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Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes A comparison with other advanced oxidation processes

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Abstract

In this work, the conductive-diamond electrochemical oxidation of several short-chain organics (2-propanol, ethanol, butyric acid and chloroacetic acid) has been studied. The results obtained have been compared with those obtained in the oxidation of these compounds with Fenton reagent and with ozone at pH 12. Significant differences have been observed among the three technologies and also between the two ranges of pollutant concentrations studied. However in both cases, the performance of the CDEO overcomes the results obtained by the oxidation with ozone and with Fenton reagent. Likewise, the oxidation with ozone seems to be more effective that the oxidation carried out by the Fenton reagent. Except for ethanol, the nature of the organic does not seem to influence on the performance of the electrochemical technology. However, the efficiencies were found to strongly depend on the concentration of pollutant. In spite of that, the CDEO is able to reduce completely the COD content of the wastes. On the contrary, important concentrations of oxidation-refractory compounds were accumulated during ozonation and Fenton treatments. The mean oxidation state of carbon of the final products obtained by the three technologies is different and this suggests significant differences in the oxidation mechanisms.

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1. Introduction

During the recent years, many works have been focused on the study of new technologies for the treatment of industrial wastes polluted with organic compounds. The treatment of these flow-streams by conventional technologies is not easy. The mixture of compounds usually dissatisfies the recovery of the organics, the low calorific power of the wastes frustrates the use of incineration, and the non-biodegradability disappoints the biological treatment. Under these circumstances the use of advanced oxidation processes (AOPs) appears as a very promising answer to solve the environmental problem generated by the discharge of these effluents. Advanced oxidation processes are defined as oxidation processes in which hydroxyl radicals are the main oxidants involved. This radical is a very powerful oxidant (E^0 ,

2.80 V vs. SHE) which leads to a very effective oxidation process. As a result, the results reported in literature [1–13] show that the technologies are very efficient. However, large amounts of oxidation-refractory compounds are usually obtained at the end of the process. This behaviour is explained in terms of the reactivity of hydroxyl radicals with some simple organic intermediates formed during the oxidation of the organic pollutants, such as acetic and oxalic acids, acetone or simple chloride derivatives as chloroform or tetrachloroethane. For this reason, in order to increase the organic matter removal, several authors propose to combine these processes with other type of treatments (f.i. biological process) [14–16] or in other cases, to add some improvements to enhance the performance of the AOPs [17,18].

In this context, during the recent years a new electrochemical technology which is also based on the use of hydroxyl radicals (and consequently can be classified as an AOP) and which does not lead to the accumulation of oxidation-refractory organics has emerged: the conductive-diamond electrochemical oxidation (CDEO). It has been widely studied for the treatment of a

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great variety of synthetic and real industrial wastes, both in lab and bench-scale plants [19–34]. The main result of these studies is that this technology allows obtaining the almost complete mineralization of the organics contained in the wastes with very high current efficiencies. These excellent results have been related to the great chemical and electrochemical stability of conductivediamond and also to the high overpotential for water electrolysis. In addition, it has been demonstrated that its large electrochemical window favors the production of hydroxyl radicals that can contribute to the oxidation process [35]. This fact has allowed classifying formally the CDEO as an AOP. In addition, it is also reported [36] that besides hydroxyl-radicals oxidation, CDEO combines others oxidation mechanisms such as direct electrooxidation on the surface and oxidation mediated by other oxidants electrogenerated on the surface from the electrolyte salts.

The coexistence of these three oxidation mechanisms gives to CDEO an important advantage in comparison with other AOPs such as Fenton oxidation and ozonation, which are going to be used in this work for comparison purposes. These technologies are some of the simplest AOPs. However, in both cases the role of the hydroxyl radicals has been largely studied and consequently they are good candidates to compare the role of these radicals. Fenton process is an advanced oxidation technology in which a mixture of hydrogen peroxide and iron(II) salts is added directly to the wastewater. This mixture promotes the appearance of hydroxyl radicals by catalytic decomposition of hydrogen peroxide, and this increases strongly the efficiency of the process (if compared with hydrogen peroxide conventional oxidation). In addition to the oxidation, the iron(III) ions generated during the oxidation stage promote the removal of other pollutants by coagulation and sedimentation. In the same way, Ozonation is one of the most widely used advanced oxidation technologies. Ozone is itself a very powerful oxidant (E^0 , 2.07 vs SHE) and, in certain conditions, it can decompose and lead to the formation of hydroxyl radicals (f.i. at pH close to 12, which is going to be the conditions used in this work). In this later case, the process efficiencies are strongly increased.

Thus, the goal of this work is to compare two simple advanced oxidation processes (ozonation at pH 12 and Fenton oxidation) with CDEO in the treatment of several short-linear-chain organics. To do this, it has been selected 2-propanol, ethanol, butyric acid and chloroacetic acid as model compounds of aliphatic alcohols and carboxylic acids. These molecules are not specially known to be refractory to oxidation by hydroxyl radicals but they are very representative compounds of the type of intermediates that can be generated during the oxidation of more complex molecules. The results obtained will be used to guess some points about the role of hydroxyl radicals on oxidation carried out by the three advanced oxidation processes.

