Catalysis Today 151 (2010) 173–177

Contents lists available at ScienceDirect

Catalysis Today

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

Use of conductive-diamond electrochemical oxidation for wastewater treatment

M.A. Rodrigo *, P. Cañizares, A. Sánchez-Carretero, C. Sáez

Department of Chemical Engineering, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

ARTICLE INFO

Article history:
Available online 1 March 2010

Keywords:
Electrochemical oxidation
Diamond
Wastewater
Hydroxyl radical

ABSTRACT

In this work, the more relevant figures about the use of conductive-diamond electrochemical oxidation (CDEO) in the treatment of industrial wastes are described. It is shown that it is a good technology to treat many industrial effluents with organic loads below 20000 mg dm^{-3}, very efficient, robust and non-selective. It has been observed that the nature of the pollutant does not affect significantly the efficiency of the process. Conversely, organic load and current density show a marked influence in the results. The efficiency of the process increases with the organic content, and mass-transfer limitations seems to be the major drawback of the technology. CDEO is more efficient that electrolysis with other anodic materials, and its main advantage against other advance oxidation technologies is that it does not lead to the formation of oxidation-refractory intermediates. The combined action of direct electrolysis, hydroxyl radicals and that of other oxidants produced from the salts contained in the wastes seems to be the responsible of this good behavior. Two observations related to the production of hydroxyl radicals help to support this: the effect of the pH and that of the anodic potential on the efficiencies of the process.

1. Introduction

In the recent years, several works have been published concerning the application of conductive-diamond electrochemical oxidation (CDEO) for the treatment of aqueous wastes. Pollutants oxidized in the studies with synthetic wastes include cyanide [1], carboxylic acids [2,3], alcohols, and aromatic and polyaromatic compounds [4–7]. However, this list is even greater if the treatment of actual wastes is also considered. Thus, CDEO has been applied to the treatment of olive-oil mills [8], wooden manufacturing factories [9–11], surphactants [12] and even to the treatment of wastes consisting of merged effluents of different industries [13,14]. In every case, a successful treatment has been obtained. Thus, it has been concluded that it is a robust and efficient technology which, in most cases, is able to achieve the complete mineralization of the organics contained in the wastes. The efficiency of the technology is very high, and it only seems to be limited by the transport of pollutants to the anodic surface.

Many approaches have been used to increase these efficiencies, such as the special design of cells [15], the combination of cathodically produced hydrogen peroxide with CDEO [16], or the use of ultrasounds [17]. All of them have shown good results, and have focused CDEO as a hot topic in industrial wastewater treatment and in the treatment of other wastewater such as those coming from soil remediation processes.

In addition, conductive-diamond electrodes show a great chemical and electrochemical stability, and an acceptable conductivity. The high overpotential for water electrolysis seems to be the more important property of conductive-diamond in its use in aqueous media. This electrochemical window is large enough to produce hydroxyl radicals with high efficiency, and this radical seems to be directly involved in the oxidation mechanisms that occur on diamond surfaces [18]. According to literature, direct oxidation models fit well the experimental data [19–22], specially for non-chlorinated or nitrogenated substituted aromatics. However, it is known that in the electrochemical oxidation of wastewaters on conductive-diamond other oxidants are generated including persulphates [23], peroxophosphates [24], oxochlorinated anions [25] and hydrogen peroxide [26], depending on the waste composition and on the operation conditions. Thus, besides direct electro-oxidation on the surface and oxidation by means of hydroxyl radicals in a region close to the electrode surface, the oxidation mediated by other oxidants electrogenerated on the surface from the electrolyte salts should be taken into account, as it can complement the mechanisms of oxidation in this kind of electrochemical technology, and it contributes to increase the global oxidation efficiency.

Consequently, CDEO has shown better perspectives towards its application than other electrochemical oxidation technologies, and even that other advanced oxidation processes. In this context, the goal of this paper is to describe the more relevant figures of CDEO related to its use in industrial applications, and to point out the important role of the oxidation mechanisms that happen inside the electrochemical reactor and that shift CDEO as a very promising

---

* Corresponding author. Tel.: +34 902204100x3411.
E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.01.058

technology for the removal of organic pollutants in industrial wastes.

