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Electrochemical treatment of the effluent of a fine chemical manufacturing plant

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Abstract

In this work, the electrochemical oxidation of an actual industrial wastewater with conductive-diamond anodes has been studied. The wastewater is the effluent of a fine chemicals plant. This effluent consists of an aqueous solution of solvents (ketones and alcohols) with a high concentration of aromatic compounds coming from the raw materials, intermediates and products of the different processes of the plant and its COD is around 6000 mg dm^{-3}. The electrolyses were carried out in a discontinuous operation mode under galvanostatic conditions, using a bench-scale plant equipped with a single compartment electrochemical flow cell. The conductive-diamond electrochemical oxidation (CDEO) allowed achieving the complete mineralization of the waste with high current efficiencies. These efficiencies seem to strongly depend on the concentration, pH and temperature but not on the current density (in the range studied). This confirms that besides the hydroxyl radicals mediated oxidation, CDEO combines other important oxidation processes such as the direct electrooxidation on the diamond surface and the oxidation mediated by other electrochemically formed compounds generated on this electrode. Other two advanced oxidation processes (ozonation and Fenton oxidation) have been also studied in this work for comparison purposes. Both technologies were able to treat the wastes, but they obtained very different results in terms of efficiency and mineralization. The efficiency of ozonation and electrochemical oxidation were very similar (especially during the first stages), although the energy consumption required by the electrochemical process to remove at fixed percentage of COD or TOC was significantly smaller than that of ozonation. The possible accumulation of carboxylic acid as final products excludes the use of Fenton oxidation as a sole treatment technology.
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Keywords: Actual wastewater; Conductive-diamond electrochemical oxidation; Fenton process; Ozonation

1. Introduction

In the recent years, electrochemical oxidation with conductive-diamond anodes has appeared as one of the most promising technologies in the treatment of industrial wastes polluted with organics. Compared with other electrode materials, conductive-diamond has shown a higher stability and efficiency. During the recent years, conductive-diamond electrochemical oxidation (CDEO) has been widely studied with synthetic industrial wastes in lab and bench-scale plants [1–17], but unfortunately only few papers have focused the electrochemical treatment of actual aqueous wastes [18]. The main conclusion 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.

Recently, it has been demonstrated that hydroxyl radicals are formed during the electrolysis on conductive-diamond anodes of aqueous electrolytes [19] and this has allowed classifying this technology as an advanced oxidation process (AOP). Besides this mechanism, the global oxidation process in conductive-diamond anodes is known to be complemented by direct electrooxidation on the surface and also mediated oxidation by other oxidants electrogenerated on the surface from the electrolyte salts [16]. The combination of these oxidation mechanisms has shown to increase the current efficiency of this technique, as compared with other electrochemical technologies. Nevertheless, the energy requirements in the oxidation of industrial wastewaters are still very high due to the large number of electrons required to completely oxidize the organic matter to carbon dioxide. In spite of this, the operation costs reported for this tech-

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Table 1
Characteristic of the fine chemicals and pharmaceutical industries (FCI) wastewaters studied

Parameter	Value
COD (mg dm^{-3})	6000
TOC (mg dm^{-3})	1600
pH	6
Conductivity (mS cm^{-1})	25
Composition	Aromatic and aliphatic compounds, ethanol, methanol

nology are even lower than those required by other electrochemical technologies [14,18,20]. However, the main drawback of this technology is the high price of conductive-diamond anodes.

Fine chemicals and pharmaceutical industries (FCI) wastewaters are characterized by the great variety of pollutants contained, as a consequence of the large variety of the raw materials used and of the complexity of the processes carried out. Normally, these plants operate in batch mode (different manufacturing processes coexist) and the effluents generally contain small quantities of reaction intermediates and products and large amounts of the dissolvent used to recover the raw materials. Thus, although the concentration and proportion of pollutants contained in the wastes can vary, the average composition and characteristics of the effluents almost does not fluctuate. The actual wastewater used in this work comes from a fine chemical plant. Its main characteristics are summarized in Table 1. As it can be observed, it is mainly composed of a great variety of organics (aromatic and aliphatic compounds) and solvents such as methanol and ethanol. Its organic load is around 6000 mg dm^{-3} of COD and the ratio TOC/COD is around 0.27. Moreover, its high conductivity can be explained in terms of a very high concentration of chloride ions.

In recent years, only few papers have engaged on the treatment of this kind of actual wastes, and they have been focused mainly on the study of ozonation [21], Fenton [22] and photochemical AOP [23], but not on conductive-diamond electrochemical oxidation. Thus, the goal of this work is to study the treatment of this actual industrial waste with conductive-diamond electrochemical oxidation (CDEO), to study the role of the main oxidative mechanisms in the electrochemical oxidation of organics with conductive-diamond electrodes and to compare the results obtained with those obtained using other AOP technologies.