2. Experimental

2.1. Analytical procedure and determination of instantaneous current efficiency (ICE)

The carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. Chemical oxygen demand (COD) was

determined using a HACH DR2000 analyzer. Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

The COD method was used for the determination of the instantaneous current efficiency (ICE). In this method, ICE is calculated [37] from the measured COD values using Eq. (1).

$$ICE = \frac{[COD_{t+\Delta t} - COD_t]FV}{8I\Delta t}$$
(1)

where COD₀, COD_t and COD_{t+ Δt} are the COD (in g O₂ dm⁻³) at times 0, *t* and *t* + Δt (in seconds), respectively, *I* is the current intensity (A), *F* is the Faraday constant (96,487 C mol⁻¹), *V* is the volume of the electrolyte (dm³) and 8 is a dimensional factor for unit consistence (32 g O₂ mol⁻¹ O₂/4 mol e⁻¹ mol⁻¹ O₂).

2.2. Determination of the mean oxidation state of carbon

The mean oxidation state of carbon (MOSC) can be calculated from the values of TOC and COD using Eq. (2):

$$MOSC = 4\left(1 - \frac{COD}{TOC}\right)$$
(2)

where COD is the chemical oxygen demand (in mol $O_2 dm^{-3}$) and TOC is the total carbon (in mol C dm⁻³), respectively. This parameter oscillates between -4 for the minor oxidation state (CH₄) and +4 for the major oxidation state (CO₂).

2.3. 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 oxygenequivalent chemical-oxidation capacity (OCC) that is defined as the kg of O₂ that are equivalent to the quantity of oxidant reagents used in each AOP to treat 1 m³ of wastewater [38]. The OCC has the same purpose that the frequently used chemical oxygen demand (COD) which quantifies the kg 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. (3)–(5).

OCC (kg O₂ m⁻³) =
$$0.298 \cdot Q (kA h m^{-3})$$
 (3)

OCC
$$(kg O_2 m^{-3}) = 1.000 \cdot [O_3] (kg O_3 m^{-3})$$
 (4)

OCC
$$(\text{kg O}_2 \text{ m}^{-3}) = 0.471 \cdot [\text{H}_2\text{O}_2] (\text{kg H}_2\text{O}_2 \text{ m}^{-3})$$
 (5)

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

2.4. Conductive diamond electrochemical oxidation

In this work, the CDEO assays were carried out in a singlecompartment electrochemical flow-cell working under a batch operation mode [26]. 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 $(0.6 \,\mathrm{dm}^3)$ and circulated through the electrolytic cell by means of a centrifugal pump (flowrate $2.5 \text{ dm}^3 \text{ min}^{-1}$). 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. Borondoped diamond films were provided by CSEM (Switzerland) and synthesized by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si (100) wafers $(0.1 \,\Omega \,\text{cm}, \text{Siltronix})$. Electrolyses were carried out in galvanostatic mode. During the electrolyses no control of pH was carried out.

2.5. 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). This reactor consist of a 2.5 dm³ jacketed cylindrical Pyrex glass tank equipped with a porous gas distribution plate and baffles to increase the capacity of absorption of ozone. A mechanical stirrer (IKA WERKER model EUROSTAR DIGITAL, Germany) and a recycle pump (Emapompe, model P 022 Plastomec) are also use to promote the absorption of ozone and to obtain good mixing conditions. Pure oxygen taken from a commercial cylinder was fed into an ozone generator (Ambizon, Model GMF-10, Sistemas y Equipos de Ozonización S.L., Madrid, Spain) which is able to produce a maximum mass flow rate of 10 g h^{-1} . In the generator outlet, the stream was dried with a sample conditioner (Sample conditioning system, model SC-010-R AFX, Sistemas y Equipos de Ozonización S.L., Madrid, Spain). The concentration of ozone in the gas at the reactor outlet and inlet was measured with an ozone meter (Ozone analyzer, Model H1 AFX, Sistemas y Equipos de Ozonización S.L., Madrid, Spain) and its calibration was carried out iodometrically [39]. Dissolved ozone concentration in the liquid phase was determined spectrophotometrically (600 nm) from discoloration of the resulting solution, by the Karman indigo method [40]. In the experiments described in this work, the ozone-oxygen mixture gas stream was sparged with a constant flow rate of $0.5 \,\mathrm{dm^3 \,min^{-1}}$ (flow controller Cole Parmer, model #: 32907-39) and the average production of ozone was around 1 g h^{-1} . The volume of wastewater treated in each assay was 2 dm^3 and it was place inside the reactor previous to the experiments. To increase the mixing conditions, the stirring rate of the mechanical stirrer was adjusted to 550 rpm and the flow recycled to $67.5 \,\mathrm{dm^3}\,\mathrm{h^{-1}}$. The ozone generator was switched on previous to the experiments, and only when the desired ozone percentage in the ozone–air gas was reached (steady state conditions) the ozone–oxygen mixture gas stream started to be sparged into the reactor. During the experiments sodium hydroxide was added to the reactor to maintain the pH in a set point close to 12 ± 0.1 . According to literature [41,42], this is an optimum pH to promote the generation of hydroxyl radicals due to the radicalary decomposition of the ozone molecules. The temperature was also maintained during operation at 25 °C using a thermostatic bath (Tectron, model 3473200 Selecta, Madrid, Spain) by circulating the water through the jacket reactor to ensure a constant temperature inside the reactor.