2. Materials and methods

2.1. Wastewater characterization

In this work, both synthetic (propanol, phenol, hydroxybenzenes, chlorophenols, nitrophenols and dyes) and actual (pharmaceutical, olive-oil mills, chemical, petrochemical and door-manufacturing) wastewaters have been studied. In the case of electrochemical oxidation 5000 mg Na_2SO_4 dm^{-3} was used as supporting electrolyte.

2.2. Analytical procedure

The chemical oxygen demand (COD) was used to monitor the organic load of the wastes. It was determined using a HACH DR200 analyzer. Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

2.3. Conductive-diamond electrochemical oxidation (CDEO)

The oxidation of each organic pollutant was carried out in a single-compartment electrochemical flow cell working under a batch operation mode [2]. Diamond-based material, graphite, lead dioxide (Pb/PbO_2) and dimensional stable anodes (DSA) were 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 each and an electrode gap of 9 mm. Boron-doped diamond (BDD) films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si ⟨1 0 0⟩ wafers (Siltronix). Lead dioxide was synthesized in our laboratory by electrochemical oxidation of lead plates at a current density (j) of 10 mA cm^{-2} in a 10% sulfuric acid solution at 25 °C for 90 min. Commercial DSA-O_2 and graphite electrodes were supplied by ElectroCell AB (Sweden).

The electrolyte was stored in a glass tank (500 ml) and circulated through the electrolytic cell by means of a centrifugal pump (flowrate 2.5 dm^3 min^{-1}). A heat exchanger 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.

Electrolyses were carried out in galvanostatic mode, controlling the current density and monitoring the anodic cell potential and cell potential. The cell potential was constant during each electrolysis, indicating that appreciable deterioration of the electrode or passivation phenomena did not take place during any test. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 30 min in a 1 M Na_2SO_4 solution at 50 mA cm^{-2} to remove any kind of impurity from its surface.

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 dm^3) equipped with a porous gas distribution plate and baffles to increase the capacity of absorption of ozone. 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. The pH was maintained in a set point close to 12 ± 0.1. A jacketed 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, Germany) with 15 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. 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. Hydrogen peroxide was measured by colorimetric determination.

3. Results and discussion

Fig. 1 shows the changes of the COD with the specific charge passed during the CDEO of four actual wastewaters. These effluents consist of aqueous wastes with a high concentration of organics, coming from the raw materials, intermediates and products of the different manufacturing plants (petrochemical, fine-chemical, door-manufacturing plants and olive-oil mills).

As it can be seen, and although the four wastes are very different in composition and organic load, the electrochemical process can remove successfully the organic load contained in the studied wastes down to zero. This means that this technology can be used not only to accomplished the typical discharge limits to municipal sewage collectors (around 1000–1500 mg dm^{-3} in Spain) but also to the direct discharge into rivers (COD around 125 mg dm^{-3}), or even for the reuse of the treated waste.

In every case, two different behaviors seem to be obtained (inset of Fig. 1). During a first stage (COD > 1500 mg dm^{-3}), the COD seems to decrease linearly with charge and after this value, the change of the COD becomes exponential. This type of variation is characteristic of electrochemical oxidation of aqueous wastes polluted with organics, and it has been well-explained in literature