2. Experimental

2.1. Analytical procedure and determination of the current efficiency

The carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. The chemical oxygen demand (COD) was determined using a HACH DR200 analyzer. The COD method was used for the determination of the current efficiency. In this method, the COD was measured during electrolysis and the instantaneous (ICE) and the average current efficiency (ACE) were calculated using the relations:

$$\mathrm{ICE} = \frac{[\mathrm{COD}_{t+\Delta t} - \mathrm{COD}_t]FV}{8I\,\Delta t},$$

$$\mathrm{ACE} = \frac{[\mathrm{COD}_0 - \mathrm{COD}_t]FV}{8It}$$

where COD_0, COD_t and $\mathrm{COD}_{t+\Delta t}$ are the COD (g O_2 dm^{-3}) at times 0, t and $t+\Delta t$ (s), respectively, I is the current intensity (A), F the Faraday constant (96487 C mol^{-1}), V the volume of the electrolyte (dm^3) and 8 is the dimensional factor for unit consistence (32 g O_2 mol^{-1} O_2/4 mol e^{-1} mol^{-1} O_2). Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

2.2. 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 kg 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 (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 equations:

$$\mathrm{OCC}\,(\mathrm{kg\,O_2\,m^{-3}}) = 0.298\,Q\,(\mathrm{kA\,h\,m^{-3}})$$
$$= 1.000[\mathrm{O_3}]\,(\mathrm{kg\,O_3\,m^{-3}}) = 0.471[\mathrm{H_2O_2}]\,(\mathrm{kg\,H_2O_2\,m^{-3}})$$

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.

2.3. Conductive-diamond electrochemical oxidation

In this work, the CDEO assays were carried out in a single-compartment electrochemical flow-cell working under a batch operation mode [16]. 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 (flowrate 2.5 dm^3 min^{-1}). A heat exchanger coupled with a controlled thermostatic bath

Table 2
Characteristic of the BDD used in this work

Parameter	Value
Scotch test adhesion	+
Electrical resistance (Ω)	5.6
BDD-film thickness (μm)	2.74
BDD-film Raman sp^3/sp^2	108
BDD-film boron concentration (ppm)	1300
CALT (kA h cm^{-3})	50

(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 vapour deposition technique (HF CVD) on single-crystal p-type Si (1 0 0) wafers (0.1 Ω cm, Siltronix). The main characteristics of the BDD used in this work are summarized in Table 2. Electrolyses were carried out in galvanostatic mode. During the electrolyses no control of pH was carried out.

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). This reactor consists of a 2.5 dm^3 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 used 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 [24]. Dissolved ozone concentration in the liquid phase was determined spectrophotometrically (600 nm) from discoloration of the resulting solution, by the Karman indigo method [25]. In the experiments described in this work, 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 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 dm^3 h^{-1}. The ozone generator was switched on before to run of 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 [26,27], 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.

2.5. 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 and Co., KG, Staufen, Germany) 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. According to literature [28,29], 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 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 with Eisenberg [30]. 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 set of experiments were carried out to determine the range of hydrogen peroxide and iron required to obtain optimum results.

3. Results and discussion

3.1. Performance of a discontinuous CDEO

Fig. 1 shows the results obtained in the electrolysis of the actual FCI wastewater (pH: natural, T: 25 °C, j: 300 A m^{-2}). It can be observed that COD decreases with the specific electrical charge passed (Q) down to zero. On the other hand, although the complete removal of the TOC concentration is achieved, a complex shape (with a plateau zone in the first stages of the oxidation process) is obtained. This fact could be explained attending to the intermediates generated in the process. In literature [16], it is proposed that the CDEO of most organic compounds leads first to the formation of carboxylic acids and later to the oxidation of