2.6. 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 15 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. According to literature [43,44], this is the optimum pH to promote the formation of hydroxyl radicals in a Fenton process. In every case, the reaction was started by adding the dose of hydrogen peroxide. Preliminary experiments were carried out to determine the reaction time needed to meet the steady state conditions. From these experiments a reaction time of 4 h was selected (more than three times higher than the worse value obtained in the previous experiments). Once the reaction time was finished TOC, COD, UV-vis spectra and hydrogen peroxide were measured in every reactor. Then, the steady state conditions were assured by a later measure (after 1 h). Hydrogen peroxide was measured according to Eisenberg [45]. This is a well-known colorimetric technique based on the reaction of hydrogen peroxide with a titanium sulphate reagent. The COD value (that takes into account both the contribution of organics and hydrogen peroxide) was corrected with the value of hydrogen peroxide to obtain the COD value associated to the organic pollutants contained in the wastes. Several set of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results.

2.7. Wastewater characterization

The synthetic wastewaters used in this work contained different concentrations (around 100, 2000 and 4000 mg dm⁻³ of COD) of aliphatic alcohols (2-propanol, ethanol) or carboxylic acids (butyric acid and chloroacetic acid) and 5000 mg Na₂SO₄ dm⁻³.

3. Result and discussion

3.1. Electrochemical oxidation of acyclic organic compounds. General behaviour

Fig. 1 shows the changes (with the specific charge passed) of the COD and TOC during the CDEO of synthetic wastes polluted with different concentrations of 2-propanol (T, 25 °C; neutral pH; j, 30 mA cm⁻²; supporting medium, Na₂SO₄ 5000 ppm).

As it can be seen, the electrochemical process can successfully remove almost all the COD and TOC contained in the synthetic wastes, even for high concentrations of 2-propanol. The decrease of the COD seems to be linear with charge for a wide range of COD (oxidation rate not depending on the concentration of COD). This means that the process is not mass-transfer controlled for high concentration of COD, but controlled by the Butler-Volmer kinetic. However, the change of the COD becomes exponential for lower COD and, as it can be observed in Fig. 2, there is a clear correlation between the instantaneous current efficiency (ICE) and the COD. This type of variation is characteristic of electrochemical oxidation of aqueous wastes polluted with organics [26] and it has been well explained in literature [19–21] in terms of the controlling mechanisms of the electrochemical process (electrodic or mass transport). In this context, the continuous line is not a trend line but the simulation of a model [19-21] which considers both behaviours,



and which assumes a maximum value of ICE for COD over a given value (COD^{mass} transfer), and a linear decrease of ICE down to zero for lower COD. It has to be taken into account that the model only assumes oxidation on the electrode surface or mediated oxidation by hydroxyl radicals in the nearness of this surface. The value of COD^{mass} transfer</sup> has been determined experimentally from a typical ferrocyanide/ferrycyanide essay (1580 mg dm⁻³) [46] and also by mathematical fitting of the experimental data obtained in the electrolyses of 2-propanol (1790 mg dm⁻³). This parameter is related with the mass transfer coefficient (k_m , $1.4 \times 10^{-5} \text{ m s}^{-1}$) and the applied current density (j_{appl} , A m⁻²) through Eq. (6), where COD (t) is the chemical oxygen demand at time t (mol O₂ m⁻³) and F is the Faraday constant (96,487 C mol⁻¹).

$$COD_{lim}^{mass\,transfer} = \frac{j_{appl}}{4Fk_m} \tag{6}$$

According to literature [26] the discrepancy in both values can be explained by the effect of mediated electrochemical oxidation processes, that extends the oxidation to the whole reaction volume and not only to the closeness of the anodic surfaces. In this context, it is known that the electrochemical oxidation of wastewaters on conductive-diamond anodes can lead to the electrosynthesis of different oxidants such as peroxosulphates [47], peroxophosphates [48], hypochlorite [49], peroxocarbonates [50], etc. depending on the waste composition (especially on the pH and on the electrolyte salts) and on the operation conditions. This chemical oxidation can play an important role in the overall electrochemical oxidation process of organics, and in several cases [29,30,34] these mechanisms can be even more important that the direct oxidation mechanism itself.

The performance observed in the electrolyses of 2-propanol is also repeated in the electrochemical oxidation of two of the other model-pollutants studied in this work (butyric and chloroacetic acids) but not for the oxidation of ethanol. This can be clearly observed in Fig. 3. In this case, the current efficiency values are significantly smaller that those predicted by the model [19–21,26] (which assumes ICE = 1 for COD over a given value, and a linear decrease of ICE down to zero for lower COD), particularly at low concentrations. In addition, the



Fig. 1. Variation of COD (a) and TOC (b) with the specific electrical charge passed in the electrochemical oxidation of a synthetic wastewater polluted with different concentrations of 2-propanol. (Δ) 4150 mg O₂ dm⁻³, (\blacktriangle) 2000 mg O₂ dm⁻³, (\bigstar) 105 mg O₂ dm⁻³ (natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻²).

Fig. 2. Variation of the instantaneous current efficiency (ICE) with the COD in the electrochemical oxidation of wastewaters polluted with different concentrations of 2-propanol. (\triangle) 4150 mg O₂ dm⁻³, (\blacktriangle) 2000 mg O₂ dm⁻³, (\blacklozenge) 105 mg O₂ dm⁻³ (natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻²).