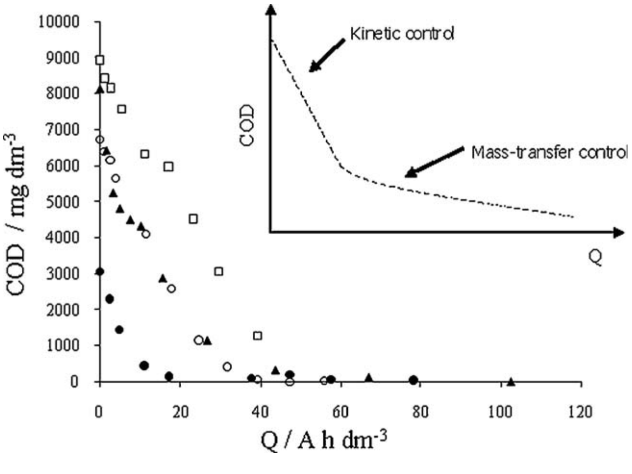

Fig. 1. Variation of the COD with the electrical charge passed during the electrochemical oxidation with BDD anodes of wastewaters generated in: olive mill process (●), petrochemical process (○), chemical plant (□) and door-manufacturing factories (▲). Inset: typical variation of the COD with the electrical charge. Experimental conditions: natural pH, j: 30 mA cm^{-2}; T: 25 °C.

[2,19] in terms of the controlling mechanisms of the electrochemical process (electrodic or mass transport): at low CODs the process is mass-transfer controlled, and the oxidation rate depends on the concentration of COD; at higher COD concentrations, the process is not mass-transfer controlled, but kinetically controlled, and a zero order kinetic defines well the behavior of the reaction system. According to literature [21], the value in which the process starts to be mass-transfer controlled depends on the mass transport coefficient of the pollutants in the electrochemical cell (Eq. (1)) and, hence, it is strongly related to its fluid-dynamic conditions:

$$\mathrm{COD_{limit}} = \frac{jA}{4Fk_m} \tag{1}$$

Over $\mathrm{COD_{limit}}$, in the kinetic-controlled range, the efficiency in the use of electric charge is maintained constant at its maximum possible value. However, for lower outstanding-COD the efficiency decreases continuously during the batch electrolysis down to an almost nil value. Taking into account mass-transfer coefficients that can be typically obtained in electrochemical cells for wastewater treatment, characteristic $\mathrm{COD_{limit}}$ are around 500–2000 mg dm^{-3}. This means that CDEO can be a very valuable technology for reducing COD down to these limits, which are around those required for the discharge into the municipal sewage collectors.

Fig. 2 compares the maximum COD removal achieved by CDEO and by other two advanced oxidation processes (AOP) commonly used in the industry (Fenton oxidation and ozonation) during the treatment of different types of actual wastewaters. Only CDEO is able to eliminate completely the organic load of the industrial effluents, and the other two AOP lead to the accumulation of significant amounts of oxidation-refractory compounds. These results can be explained taking into account the oxidation mechanisms involved in the three AOPs. It is known that besides hydroxyl radicals formation [18,27], CDEO combines other types of oxidation mechanism: direct electro-oxidation on the conductive-diamond surface and mediated oxidation by other electrochemically formed compounds such as persulphate [23], perphosphate [27] or hypochlorite [25,28] depending on the electrolyte. Conversely, in Fenton process and ozonation at alkaline pH, just the hydroxyl radical and the molecular ozone (for the ozonation) or the hydrogen peroxide (for Fenton process) are the oxidant agents involved in the treatment. Likewise, these two former technologies seem to be strongly influenced for the composition of the waste. Thus, it can be pointed that CDEO competes favourably with ozonation and Fenton oxidation due to the complexer and more efficient oxidation processes that develops in the electrochemical process. Presently, CDEO is the only technology than can deserve the completely removal of the pollutants contained in an actual wastes.