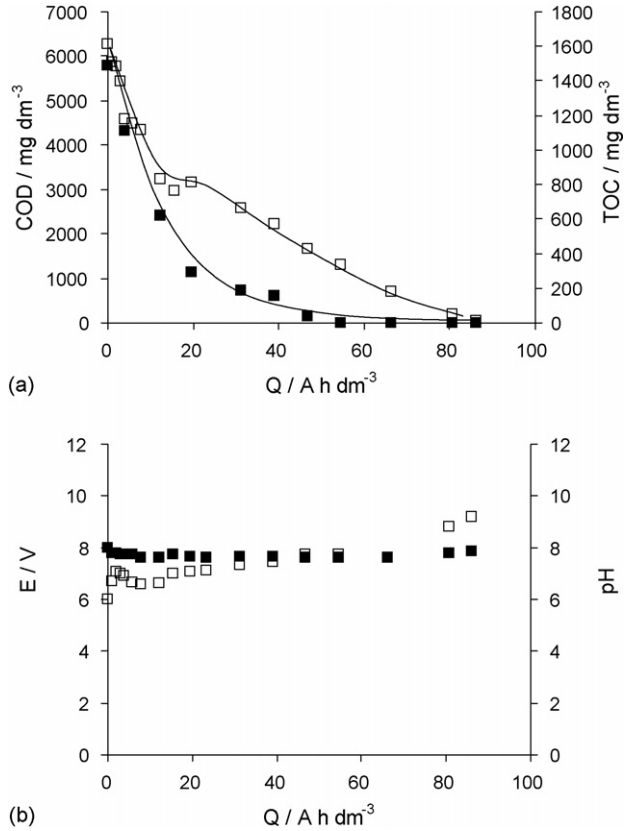

Fig. 1. (a) Variation of COD (■) and TOC (□) with the specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. (b) Variation of the cell potential (■) and pH (□) with the specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. Experimental conditions: natural, pH; T, 25 °C; j, 300 A m^{-2}.

these organic acids to carbon dioxide. Generally the oxidation of carboxylic acid is the limiting step due to their lower oxidizability. Thus, the accumulation of these acids with very low COD and a significant TOC concentration allow explaining the abrupt change obtained in COD and the slower decrease of the TOC concentration.

Fig. 1b shows the changes in pH and potential during the same electrolysis. As it can be observed, the pH of the waste increases slightly at the beginning of the oxidation process. These changes can be explained in terms of the anodic and cathodic reactions that take place in the cell. The water reduction on the cathode leads to the generation of hydroxyl anions. Conversely, on the anode the oxidation of organics (and/or inorganic compounds) and the generation of protons from water oxidation coexist. As a consequence of the competing reaction, the proton generation rate on the anode is lower than that of hydroxyl anions. Thus, the generation of protons only compensates partially the cathodic anions generated and, consequently, the pH increases. It can be also seen that the cell potential is maintained almost constant during all the electrolysis, indicating that the formation of non-conductive layers on the surface of the electrodes or the electrodes corrosion did not occur.

Fig. 2 shows the changes in the average and the instantaneous current efficiencies during the same electrolysis experiment. It can be observed that maximum efficiencies are obtained during

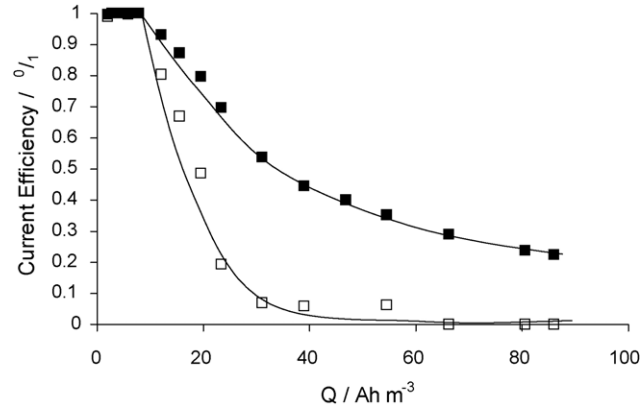

Fig. 2. Variation of the instantaneous (□) and average current efficiency (■) with the specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. Experimental conditions: natural pH; T, 25 °C; j, 300 A m^{-2}.

the initial stages of the process, and that there is a continuous decrease of the efficiencies during the experiment. This behaviour is characteristic of discontinuous CDEO of wastewaters and it is usually explained in terms of mass transfer limitations assuming that the main mechanism involved in the electrochemical oxidation on conductive-diamond anodes is a direct or a hydroxyl radical mediated electrochemical oxidation process [5,16,19].

3.1.1. Influence of the operation conditions in the CDEO

Figs. 3 and 4 show electrolyses of the FCI wastewater carried out at different current densities. As it can be seen, an increase in the current density leads to an increase in the oxidation rate. However, similar electrical charges are required in all cases to remove the same amount of organic matter and consequently the ICE versus COD profiles are almost overlapped. This means that the current density does not influence on the efficiency in the range studied (150–600 A m^{-2}) and, it also suggests that chemical oxidation by stable electrogenerated oxidants (mediated electrochemical oxidation) plays an important role in the overall electrochemical oxidation process of organics. In this case, this mechanism can be even more significant that the direct oxidation of pollutants on the electrode surface, and it can be also

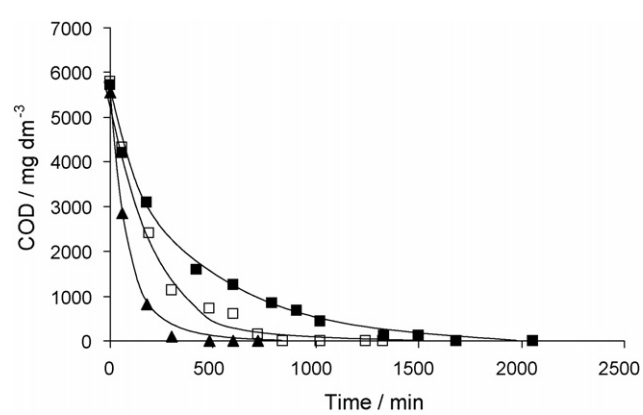

Fig. 3. Variation of COD with time in the electrochemical oxidation of an FCI wastewater. Experimental conditions: natural pH; T, 25 °C. Current density: (□) 300 A m^{-2}; (■) 150 A m^{-2}; (▲) 600 A m^{-2}.