Fig. 3. Variation of the instantaneous current efficiency (ICE) with the COD in the electrochemical oxidation of wastewaters polluted with different concentrations of ethanol. (Δ) 4000 mg O₂ dm⁻³, (\blacktriangle) 2000 mg O₂ dm⁻³, (\bigstar) 100 mg O₂ dm⁻³ (natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻²). Continuous line: ethanol. Discontinuous line: 2-propanol.

changes of the ICE with the COD^{effect} is not linear but exponential. According to literature [36], this fact can be indicative of a more complex oxidation phenomenon with a larger influence of the direct electro-oxidation process (and especially of the adsorption of ethanol onto the diamond surface, which can control the later oxidation process). The formation of solid materials (probably of polymeric nature) during the very initial stages of the ethanol electrolysis can support this assumption, that was previously formulated [36] for the oxidation of phenol at a very low overpotentials in conditions in which the effect of hydroxyl radical oxidation could be neglected.

3.2. Oxidation of 2-propanol solutions with Fenton reagent and with ozone (pH 12). Comparison with the CDEO

Results obtained in the electrolysis of 2-propanol solutions have been compared to those obtained in the oxidation of this synthetic waste with Fenton reagent and with ozone (at pH around 12). In both technologies, the primary oxidation mechanism is assumed to be the oxidation by hydroxyl radicals [2,9]. Consequently, the comparison of the results obtained by these technologies with the ones obtained by the electrochemical oxidation can be used to guess some insights about the oxidation mechanisms in this later process.

To compare the results obtained with different oxidation technologies in terms of equivalent doses of oxidants, a new parameter has been recently proposed in literature: the OCC (oxygen-equivalent chemical-oxidation capacity) [38]. This parameter informs about the chemical efficiency of the oxidants used in each process and it quantifies the oxidants added to the waste with the same arbitrary units (kg O_2 m⁻³ of wastewater).

Figs. 4 and 5 show, for the three oxidation technologies, the changes of the COD and TOC with the dose of the oxidant added, in the treatment of solutions of 2-propanol with low (COD around 10^2 mg dm⁻³) and high (COD around 2×10^3 mg dm⁻³) initial concentration of this compound. In the first case, the electrochemical process is clearly mass-transport controlled while in the second there is a long period in which the treatment is not controlled by mass transport.



Fig. 4. Changes in the removal percentage of COD (a) and of TOC (b) with the OCC parameter, during the oxidation of a synthetic wastewater polluted with 2-propanol (COD⁰: 105 mg dm⁻³) by CDEO (\triangle), Fenton oxidation (\square) and Ozonation (\blacktriangle). Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process, pH 3; *T*, 25 °C; Fe²⁺, 42 mg dm⁻³. Ozonation: ozone production, 1 g h⁻¹; *T*, 25 °C; pH 12.

Significant differences are observed between both figures, especially in the results obtained by the electrochemical process. However in both cases, the performance of the CDEO overcomes the results obtained by the oxidation with ozone and with Fenton reagent. Likewise, the oxidation with ozone seems to be more effective that the oxidation carried out by the Fenton reagent.

At low pollutant concentrations, the CDEO allows obtaining almost quantitative removal of the COD for OCC doses over $2 \text{ kg O}_2 \text{ m}^{-3}$. However, for these OCC the complete mineralization of the wastes is not reached, and the TOC removal continues increasing with the dose of oxidant added. This fact can only be explained in terms of the formation of intermediates with a very low ThOD/TOC ratio (maybe, very oxidized carboxylic acids, although no intermediates could be identified by HPLC). The oxidation of these compounds could produce a large decrease of total organic carbon without a significant change in the COD. Oxidation with ozone (pH 12) and with Fenton reagent lead to less efficient processes and an accumulation of oxidation-refractory compounds is observed in both cases. This accumulation is especially important in the case of the Fenton process in which the maximum COD removal is under 60%. The TOC changes are similar to those obtained in the electrochemical processes, and this can only be interpreted in terms of the formation of intermediates with a higher ThOD/TOC ratio and with a very low oxidation rate. These results are in agreement with other works in literature, which shows a difficult



Fig. 5. Changes in removal percentage of COD (a) and of TOC (b) vs. the OCC parameter, during the oxidation of a synthetic wastewater polluted with 2-propanol (COD⁰: 2000 mg dm⁻³) by CDEO (\triangle), Fenton oxidation (\Box) and Ozonation (\blacktriangle). Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process: pH 3; *T*, 25 °C; Fe²⁺, 2000 mg dm⁻³. Ozonation: ozone production, 1 g h⁻¹; *T*, 25 °C; pH 12.

oxidazability of aliphatic compounds by Fenton and by ozonation with very low efficiencies [51,52]. Likewise, very similar results have been found in the ozonation and Fenton oxidation of the other compounds studied in this work (ethanol, butyric acid and chloroacetic acid). These results will be discussed in the next section of this paper.

At high initial COD, the results found were very different. As it can be seen almost the complete elimination of the COD and even the complete mineralization of the organic matter contained in the waste is obtained by CDEO. The ozonation process improved the removal percentage for both COD and TOC but still it is less efficient that the electrochemical process. However, the results obtained by Fenton treatment are very similar to those obtained at low initial concentration and an important fraction of refractory carbon remains at the end of the treatment. The presence of these refractory compounds is a major disadvantage for the introduction of theses technologies at industrial scale and for the treatment of highly-loaded wastes, since it leads to the use of a refining process to reduce the oxidation-refractory COD.