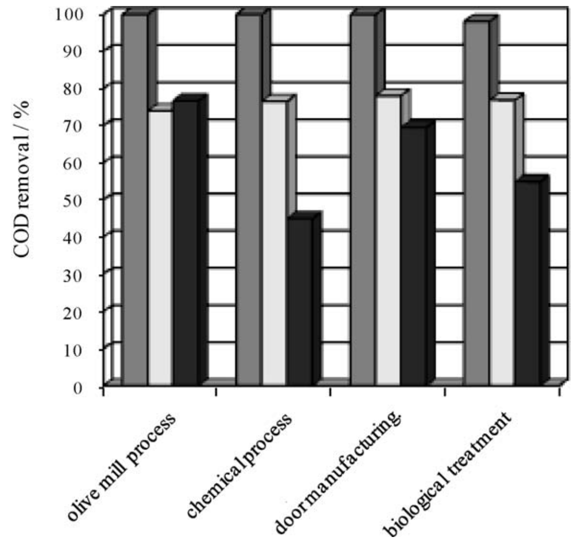

Fig. 2. Changes in the removal percentage of COD of wastewaters come from olive mill process, chemical plant, door-manufacturing process and biological treatment, during CDEO (■), Fenton oxidation (▨) and ozonation (■). Experimental conditions CDEO: natural pH, j: 30 mA cm^{-2}; T: 25 °C. Experimental condition Fenton oxidation: pH 3; T: 25 °C; Fe^{2+}: 850 mg dm^{-3}. Ozonation: pH 12; T: 25 °C; ozone production: 0.99 g h^{-1}.

Fig. 3 shows the efficiency of CDEO in the use of electric charge (expressed in terms of kg removed COD per kAh supplied) for a great variety of synthetic (propanol, naphtol, tiophene, phenol, hydroxybenzenes, chlorophenols, nitrophenols and dyes) and actual (fine-chemical, olive-oil mills, petrochemical and door-manufacturing) wastewaters. This parameter has been calculated within the range of COD in which the efficiency remains constant at its maximum value.

As it can be observed, independently of the type of wastewater, the efficiency follows a marked trend with the pollutant concentration (COD): the higher the organic load, the higher the efficiency of the process. Thus, for a concentrated wastewater, a particular amount of electrical charge is able to remove a higher organic content than in the case of a diluted waste. This means that CDEO is more efficient for strongly polluted wastes, and it also suggests that mediated oxidation should play an important role in the removal of pollutants from the raw waste.

However, in this point, it also has to be taken into account that the energy required to remove COD depends directly on the concentration of pollutants in the raw wastewater. This can be clearly seen in Fig. 4, where it is shown the energy consumption required by CDEO to diminish the COD of different wastewaters down to the typical discharge limit in municipal sewage collectors (1500 mg dm^{-3}).

Data fits well a potential model, with increasing energy requirements with the concentration of COD in the raw waste. In this point, it is easy to mark the higher limit of COD concentration in which the use of CDEO can be recommended, by comparison of the energy requirements of the CDEO with the energy requirements of other technologies. It is important to mark that the treatment of many type of wastewaters polluted with organics can be carried out with electric vacuum evaporation [29], with a typical energy demand around 150–200 kWh m^{-3}. This technology usually leads to good results, and presently it is one of the more serious competitors of the CDEO, even more than

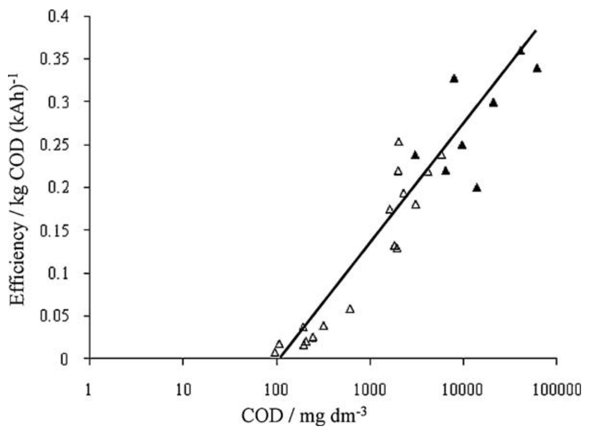

Fig. 3. Efficiency of the electrochemical oxidation with BDD anodes of (△) synthetic wastewaters (polluted with propanol, naphtol, tiophene, phenol, hydroxybenzenes, chlorophenols, nitrophenols or dyes) and (▲) actual wastewaters (pharmaceutical, olive-oil mills, chemical and door-manufacturing). Experimental conditions: natural pH, j: 30 mA cm^{-2}; T: 25 °C.

ozonation or Fenton oxidation, that are seriously limited by the formation of oxidation-refractory species. According to the authors' opinion, when this competing technology is available, this marks a boundary in the use of CDEO: the electrochemical technology should only be applied for concentrations of COD smaller than 15000–20000 mg dm^{-3}.