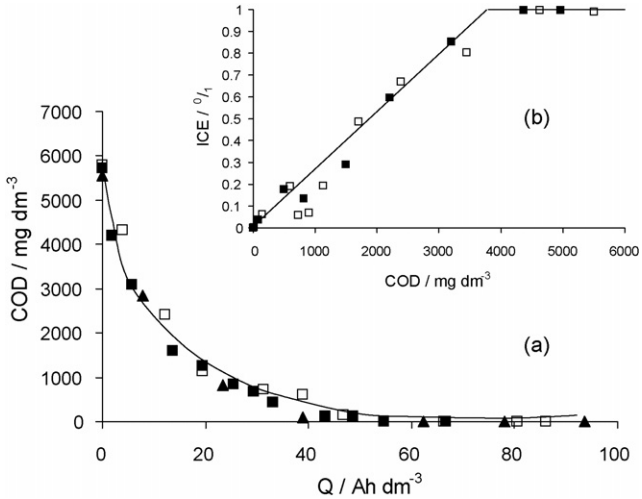

Fig. 4. (a) Variation of COD with specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. (b) Variation of the instantaneous current efficiency (ICE) with the COD in the electrochemical oxidation of an FCI wastewater. Experimental conditions: natural pH; T, 25 °C. Current density: (□) 300 A m^{-2}; (■) 150 A m^{-2}; (▲) 600 A m^{-2}.

more important that the oxidation mediated by hydroxyl radicals (taking into account the low average lifetime of hydroxyl radicals, the oxidation carried out by these species can be considered as a direct process from the mass-transport point of view). In literature, it is proposed that the conductive-diamond electrochemical oxidation of wastes containing salts leads to the formation of some oxidized reagents such as peroxodisulphates [31], peroxodiphosphates [32] and of course of hypochlorite [10,16] (or hypochlorous acid as a function of the pH) depending on the salt contained in the wastewater. The high concentration of chloride ions in the actual FCI wastewater can promote the formation of active chloro species and they can explain the small influence of the current density: the stability of the chlorinated oxidants and their high oxidation capacity extend the oxidation reaction through the complete reaction volume.

Fig. 5 shows the influence of temperature on the electrolytic process. As it can be seen, an increase in the temperature leads to more efficient processes. Since direct oxidation processes

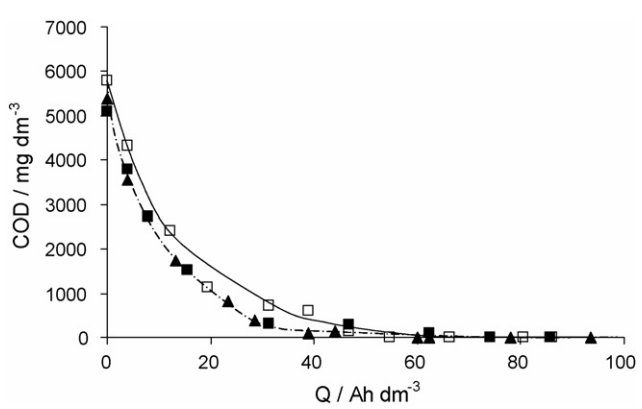

Fig. 5. Variation of COD with specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. Experimental conditions: natural pH; j, (□) 300 A m^{-2}; T, (□) 25 °C, (■) 40 °C, (▲) 60 °C.