The different behaviour observed for the three oxidation technologies studied in this work, has to be explained in terms of the oxidation mechanisms involved in each technique. It is assumed that in these three processes, the hydroxyl radicals are implicated in the oxidation [2,9,35], but according to the results, these huge differences have to be explained by the action of other oxidants. As it is known, the hydroxyl radical is a powerful oxidant but it has been found that, for different causes, it is inefficient in the oxidation of some of the simplest organic compounds, such as acetic and oxalic acids, acetone or simple chloride derivatives as chloroform or tetrachloroethane [1,8]. In the case of CDEO, the higher efficiencies help to confirm that there are other important oxidation processes that complement the hydroxyl radicals mediated oxidation [36]. Among them, two can be of special importance: the direct electro-oxidation on the BDD surface and the oxidation mediated by other electrochemically-formed compounds generated in this electrode, due to the oxidation of salts present in the electrolyte. Thus, in the recent years it has been demonstrated the formation of powerful oxidants such as peroxosulphates, peroxophosphates, hypoclorites or peroxocarbonates, etc by oxidation of sulphates, phosphates, chloride anions or carbonates, respectively [47-50]. In the same way, the better results observed in the oxidation with ozone can be explained by the effect of the molecular ozone, which is very different to the effect of hydroxyl radical [7–9,11,12]. The low oxidation power of the molecular hydrogen peroxide explains the worse results obtained by the Fenton technology, in which the effect of the hydroxyl radicals is, probably, the lone oxidative mechanism.

3.3. Comparison of the three technologies in the oxidation of short-linear-chain organics

Figs. 6 and 7 compare for low (COD around 10^2 mg dm^{-3}) and high (COD around $2 \times 10^3 \text{ mg dm}^{-3}$) initial concentration of pollutants, respectively, the maximum removal percentages of COD and TOC obtained in the treatment of aqueous solutions of the model-compounds by the three studied oxidation technologies.

As it was previously discussed in the case of 2-propanol, significant differences can be observed among the three technologies and between the two ranges of pollutant concentrations. However, the main conclusions obtained for 2-propanol are valid for the other compounds studied in this work.

In the oxidation of weakly-loaded synthetic wastes (Fig. 6), the CDEO allows obtaining the highest removal percentages for both COD and TOC, with almost quantitative removal of the COD and very high removals of TOC (the electrochemical experiments were finished when the oxidation rates become almost negligible, but a certain oxidation capability existed still in that moment). The ozonation process achieves significant removal percentages of COD but an important concentration of oxidation-refractory compounds appears. These circumstances are magnified in the case of the Fenton oxidation, where the ratio of refractory compounds is always over 25% in terms of COD and over 50% in terms of TOC. It is important to note that the formation of refractory compounds is higher in the oxidation of ethanol suggesting an important role of the nature of the organics in the oxidation pathway. Thus, due to its simplicity the oxidation of the molecule of ethanol can only lead to very small number of intermediates, while the possibilities of formation of other compounds increase significantly for the others compounds. This helps to explain the accumu-

(a) 100



80 Removal percentage of COD / % 60 40 20 ethanol butyric acid chloroacetic 2-propanol acid (b) 100 80 Removal percentage of 60 TOC / % 40 20 2-propanol ethanol butyric acid chloroacetic

Fig. 6. Removal percentage of COD (a) and TOC (b) during the oxidation of synthetic wastewater polluted with 2-propanol, ethanol, butyric acid and chloroacetic acid by CDEO (\mathbb{Z}), Fenton oxidation (\square) and ozonation (\square). Initial concentration: 100 mg dm⁻³ of COD. Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process: pH 3; *T*, 25 °C; Ozonation: ozone production, 1 g h⁻¹; *T*, 25 °C; pH 12. Fe²⁺: 2-propanol (42 mg dm⁻³), ethanol (50 mg dm⁻³), butyric acid (100 mg dm⁻³), chloroacetic acid (50 mg dm⁻³).

lation of oxidation-refractory compounds in the treatment of ethanol.

In the oxidation of highly-loaded synthetic wastes (Fig. 7) the CDEO gets again the best removal percentages and also ozonation and mainly the Fenton leads to the accumulation of refractory compounds. Usually, the trends are similar to the obtained working at low initial concentration, even though the removal percentages are significantly increased, especially in the Fenton oxidation.

From the results discussed, it is clear that a certain accumulation of oxidation-refractory organics appear during the treatments. Fig. 8 shows the changes in the MOSC (mean oxidation state of carbon) from the initial to the final step of the oxidation processes. This parameter ranges between -4 for the minor oxidation state of carbon (CH₄) and +4 for the major oxidation state (CO₂) and informs qualitatively about the nature of the organics from measurements of TOC and COD. As it can be expected, CDEO achieves the almost complete mineralization of carbon (MOSC close to +4) in every case. The MOSC of the final products obtained by ozonation (around +3) is normally higher that the ones obtained by Fenton (around +2). These values suggest that the refractory compounds formed in the oxidation technologies are of different nature and they also indicate the necessity of complementing both treatments with

Fig. 7. Removal percentage of COD (a) and TOC (b) during the oxidation of synthetic wastewater polluted with 2-propanol, ethanol, butyric acid and chloroacetic acid by CDEO (\boxtimes), Fenton oxidation (\square) and Ozonation (\square). Initial concentration: 2000 mg dm⁻³ of COD. Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process: pH 3; *T*, 25 °C; ozonation: ozone production, 1 gh⁻¹; *T*, 25 °C; pH 12. Fe²⁺: 2-propanol (2000 mg dm⁻³), ethanol (500 mg dm⁻³), butyric acid (1000 mg dm⁻³), chloroacetic acid (1000 mg dm⁻³).

acid

other technologies to complete the treatment of wastes polluted with aliphatic compounds.