Fig. 5 compares the efficiency of the electrochemical oxidation using different electrodic materials: graphite, DSA, Pb/PbO$_2$ and conductive-diamond during the oxidation of a particular actual wastewater. In all cases, the efficiency has been calculated in the first stages of the treatment, where the COD decreases linearly with the electrical charge passed. As it can be observed, the material used for the anode is a key parameter in the electro-oxidation of wastewaters. Graphite and DSA electrodes show worse performance than Pb/PbO$_2$ and conductive-diamond ones. In fact, in literature [30] two limiting types of anode behavior have been identified depending on the tendency of the electrode surface to undergo chemical transformation during the oxidation process. Thus, graphite and DSA can be transformed (burned or further oxidized) during the electrochemical process, while diamond electrodes and fully oxidized metal oxides such as PbO$_2$ do not experience any change when they are used as anode. These former electrodes generally achieve greater current efficiencies and lead to almost complete conversion of the organic matter to carbon dioxide. Conversely, the use of DSA electrodes frequently leads to the formation of polymers, which in turn deactivate the anode surface and minimize the energetic efficiency of the process. However, it is important to remark that the yield and the efficiency of the electrochemical oxidation with DSA can be improved using sodium chloride as supporting electrolyte. It is known [31] that this electrode can oxidize chloride ions to hypochlorite that react with the organics and contribute to the global oxidation process. Likewise, it is important to note that during the use of PbO$_2$ anodes is common the release of lead species which prevents against the use of this type of anode material in an actual application of the electrolytic technology.

Fig. 6 shows the influence of the pH on the efficiency of the electrochemical treatment of synthetic (phenol and chlorophenol) and of actual (pharmaceutical and chemical) wastewaters. At the light of these results, neutral pH seems to lead to less efficient process, whereas alkaline (around 12) and acidic (around 3–4) pH values improve the yield of the treatment. This behavior is difficult to explain but it may be related to the mediated oxidation mechanism carried out by hydroxyl radicals [27]. As it is reported in literature [32], acid pH values (around 3) promote the formation of hydroxyl radicals. Equally, the high concentration of hydroxide ions at alkaline media can also favor the formation of large amount of hydroxyl radicals in the reaction system in the absence of carbonates [33]. It is also important to note in this figure that the nature of the pollutant is not important in the results of the CDEO. This marks the low selectivity of the CDEO technology in the oxidation of industrial wastes.

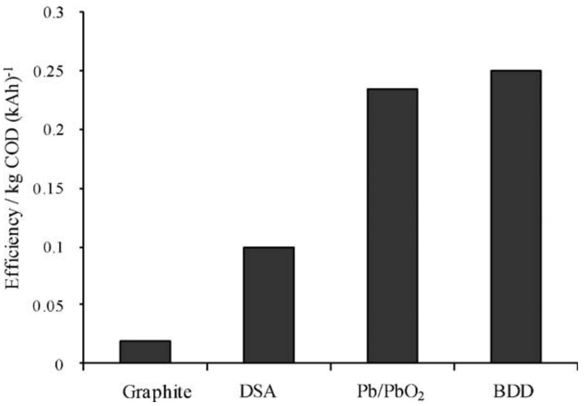

Fig. 5. Efficiency of the electrochemical oxidation of an actual chemical wastewater (30 mA cm^{-2}) as a function of the anodic material. Experimental conditions: natural pH, j: 30 mA cm^{-2}; T: 25 °C.

To verify the role of the hydroxyl radical in the conductive-diamond electrolyses, several essays were carried out in a potential range around water oxidation (above and below) using the electrochemical oxidation of a well-known organic model pollutant (phenol). The experiments were carried out galvanostatically but the cell potential was observed to be constant during all the experiments. A reference electrode was placed close to the anode in order to estimate the anode potential. Due to the cell configuration, the values obtained are clearly affected by ohmic losses caused by the electrolyte resistance, and so they only can be taken as a first approximation.