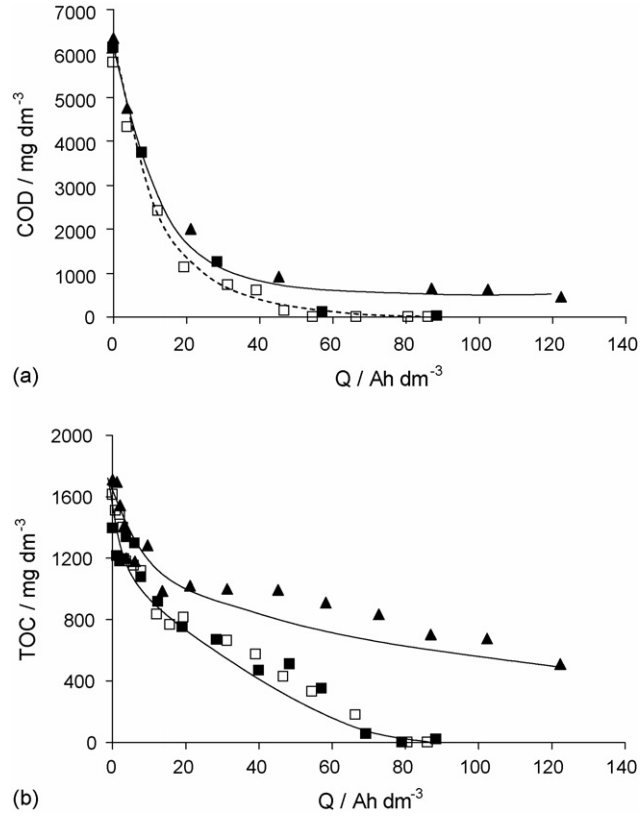

Fig. 6. Variation of COD (a) and TOC (b) with the specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. Experimental conditions: T, 25 °C; j, 300 A m^{-2}; pH, (□) natural, (■) 12, (▲) 2. Solid line: trend line.

remain almost unaffected by temperature (mass-transfer coefficients are not going to be greatly modified in the range of temperatures studied), this fact should be also explained in terms of mediated oxidation processes by inorganic electrogenerated reagents (chlorine, hypochlorous acid or hypochlorite), whose rate should be greatly improved by temperature. The small change observed between 40 and 60 °C can be explained by the thermal decomposition of several oxidants that it is reported to occur in this range [10].

The influence of the pH of the waste in the electrochemical oxidation process is shown in Fig. 6. Acidic pH leads to less efficient processes both in terms of COD and TOC elimination. However, changes in the pH from neutral to alkaline do not seem to affect to the oxidation rates. These observations can be explained in terms of the primary active chloro species. At pH 2 the primary active chloro species is Cl_2. This compound can be formed in the reactor but the experimental setup used in this work promotes its desorption in the storage tank. Consequently, at strongly acidic conditions the mediated electrochemical oxidation by active chlorine electrogenerated is not favoured and the direct oxidation (or the hydroxyl mediated oxidation) should be the primary mechanism. At natural pH (pH around 6), and at alkaline pH, the primary active chloro species are HClO and ClO^-, respectively. These species are almost not affect by desorption of gases and they can act as oxidizing reagents in the whole volume of wastewater. The effect

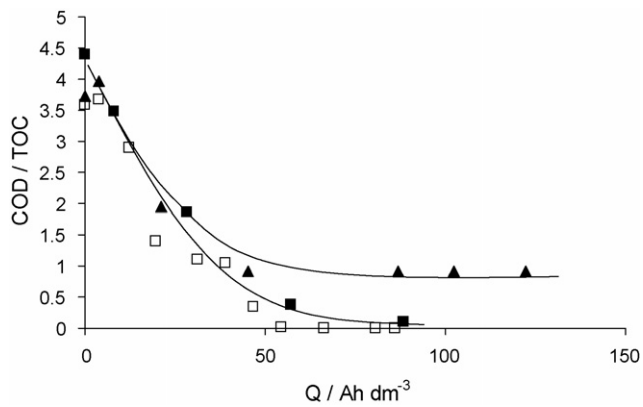

Fig. 7. Variation of COD/TOC with the specific electrical charge passed in the electrochemical oxidation of an FCI wastewater. Experimental conditions: T, 25 °C; j, 300 A m^{-2}; pH, (□) natural, (■) 12, (▲) 2.

of the oxidation mechanisms can be also observed in the oxidation products. Thus, Fig. 7 shows the changes in the COD/TOC ratio during the former electrolyses. It can be observed that in alkaline and neutral conditions the complete mineralization of the organics is obtained while acidic conditions lead to a final COD/TOC ratio around 1, which can correspond to the accumulation of carboxylic acids. It is known that the oxidation of carboxylic acids by chlorine is very effective. However, it is not very efficient in the case of hydroxyl radicals (oxidation rate even three-folder lower than those of phenol and hydroquinone) or in case of direct electrooxidation (anodic oxidation potential even above water oxidation).

Fig. 8 shows the energy required to reduce the organic load (COD) of the FCI wastes at different operation conditions. As it can be observed, almost all the experimental data lay over the same curve. Only data corresponding to the essay carried out at acidic pH differs slightly. In these curves two zones can be distinguished. In the first zone, the energy requirement increases linearly up to removal around 90% and then it starts to increase exponentially to get the 100% of removal. This means that this technique can be used in an economically adequate way for a pretreatment of the waste and that although a big removal of COD is feasible to be obtained from the technical point of view, the energy cost made this technique unsuitable for its use in a refining process.