In addition to the treatment (removal of COD) and the mineralization (removal of TOC) capacities, other important parameter which helps to compare oxidation technologies is the efficiency in the use of the oxidant reagents (dose of oxidant required to remove a given amount of COD or TOC). As it has been shown the efficiency depends on the concentration of organics and this dependency is especially important for very low concentrations. For this reason, in this work this parameter has only been evaluated for the oxidation essays of highly polluted wastes and for removal percentages of 50%. These conditions were arbitrarily selected, since for all these cases there was a linear correlation between the COD and the dose of oxidant added, and consequently the efficiency does not depend importantly on the concentration of pollutant. The efficiency in the removal of COD (ε_{COD}) ranges from 0 to 1 g of COD per g of OCC while the efficiency in the removal of TOC (ε_{TOC}) ranges from 0 to 0.25 g of COT g^{-1} of OCC.

Fig. 9 shows the values calculated for both parameters. As it can be observed in part a, the CDEO obtains the highest ε_{COD} for all the compounds studied. These efficiencies were close to the maximum for the oxidation of 2-propanol, butyric acid and chloroacetic acid and they decrease to 0.5 g of COD g⁻¹ of



Fig. 8. Variation between the initial (\blacksquare) and the final mean oxidation state of carbon during the oxidation of synthetic wastewaters polluted with 2-propanol, ethanol, butyric acid and chloroacetic acid by CDEO (\boxtimes), Fenton oxidation (\blacksquare) and ozonation (\square). (a) Initial concentration: 100 mg dm⁻³ of COD; Fe²⁺, 2-propanol (42 mg dm⁻³), ethanol (50 mg dm⁻³), butyric acid (100 mg dm⁻³), chloroacetic acid (50 mg dm⁻³). (b) Initial concentration: 2000 mg dm⁻³ of COD. Fe²⁺: 2-propanol (2000 mg dm⁻³), ethanol (500 mg dm⁻³), butyric acid (1000 mg dm⁻³), chloroacetic acid (1000 mg dm⁻³). Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process: pH 3; *T*, 25 °C; ozonation: ozone production, 1 g h⁻¹; *T*, 25 °C; pH 12).

OCC in the oxidation of the synthetic wastewater polluted with ethanol. As it has been previously discussed, the formation of polymeric materials during the first stages and the reversibility of some of the oxidation reactions on the cathodic surface can explain this lower value. Results obtained by the Fenton and the ozonation technologies are worse than the obtained by the electrochemical technologies and they seem to depend on the nature of the pollutant. The maximum ε_{COD} obtained in the ozonation was $0.3 \text{ g} \text{ COD g} \text{ OCC}^{-1}$ and the efficiencies decrease in the sequence alcohol - carboxylic acid - chlorosubstituted carboxylic acid. This series can be explained taking into account that the Cl- and -COOH groups are electronwithdrawing groups and these groups are weakly reactive to ozone [51]. The Fenton process obtains the lowest efficiency values in most cases. This can be explained in terms of the lower oxidation capacity of hydroxyl radicals towards these compounds [52], and it also suggests the existence of other additional oxidation mechanisms in the oxidation with ozone and in the electrochemical oxidation with diamond anodes [11,12,36]. Table 1 shows the reaction rate of hydroxyl radicals with several aliphatic alcohols and carboxylic acids. The higher value of ε_{COD} in the oxidation of butyric acid is an important dif-



Fig. 9. Effectivity of the use of oxidant reagents in the elimination of the COD and the TOC in the treatment of synthetic wastewaters polluted polluted with 2-propanol, ethanol, butyric acid and chloroacetic acid by CDEO (\boxtimes), Fenton oxidation (\square) and ozonation (\square). Initial concentration: 2000 mg dm⁻³ of COD. Operation conditions. CDEO: natural pH; 5000 mg Na₂SO₄ dm⁻³; *T*, 25 °C; *i*, 30 mA cm⁻². Fenton process: pH 3; *T*, 25 °C; ozonation: ozone production, 1 g h⁻¹; *T*, 25 °C; pH 12. Fe²⁺: 2-propanol (2000 mg dm⁻³), ethanol (500 mg dm⁻³), butyric acid (1000 mg dm⁻³), chloroacetic acid (1000 mg dm⁻³).

ference with ozonation and it can be explained by the higher action of hydroxyl radicals (promoted in the Fenton process) with the increasing number of carbons in the aliphatic molecule (see Table 1).