Results show that there is an abrupt change in the efficiencies of the processes in the kinetic-control zone and two different limit behaviours can be obtained (Fig. 7). For anodic cell potentials below a certain value (in the range 2–2.5 V) it is possible to remove around 0.06 kg of COD per kAh supplied, and for higher cell potentials the current efficiency obtained increases sharply to values over 0.10 kg COD per kAh. This change can be interpreted in terms of the contribution of hydroxyl radicals for higher potentials. In this respect, it can be suggested that working over a given anodic potential (over 2.5 V vs. SCE) should cause the formation of large

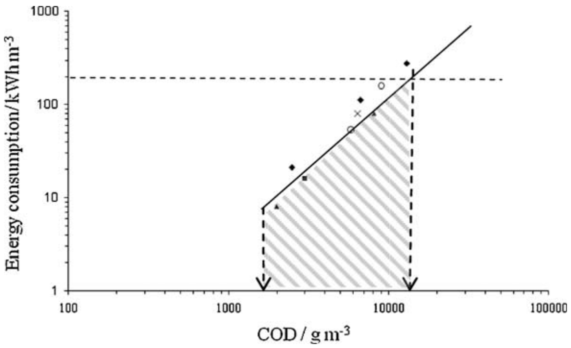

Fig. 4. Variation of the energy consumption with the COD concentration in the electrochemical oxidation with BDD of wastewaters generated in: mechanized process (◆), olive mill process (■), chemical plant (○), door-manufacturing process (▲) and petrochemical process (×). Experimental conditions: natural pH, j: 30 mA cm^{-2}; T: 25 °C.

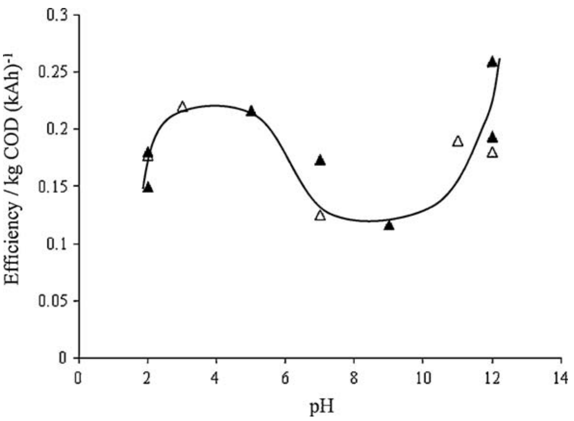

Fig. 6. Efficiency of the electrochemical oxidation of wastewaters: (▲) phenolic synthetic wastewater (3000 mg dm^{-3} of COD); (△) petrochemical wastewater (7000 mg dm^{-3} of COD). Experimental conditions: natural pH, j: 30 mA cm^{-2}; T: 25 °C.

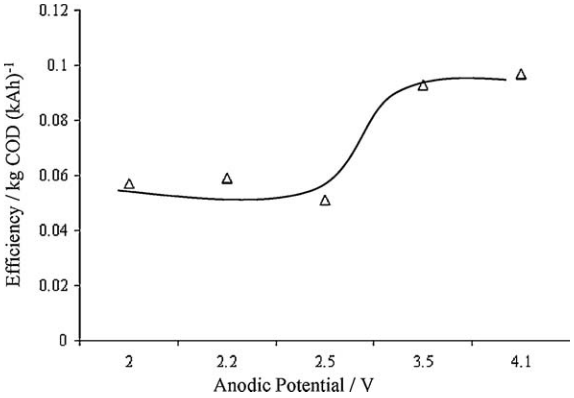

Fig. 7. Efficiency of the electrochemical oxidation of phenol aqueous wastes as a function of the anodic potential. Experimental conditions: 1000 mg dm^{-3} of COD, natural pH, *j*: 30 mA cm^{-2}; *T*: 25 °C.

amounts of hydroxyl radicals on the anodic surface that can then promote the changes observed in the bulk oxidation.

4. Conclusions

The main conclusions that can be drawn from this work are:

The electrochemical oxidation with conductive-diamond can be used to remove the organic content of a great variety of synthetic and actual wastewaters. Opposite to Fenton oxidation or ozonization, this technology does not lead to the formation of oxidation-refractory species and it allows diminishing the organic load of any effluent down to any required discharge limit.

