Chemical Engineering Journal 161 (2010) 167–172

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes

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ARTICLE INFO

Article history:
Received 16 March 2010
Received in revised form 27 April 2010
Accepted 28 April 2010

Keywords:
Chlorpyrifos
Electrochemical degradation
Boron-doped diamond
Lead dioxide
Hydroxyl radicals

ABSTRACT

Laboratory experiments were carried out on the kinetic of the electrochemical degradation of aqueous solutions containing chlorpyrifos as model compounds of organophosphorus pesticides. The process was studied under galvanostatic polarization mode in acidic medium using boron-doped diamond (BDD) anodes and graphite carbon bar as cathode. The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the instantaneous current efficiency. The results showed that the degradation of this pesticide is dependent on its initial concentration, current density and temperature. COD decay follows a pseudo first-order kinetic and the process was under mass transport control within the range studied, regardless of the experimental conditions. The removal rate of COD increases with applied current density until 20 mA cm^{-2} and decreases for higher values. The degradation rate increased significantly with increasing temperature and initial concentration of chlorpyrifos. The best obtained conditions for COD removal on the BDD anode to degrade chlorpyrifos solutions (COD(0) = 456 mg L^{-1}) include operating at 20 mA cm^{-2} and 70 °C. This arrangement allows to completely degrade chlorpyrifos in just 6 h. Compared with PbO_2, BDD anode has shown more performance and rapidity in the COD removal in the same electrolysis device.

1. Introduction

The intensive use of pesticides in agriculture and the improper storage or disposal of obsolete pesticides are a source of contamination of soil, ground water, rivers, lakes, rainwater and air. Various innovative technologies have been proposed for the removal of pesticides from water. Among these technologies, the electrochemical processes constitute the emergent methods for the degradation of pesticides. These methods are environmentally friendly and they do not form new toxic wastes.

In anodic oxidation, organic pollutants are directly destroyed by reaction with hydroxyl radical ($HO^{\bullet}$) formed at the anode surface from water oxidation [1–4]:

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \quad (1)$$

Several anode materials such as Pt [5–10], SnO_2 [11,12], PbO_2 [12–14] and BDD [10,12,15,16] have been used for pesticides removal. The new anode material (BDD) possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium [17,18]. BDD anode has much higher O_2 overvoltage than that of conventional anodes such as PbO_2, doped SnO_2, IrO_2 and Pt, then producing larger amount of $HO^{\bullet}$ on the anode surface by reaction (1) giving a more rapid destruction of pollutants [14,17,18].

Some investigations have also intended to compare the behaviour of BDD with other electrodes, such as SnO_2, PbO_2 and IrO_2 for the oxidation of organic pollutants. Chen et al. [19] reported that the current efficiency obtained with Ti/BDD in oxidizing acetic acid, maleic acid, phenol, and dyes was 1.6–4.3-fold higher than that obtained with the typical $Ti/Sb_2O_5–SnO_2$ electrode. Other papers showed that Si/BDD electrodes are able to achieve faster oxidation and better incineration efficiency than PbO_2 in the treatment of naphthol [20,21], 4-chlorophenol [22] and chloranilic acid [23].

Recently, Martínez-Huitle et al. [12] demonstrated that the pesticide methamidophos can be electrochemically removed from aqueous solutions using Pb/PbO_2, Ti/SnO_2, and Si/BDD electrodes. They found that current density influence is remarkably clear on the Si/BDD electrodes where it was evident that the most efficient current density toward a complete methamidophos mineralization was reached with the application of 50 mA cm^{-2}.

Chlorpyrifos is one of the most widely used organophosphorus pesticides in agriculture (Fig. 1). The use of chlorpyrifos has been vastly restricted in U.S. and some European countries, even for agricultural purposes. However, it is still widely used in about 100 other countries. Like other organophosphorus pesticides, chlorpyrifos inhibits the cholinesterase enzyme systems essential in the normal

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doi:10.1016/j.cej.2010.04.060

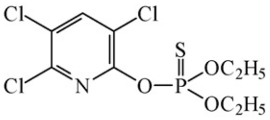

Fig. 1. Chemical structure of chlorpyrifos.

functioning of the nervous system. The most commonly reported effects of chlorpyrifos poisoning include: headache, nausea, dizziness, salivation, excess sweating, blurred vision, muscle weakness, abdominal cramps, diarrhoea, and in some extreme cases even death [24].