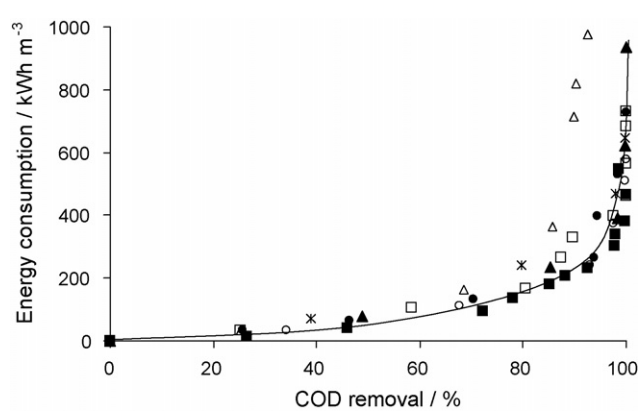

Fig. 8. Variation of the energy consumption with the percentage of COD removal in the electrochemical oxidation of an FCI wastewater. Experimental conditions: (□) natural pH, T 25 °C; j 300 A m^{-2}; (■) natural pH, T 25 °C, j 150 A m^{-2}; (▲) natural pH, T 25 °C, j 600 A m^{-2}; (*) pH 12, T 25 °C, j 300 A m^{-2}; (△) pH 2, T 25 °C, j 300 A m^{-2}; (◯) natural pH, T 40 °C, j 300 A m^{-2}; (●) natural pH, T 60 °C, j 300 A m^{-2}.

3.1.2. Comparison with other advanced oxidation process (AOP)

Fig. 9 shows the COD and TOC profiles during the discontinuous ozonation (at alkaline pH) of the FCI wastewater studied in this work. As it can be observed, the ozonation process can treat successfully this kind of actual wastewater. However, the complete removal of organic load is not achieved and a small concentration of organic carbon (9%) remains at the end of the process. Unlike the CDEO, the COD value is significant and the ratio COD/TOC is still higher at the end of the treatment. To explain this observation, it has to be taken into account that the wastewater studied in this work contains large amounts of chloride and that these species can influence on the value of the COD. Thus, the outstanding concentration of these inorganic species can explain the high value of COD obtained at the end of the process in comparison with that of TOC and with the results obtained in the CDEO. Fig. 9b shows the changes in the global and instantaneous efficiency during the discontinuous ozona-

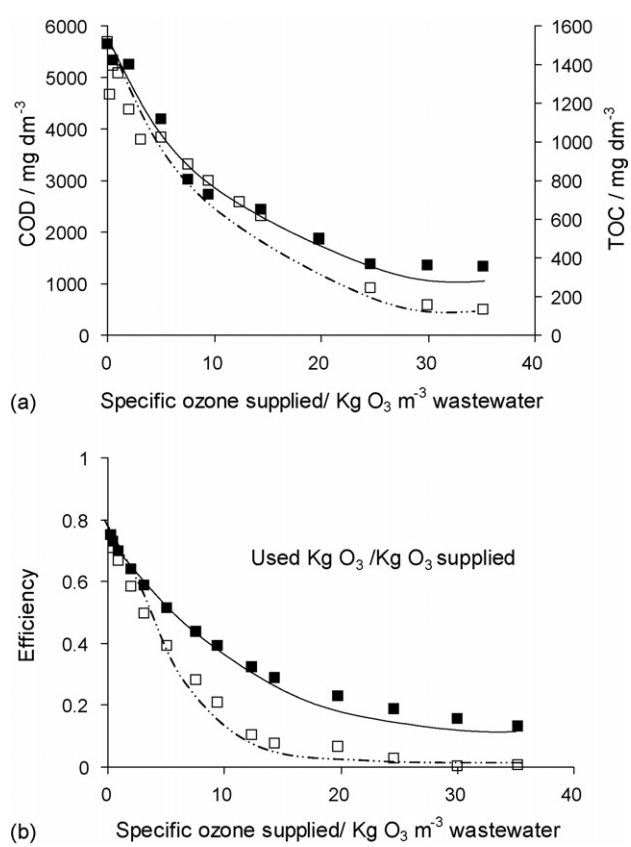

Fig. 9. (a) Variation of the COD (■) and TOC (□) with specific ozone supplied in the ozonation process of an FCI wastewater. (b) Variation of the global (■) and instantaneous (□) efficiency (used kg O_3/kg O_3 supplied) with specific ozone supplied in the ozonation process of an FCI wastewater. Experimental conditions: pH 12; T, 25 °C; ozone production, 0.99 g h^{-1}.