The electrochemical oxidation of industrial wastes is strongly influenced by the type of anodic material. Graphite and DSA electrodes show worse performance than Pb/PbO$_2$ and conductive-diamond ones. The higher stability of conductive-diamond makes CDEO as the reference technology in the electrochemical treatment of industrial wastes.

In the case of using conductive-diamond anodes, mediated oxidation can play an important role in the overall electrochemical oxidation process of organics, and it can be even more important that the direct oxidation mechanism itself.

-During the electrolyses of actual wastewaters, the energy requirements increase with the COD concentration of the raw waste. CDEO is a very valuable technology for the treatment of industrial waste within the range 1500–20000 mg dm^{-3} of COD.

Acknowledgment

The financial support of Spanish government through project CTM2007-60472/TECNO is gratefully acknowledged.

References

[1] P. Cañizares, M. Díaz, J. Domínguez, J. Lobato, M.A. Rodrigo, Electrochemical treatment of diluted cyanide aqueous wastes, J. Chem. Technol. Biotechnol. 80 (2005) 565–573.
[2] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Saéz, Electrochemical oxidation of phenolic compound waste with BDD anodes, Water Res. 39 (2005) 2687–2705.
[3] E. Weiss, K. Groenen-Serrano, A. Savall, C. Comninellis, A kinetic study of the electrochemical oxidation of maleic acid on boron doped diamond, J. Appl. Electrochem. 37 (2007) 41–47.
[4] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes. A comparison with other advanced oxidation processes, Electrochim. Acta 53 (2008) 2144–2153.
[5] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, Electrochemical oxidation of wastewaters polluted with aromatics and heterocyclic compounds. A comparison with other AOPs, J. Electrochem. Soc. 154 (1) (2007) E165–E181.
[6] I. Sires, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodriguez, C. Arias, E. Brillas, Electrochemical degradation of clofibric acid in water by anodic oxidation: comparative study with platinum and boron-doped diamond electrodes, Electrochim. Acta 52 (1) (2006) 75–85.
[7] A.M. Polcaro, M. Mascia, S. Palmas, A. Vacca, Electrochemical degradation of diuron and dichloroaniline at BDD electrode, Electrochim. Acta 49 (4) (2004) 649–656.
[8] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinoss, Electrochemical oxidation of olive oil mill wastewaters, Water Res. 39 (2005) 4177–4187.
[9] P. Cañizares, R. Paz, J. Lobato, C. Sáez, M.A. Rodrigo, Electrochemical treatment of the effluent of a fine chemical manufacturing plant, J. Hazard. Mater. B 138 (2006) 173–181.
[10] P. Cañizares, J. Lobato, R. Paz, C. Sáez, M.A. Rodrigo, Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere 67 (2007) 832–838.
[11] A. Beteta, P. Cañizares, M.A. Rodrigo, L. Rodriguez, C. Sáez, Treatment of door manufacturing factories wastewaters using CDEO and other AOPs. A comparison, J. Hazard. Mater. 168 (2009) 358–363.
[12] M. Panizza, M. Delucchi, G. Cerisola, Electrochemical degradation of anionic surfactants, J. Appl. Electrochem. 35 (2005) 357–361.
[13] C. Barrera-Díaz, F. Ureña-Nuñez, E. Campos, M. Palomar-Pardavé, M. Romero-Romo, A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater, Radiat. Phys. Chem. 67 (2003) 657–663.
[14] B.K. Körbahti, A. Tanyolaç, Continuous electrochemical treatment of simulated industrial textile wastewater from industrial components in a tubular reactor, J. Hazard. Mater. 170 (2009) 771–778.