Part b of Fig. 9 shows the influence of the nature of the pollutant on the values of ε_{TOC} . The CDEO again presents the highest efficiency values, although in this case the COT OCC⁻¹ values are lower comparatively than the COD OCC⁻¹ values, and they are far away from the maximum value. This can be interpreted in terms of the accumulation of intermediates during the first stages of the electrochemical oxidation, with a small carbon dioxide generation. Hence the oxidation of these intermediates should be less favored than the oxidation of the initial compounds. For the ozonation and Fenton oxidation, the low values of the ε_{TOC}

Table 1 Reaction rate of hydroxyl radicals with organics

| Organic | Rate/dm ³ (mol s) ^{-1} | Reference |
|--------------------|---|-----------|
| 2-propanol | 1.9×10^{9} | [53] |
| Ethanol | 1.9×10^{9} | [53] |
| Butyric acid | 2.2×10^{9} | [54] |
| Propionic acid | 6.2×10^{8} | [54] |
| Acetic acid | 1.7×10^{7} | [55] |
| Chloro-acetic acid | 4.3×10^{7} | [56] |

indicate the formation of huge amounts of intermediates and the low tendency to mineralize the waste [1-18].

4. Conclusions

From this work the following conclusions can be drawn:

- Results obtained in the oxidation of 2-propanol, ethanol, butyric acid and chloroacetic acid with Fenton reagent, ozone at pH 12, and with electrochemical oxidation with diamond anodes, show significant differences. Due to the importance of mass transport in the electrolytic technology, the pollutant concentrations also influence importantly on the performance comparison.
- In the oxidation of weakly-loaded synthetic wastes, the CDEO allows obtaining the highest removal percentages for both COD and TOC, with almost quantitative removal of the COD and very high removals of TOC. The ozonation process achieves significant removal percentages of COD but an important concentration of oxidation-refractory compounds appears. These circumstances are magnified in the case of the Fenton oxidation, where the ratio of refractory compounds is always over 50% in terms of TOC.
- In the oxidation of highly-loaded synthetic wastes the CDEO obtains again the best removal percentages and also ozonation and mainly the Fenton process lead to the accumulation of refractory compounds. Usually, the trends are similar to the obtained working at low initial concentration, even though the removal percentages are significantly increased, especially in the Fenton oxidation.
- The final products formed in the three oxidation technologies are of different nature. CDEO achieves the almost complete mineralization of carbon (MOSC close to +4) in every case. The MOSC of the final products obtained by ozonation (around +3) is normally higher that the ones obtained by Fenton (around +2). These huge differences in the final products suggest significant differences in the oxidation mechanisms.
- Although it is assumed that the hydroxyl radicals are implicated in the three oxidation technologies, the different behaviour observed have to be explained by the action of other oxidants. The low oxidation power of the molecular hydrogen peroxide can explain the worse results obtained by the Fenton technology, in which the effect of the hydroxyl radicals is, probably, the lone oxidative mechanism. In the oxidation with ozone the better results can be explained by the effect of the molecular ozone, which is known to be very different to the effect of hydroxyl radical. In the case of CDEO, the direct electro-oxidation on the diamond surface and the oxidation mediated by other electrochemically-formed compounds generated on this electrode (due to the oxidation of salts present in the electrolyte) can contribute to improve the mineralization and the efficiency of the process.