Various innovative technologies have been proposed for wastewater treatment containing chlorpyrifos. These include the use of the ionizing radiation [25], photocatalytic degradation using TiO_2 as catalyst [26], photo-Fenton process [27], high-pressure arc discharge plasma process [28], biodegradation [29,30] and chemical oxidation using hypochlorous acid (HOCl) as the primary oxidant [31]. However, there is no work related to the electrochemical degradation of chlorpyrifos. This article therefore, aims to study the electrochemical process for the total degradation of chlorpyrifos in aqueous solutions. The process was studied under galvanostatic polarization mode in acidic media using BDD anodes. The degradation rate of the studied pesticide and the efficiency and limits of such a technique were investigated according to experimental parameters such as the initial concentration of chlorpyrifos, the anodic current density and the temperature.

2. Experimental

2.1. Chemicals

In this work, all solutions were prepared in the laboratory. These solutions contain quantities of chlorpyrifos taken from an emulsifiable concentrate (DURSBAN* 4, from Dow Agrosciences) containing 480 g L^{-1} (44.6%, w/w) chlorpyrifos. All solutions were freshly prepared with double distilled water. Sulfuric acid and sodium hydroxide of analytical grade were employed as conductive electrolytes and for pH adjustment.

2.2. Boron-doped diamond Si/BDD electrodes

The boron-doped diamond electrodes were provided by CSEM (Centre Suisse d'Electronique et de Microtechnique, Neuchâtel, Switzerland). It was synthesized by the hot filament chemical vapour deposition technique (HF-CVD) [32] on single-crystal p-type Si ⟨1 0 0⟩ wafers (1–3 mΩ cm, Siltronix). The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm. The resulting diamond film thickness was about 1 μm with a resistivity of 10–30 mΩ cm. The electrode area is 6 cm^2. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 30 min with a 1 M H_2SO_4 solution at 50 mA cm^{-2} to remove any kind of impurity from its surface.

2.3. Preparation of Nb/PbO_2 electrode

The electrode used for a comparison with the BDD anode was made of niobium rectangular plates (70 mm × 10 mm × 1 mm) covered with a layer of lead dioxide obtained by electrochemical oxidation of a lead nitrate aqueous solution. In order to obtain a rough substrate surface to ensure the adhesion of PbO_2 deposits, the niobium plates underwent sandblasting using silica grains with an average diameter of 0.3 mm projected under 5 bar pressure. The substrate was then ultrasonically rinsed in doubly distilled water and chemically etched with HF 40% (weight) for 30 s at room temperature. The lead dioxide was then galvanostatically deposited using a two-compartment cell (V = 500 cm^3) containing a lead nitrate solution (1 mol L^{-1}). The cathode is a graphite carbon-PTFE bar (ϕ = 5 mm; L = 60 mm) placed in a porous ceramic cylinder (Norton, RA 84) containing 1 mol L^{-1} sulfuric acid solution. The deposition of PbO_2 was carried out for 2.5 h, at 65 °C and using an anodic current density of 20 mA cm^{-2}. The average mass of PbO_2 deposited per unit of surface area was 0.22 g cm^{-2}. The deposit obtained was mat grey, adherent, regular and uniform. The surface of this electrode was 6 cm^2.

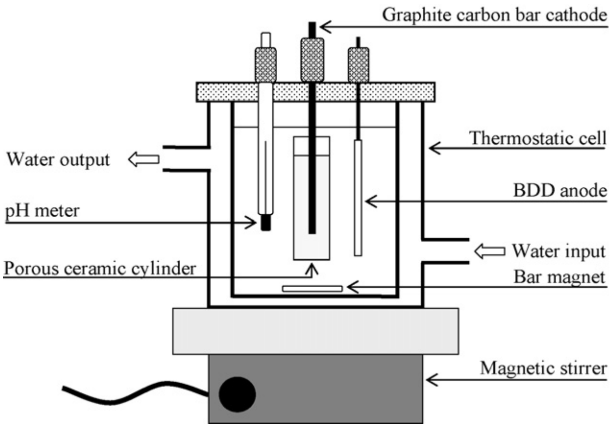

Fig. 2. Electrolytic cell.