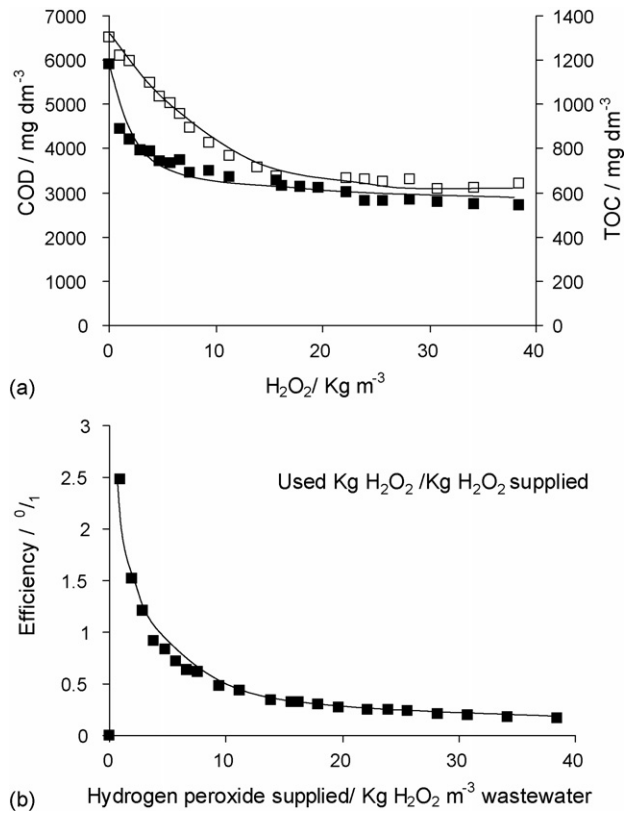

Fig. 10. (a) Variation of the COD (■) and TOC (□) with hydrogen peroxide in the Fenton oxidation of an FCI wastewater. (b) Variation of the efficiency (used kg H_2O_2/kg H_2O_2 supplied) in the Fenton oxidation of an FCI wastewater. Experimental conditions: pH 3; *T*, 25 °C; Fe^{2+}, 850 mg dm^{-3}.

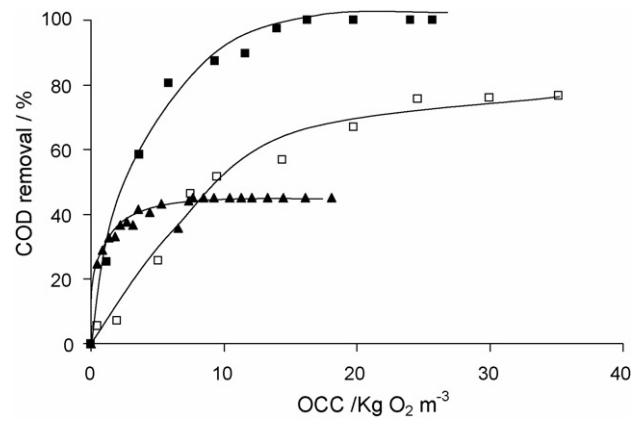

Fig. 11. Changes in the removal percentage of COD the OCC during CDEO (■), ozonation (□) and Fenton oxidation (▲) of an FCI wastewater. Experimental conditions of BDD electrolysis: natural pH; *T*, 25 °C; *j*, 300 A m^{-2}. Experimental conditions of ozonation: pH 12; *T*, 25 °C; ozone production, 0.99 g h^{-1}. Experimental conditions of Fenton oxidation: pH 3; *T*, 25 °C; Fe^{2+}, 850 mg dm^{-3}.

tion process. As it can be observed, a maximum of 80% of the ozone supplied is employed in the oxidation process, and this percentage decreases with the initial COD concentration.

Fig. 10 shows the variation of TOC and COD in the Fenton oxidation of the FCI waste. It can be observed that an important fraction of both refractory carbon and inorganic compounds (high TOC and COD) remain at the end of the treatment (50% of the organic carbon). These high concentrations of refractory carbon also appear in the Fenton oxidation of other kind of aqueous wastes [14,18] and seem to be characteristic of this oxidation process. As it can be observed in part b of Fig. 10, at the initial stages of the process, efficiencies over 100% (calculated as kg H_2O_2 used/kg H_2O_2 supplied) are obtained. This fact can be explained in terms of slide coagulation processes caused by the action of iron ions added to the solution.

These results suggest that the mechanisms involved in the three technologies are different, and it also confirms that the mechanisms of oxidation in the three technologies are not only based in the production and use of hydroxyl radicals, but they must also include other kinds of oxidation mechanisms specific of each technology. In the case of ozonation process under alkaline conditions, molecular ozone and other radicals can also contribute to the global oxidation process although in a lesser extension. Likewise, electrochemical technology combines other important oxidation processes such as the direct electrooxidation on the BDD surface and the oxidation mediated by other electrochemically formed compounds generated in this electrode [10,16,31,32]. Conversely, in Fenton oxidation hydroxyl radical oxidation is the sole oxidation mechanism and, thus, lower efficiencies are obtained (Fig. 10b). This fact could be indicative of the lower action of the hydroxyl radicals in the oxidation of the pollutants contained in the actual waste.