[15] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, R. Pompei, S. Laconi, Characterization of a stirred tank electrochemical cell for water disinfection processes, Electrochim. Acta 52 (2007) 2595–2602.
[16] E. Guinea, C. Arias, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, F. Centellas, E. Brillas, Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide, Water Res. 42 (2008) 499–511.
[17] G. Zhao, S. Shen, M. Li, M. Wu, T. Cao, D. Li, The mechanism and kinetics of ultrasound-enhanced electrochemical oxidation of phenol on boron-doped diamond and Pt electrodes, Chemosphere 73 (2008) 1407–1413.
[18] B. Marselli, J. Garcia-Gomez, P.A. Michaud, M.A. Rodrigo, C. Comninellis, Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes, J. Electrochem. Soc. 150 (3) (2003) 79–83.
[19] M.A. Rodrigo, P.A. Michaud, I. Duo, M. Panizza, G. Cerisola, C. Comninellis, Oxidation of 4-chlorophenol at boron-doped diamond electrode for wastewater treatment, J. Electrochem. Soc. 148 (5) (2001) D60–D64.
[20] L. Gherardini, P.A. Michaud, M. Panizza, C. Comninellis, N. Vatistas, Electrochemical oxidation of 4-chlorophenol for wastewater treatment. Definition of anode activity parameter (φ), J. Electrochem. Soc. 148 (2001) D78–D82.
[21] M. Panizza, P.A. Michaud, G. Cerisola, C. Comninellis, The anodic oxidation of 2-naphthol at boron-doped diamond electrodes, J. Electroanal. Chem. 507 (2001) 206–214.
[22] P. Cañizares, M. Díaz, J.A. Domínguez, J. García-Gómez, M.A. Rodrigo, Electrochemical oxidation of aqueous phenol wastes on synthetic diamond thin-film electrodes, Ind. Eng. Chem. Res. 41 (2002) 4187–4194.
[23] K. Serrano, P.A. Michaud, C. Comninellis, A. Savall, Electrochemical preparation of peroxodisulfuric acid using boron doped diamond thin film electrodes, Electrochim. Acta 48 (2002) 431–436.
[24] P. Cañizares, F. Larrondo, J. Lobato, M.A. Rodrigo, C. Sáez, Electrochemical synthesis of peroxodiphosphate using boron-doped diamond anodes, J. Electrochem. Soc. 152 (11) (2005) D191–D196.
[25] A.M. Polcaro, A. Vacca, M. Mascia, F. Ferrara, Product and by-product formation in electrolysis of dilute chloride solutions, J. Appl. Electrochem. 38 (2008) 979–984.
[26] E. Brillas, F. Alcaide, P.L. Cabot, A small-scale flow alkaline fuel cell for on-site production of hydrogen peroxide, Electrochim. Acta 48 (2002) 331–340.
[27] P. Cañizares, C. Sáez, J. Lobato, R. Paz, M.A. Rodrigo, Effect of the operating conditions on the oxidation mechanisms in conductive-diamond electrolyses, J. Electrochem. Soc. 154 (3) (2007) E37–E44.
[28] M. Panizza, G. Cerisola, Electrochemical oxidation of 2-naphthol with in situ electrogenerated active chlorine, Electrochim. Acta 48 (2003) 1515–1519.
[29] P. Cañizares, J. García-Gómez, F. Martínez, M.A. Rodrigo, Evaluation of a simple batch distillation process for treating wastes from metalworking industries, J. Chem. Technol. Biotechnol. 79 (2004) 533–539.
[30] G. Foti, D. Gandini, C. Comninellis, A. Perret, W. Haenni, Oxidation of organics by intermediates of water discharge on IrO$_2$ and synthetic diamond anodes, Electrochem. Solid-State Lett. 2 (1999) 228–230.
[31] P.M. Robertson, W. Gnehm, L. Ponto, High efficiency hypochlorite generation, J. Appl. Electrochem. 13 (2005) 307–315.
[32] A.M.F.M. Guedes, L.M.P. Madeira, R.A.R. Boaventura, C.A.V. Costa, Fenton oxidation of cork cooking wastewater—overall kinetic analysis, Water Res. 37 (2003) 3061–3069.
[33] F. Al Momani, C. Sans, S. Esplugas, A comparative study of the advanced oxidation of 2,4-dichlorophenol, J. Hazard. Mater. 107 (2004) 123–129.