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References

- [1] R.J. Bigda, Chem. Eng. Prog. 91 (1995) 62.
- [2] R.J. Bigda, J. Adv. Sci. Eng. 6 (1996) 34.
- [3] E. Brillas, E. Mur, R. Sauleda, L. Sànchez, J. Peral, X. Domènech, J. Casado, Appl. Catal. B: Environ. 16 (1998) 31.
- [4] F.J. Rivas, F.J. Beltran, J. Frades, P. Buxeda, Water Res. 35 (2001) 387.
- [5] V. Kavitha, K. Palanivelu, Water Res. 39 (2005) 3062.
- [6] T.E. Agustina, H.M. Ang, V.K. Vareek, J. Photochem. Photobio. C-Photochem. Rev. 6 (2005) 264.
- [7] Y. Ku, J.J. Hung, W.Y. Wang, Water Environ. Res. 78 (9) (2006) 901.
- [8] Y. Ku, M.X. Lin, H.W. Chen, J. Environ. Eng.-Asce 132 (12) (2006) 1670.
- [9] E.J. Rosenfeldt, K.G. Linden, S. Canonica, U. Von Gunten, Water Res. 40 (2006) 3695.
- [10] T.P. Sauer, L. Casaril, A.L.B. Oberziner, H.J. José, R.D.P.M. Moreira, J Hazard. Mater. 135 (2006) 274.
- [11] W.R. Chen, C.M. Sharpless, K.G. Linden, I.H.M. Suffet, Environ. Sci. Technol. 40 (2006) 2734.
- [12] N. Kishimoto, Y. Yasuda, H. Mizutani, Y. Ono, Ozone-Sci. Eng. 29 (2007) 13.
- [13] H. Kusic, A.L. Bozic, N. Koprivanac, Dyes Pigments 74 (2007) 380.
- [14] F.J. Benitez, J. Beltran-Heredia, J. Torregrosa, J.L. Acero, J. Chem. Technol. Biotechnol. 74 (1999) 639.
- [15] S. Contreras, M. Rodríguez, F. Al Momani, C. Sanz, S. Espulgas, Water Res. 37 (2003) 3164.
- [16] J.B. De Heredia, J. García, Ind. Eng. Chem. Res. 44 (2005) 8750.
- [17] M. Sánchez-Polo, E. Salhi, J. Rivera-Utrilla, U. von Gunten, Ozone-Sci. Eng. 28 (2006) 234.
- [18] H. Kusic, A.L. Bozic, N. Koprivanac, S. Papic, Dyes Pigments 74 (2007) 388.
- [19] M.A. Rodrigo, P.A. Michaud, I. Duo, M. Panizza, G. Cerisola, Ch. Comninellis, J. Electrochem. Soc. 148 (2001) D60.
- [20] M. Panizza, P.A. Michaud, G. Cerisola, Ch. Comninellis, J. Electroanal. Chem. 507 (2001) 206.
- [21] L. Gherardini, P.A. Michaud, M. Panizza, Ch. Comninellis, N. Vatistas, J. Electrochem. Soc. 148 (2001) D78.
- [22] P. Cañizares, J. García-Gómez, C. Sáez, M.A. Rodrigo, J. Appl. Electrochem. 34 (2004) 87.
- [23] P. Cañizares, C. Sáez, J. Lobato, M.A. Rodrigo, Ind. Eng. Chem. Res. 43 (2004) 6629.
- [24] A.M. Polcaro, M. Mascia, S. Palmas, A. Vacca, Electrochim. Acta 49 (2004) 649.
- [25] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, Electrochim. Acta 50 (2005) 1841.
- [26] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Water Res. 39 (2005) 2687.
- [27] I. Sires, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodriguez, C. Arias, E. Brillas, Electrochim. Acta 52 (2006) 75.
- [28] P. Cañizares, C. Sáez, J. Lobato, M.A. Rodrigo, J. Chem. Technol. Biotechnol. 81 (2006) 352.
- [29] P. Cañizares, L. Martínez, R. Paz, C. Sáez, J. Lobato, M.A. Rodrigo, J. Chem. Technol Biotechnol. 81 (2006) 1661.
- [30] P. Cañizares, R. Paz, J. Lobato, C. Sáez, M.A. Rodrigo, J. Hazard Materer. B 138 (2006) 173.
- [31] P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, Ind. Eng. Chem. Res. 45 (2006) 3468.
- [32] E. Weiss, K. Groenen-Serrano, A. Savall, J. New Mat. Electrochem. Syst. 9 (2006) 249.
- [33] M. Panizza, G. Cerisola, Int. J. Environ. Pollut. 27 (2006) 64.
- [34] P. Cañizares, C. Sáez, J. Lobato, R. Paz, M.A. Rodrigo, Chemosphere 67 (2007) 832.
- [35] B. Marselli, J. García-Gómez, P.A. Michaud, M.A. Rodrigo, Ch. Comninellis, J. Electrochem. Soc. 150 (2003) D79.

- [36] P. Cañizares, C. Sáez, J. Lobato, R. Paz, M.A. Rodrigo, J. Electrochem. Soc. 154 (2007) E37.
- [37] Ch. Comninellis, C. Pulgarin, J. Appl. Electrochem. 21 (1991) 703.
- [38] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M.A. Rodrigo, C. Saez, Electrochim. Acta 52 (2006) 325.
- [39] I.M. Kolthoff, R. Belcher, Volumetric Analysis, vol. III, Interscience Inc. Publishers, New York, 1957.
- [40] M. Bader, J. Hoigné, Water Res. 15 (1981) 449.
- [41] A. Mokrini, D. Ousse, S. Espulgas, Water Sci. Technol. 35 (1997) 95.
- [42] F. Al Momani, C. Sans, S. Esplugas, J. Hazard. Mater. B107 (2004) 123.
- [43] Y.W. Kang, K.Y. Hwang, Water Res. 34 (2000) 2786.
- [44] A.M.F.M. Guedes, L.M.P. Madeira, R.A.R. Boaventura, C.A.V. Costa, Water Res. 37 (2003) 3061.
- [45] G.M. Eisenberg, Ind. Eng. Chem. Anal. 15 (1943) 327.
- [46] P. Cañizares, J. García-Gómez, I.F. Marcos, M.A. Rodrigo, J. Lobato, J. Chem. Ed. 83 (2006) 1204.
- [47] K. Serrano, P.A. Michaud, Ch. Comninellis, A. Savall, Electrochim. Acta 48 (2002) 431.

- [48] P. Cañizares, F. Larrondo, J. Lobato, M.A. Rodrigo, C. Sáez, J. Electrochem. Soc. 152 (2005) D191.
- [49] M. Panizza, G. Cerisola, Electrochim. Acta 51 (2005) 191.
- [50] M.S. Saha, T. Furuta, Y. Nishiki, Electrochem. Commun. 6 (2004) 201.
- [51] M.A. Boncz, Thesis Wageningen University, Wageningen, the Netherlands, with references, with summary in Dutch, 2002, 168 p., ISBN 90-5808-758-1.
- [52] T. Turan-Ertas, M.D. Gurol, Chemosphere 47 (2002) 293.
- [53] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.
- [54] G. Scholes, R.L. Willson, Trans. Faraday Soc. 63 (1967) 2983.
- [55] M. Chin, P.H. Wine, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, CRC Press, Inc., Boca Raton, FL, 1994, p. 85.
- [56] G.E. Adams, J.W. Boag, J. Currant, B.D. Michael, in: M. Ebert, J.P. Keene, A.J. Swallow, J.H. Baxendale (Eds.), Pulse Radiolysis, Academic Press, New York, 1965, p. 131.