As it was previously mentioned, one of the goals of the present paper was to compare the three technologies in the best conditions. Unfortunately, the lack of literature about the comparison of different AOP technologies leads to the lack of parameters for comparison of these technologies. To solve this, a new parameter called oxygen-equivalent chemical oxidation capacity (OCC) was recently proposed in literature [33] by our research group. 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 O_2/m^3 of wastewater). Fig. 11 shows the changes in the COD removal with the quantity of oxidant added in the three AOP studied. As it can be observed, the initial efficiency in the COD removal is slightly higher in the Fenton oxidation and significantly less efficient in the ozonation. However, Fenton process is not able to achieve percentage of COD elimination higher than 50%, while ozonation and CDEO allow obtaining the almost complete COD removal.

On the other hand, 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. Fig. 12 shows the changes in the TOC and COD versus the energy consumption for the ozonation and electrochemical oxidation of an FCI waste. It can be observed that the energy requirements are significantly lower for the electrochemical oxidation. This indicates that electrochemical technology could compete successfully with other AOP commonly used (like ozonation). However, to include in this comparison the operating cost of the Fenton oxidation is very difficult and it overcomes the goal of a scientific work. The cost of the raw materials (hydrogen peroxide and iron), of the sludge treatment, of the reagents used to change the pH can vary a lot and they depend on the country, the year and many other

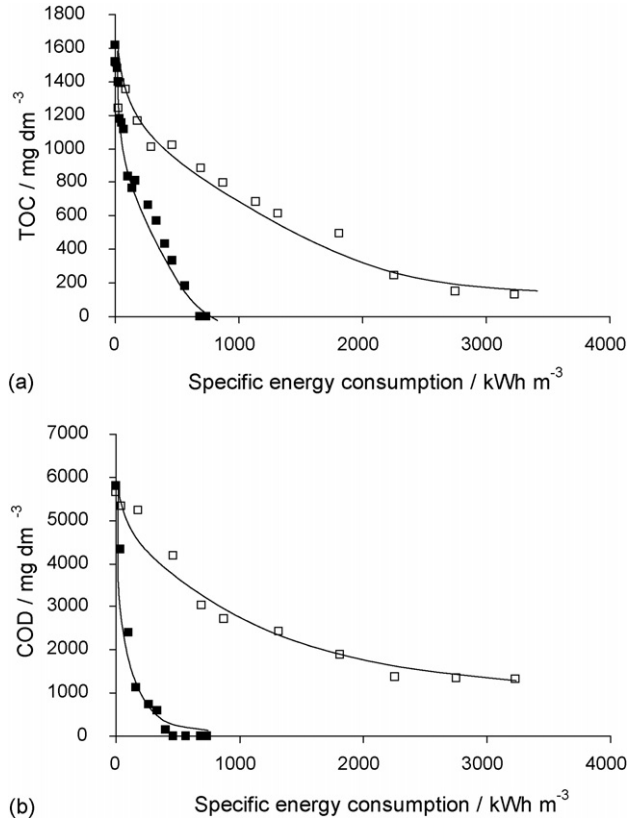

Fig. 12. Variation of the COD and TOC with specific energy consumption in the electrochemical oxidation with BDD (■) and ozonation (□) of an FCI wastewater. Experimental conditions of BDD electrolysis: natural pH; T, 25 °C; j, 300 A m^{-2}. Experimental conditions of ozonation: pH 12; T, 25 °C; ozone production, 0.99 g h^{-1}.

parameters that, in our opinion, should not be included in a scientific work and consequently they are out of the scope of the paper.

4. Conclusions

The following conclusions can be drawn from the work described here:

- Electrochemical oxidation with BDD electrodes can be used successfully to remove the COD and TOC of actual wastewater from a FCI. The global efficiencies of the process depend strongly on the pH and on the temperature.
- The influence of the current density is less important, atleast in the range studied (150–600 A m^{-2}). It also suggests that chemical oxidation by stable electrogenerated oxidants (mediated electrochemical oxidation) plays an important role in the overall electrochemical oxidation process. The presence of large amounts of inorganic salts in the actual aqueous waste (high concentration of chloride) favours the rate of the electrochemical processes and increases the mineralization efficiency significantly. This fact confirms the importance of mediated oxidation processes by active chloro species in the overall electrochemical oxidation process of fine chemical wastewaters.
- During the electrolyses of actual wastes, the energy requirements increases linearly up to an 80% removal and then they started to change exponentially. This means that this technique can be used in an economically adequate way for a pretreatment of the waste and that although a big removal of COD is feasible to be obtained from the technical point of view, the energy cost made this technique unsuitable for a refining process.
- 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 a fine chemical aqueous waste with the three technologies leads to very different results. This confirms that other kinds of oxidation mechanisms specific of each technology (f.i. persulphate and direct electrooxidation in CDEO, chemical ozone oxidation, etc.) must be considered.

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