solved with different oxidants and, from this point of view, the electrochemical technology presents an important advantage.

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