2.4. Bulk electrolysis

Galvanostatic electrolyses of chlorpyrifos aqueous solutions (150 cm^3) have been carried out in a two-compartment thermostatted cell (Fig. 2). The cathode is a graphite carbon-PTFE bar (ϕ = 5 mm; L = 60 mm) placed in a porous ceramic cylinder (Norton, RA 84) containing a 1 M sulfuric acid solution. The anode is 6 cm^2 Si/BDD or PbO_2 plate placed in front of the cathode. Chlorpyrifos solutions were electrolyzed in galvanostatic mode by applying current densities of 10–30 mA cm^{-2} using a DC power supply (model ABTP 530 Française d'Instrumentation, France). The pH of the solution was kept constant (pH = 2) by the continuous introduction of concentrated sulfuric acid or sodium hydroxide solutions to the cell.

2.5. Analysis

The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the instantaneous current efficiency. COD was determined by the dichromate method. The appropriate amount of sample was introduced into prepared digestion solution (0–1500 mg L^{-1}) containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 2 h at 150 °C in a WTW CR 2200 thermoreactor (Germany) for COD and thermal digestions. COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of the organic compounds. ICE during electrolysis can be performed from the decrease of COD by means of the following relation [1]:

$$\mathrm{ICE} = FV\frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{8I\,\Delta t} \qquad (2)$$

where F is the Faraday constant (96,487 C mol^{-1}), V the volume of the solution (L), COD_t and $COD_{t+\Delta t}$ are the chemical oxygen

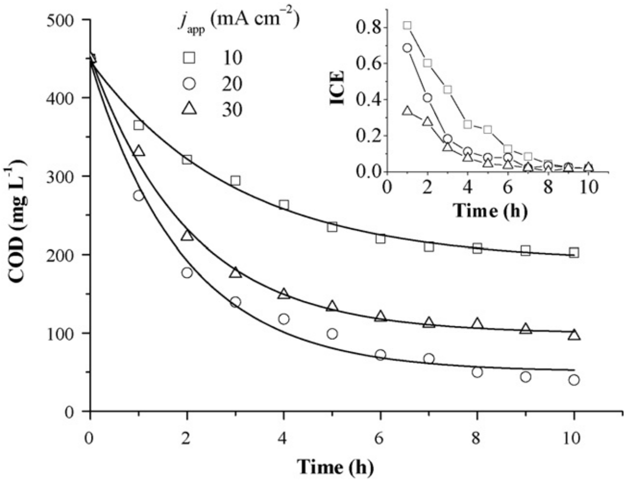

Fig. 3. Influence of the applied current density on the trends of COD and ICE during electrolysis of chlorpyrifos (COD(0) = 450 mg L^{-1}) using a 6 cm^2 BDD anode. pH = 2 and T = 50 °C.

demands at times t and $t+\Delta t$ (in g O$_2$ L^{-1}), respectively, and I is the current (A).

3. Results and discussion

3.1. Effect of current density

The influence of the current density on the COD removal during the electrochemical oxidation of chlorpyrifos at the BDD anode is shown in Fig. 3. Increasing the current density until 20 mA cm^{-2} resulted in an enhancement of the oxidation rate. After 10 h time of electrolysis, the COD percent removal increased from 55% to 91% when the current density increased from 10 to 20 mA cm^{-2}. However, for current higher than 20 mA cm^{-2}, the oxidation rate decreased.

On the other hand, as shown in the inset of Fig. 3, increasing current density resulted in a decrease in the instantaneous current efficiency. ICE can also be defined by Eq. (3) [33]:

$$\mathrm{ICE} = \frac{j_{\mathrm{lim}}(t)}{j_{\mathrm{app}}} \tag{3}$$

where $j_{\mathrm{lim}}(t)$ is the limiting current density (A m^{-2}) at a given time t, j_{app} is the applied current density (A m^{-2}). This limiting current density for the electrochemical degradation of the organic matter in the solution can be related to the COD of the solution during electrolysis by Eq. (4) [17,22,33]:

$$j_{\mathrm{lim}}(t) = 4Fk_{\mathrm{m}}\mathrm{COD}(t) \tag{4}$$

At the beginning of the electrolysis (t = 0), the initial limiting current density is given by the following equation:

$$j_{\mathrm{lim}}(0) = 4Fk_{\mathrm{m}}\mathrm{COD}(0) \tag{5}$$

where COD(0) is the initial chemical oxygen demand (mol O$_2$ m^{-3}). Eq. (3) can be written as

$$\mathrm{ICE} = \frac{j_{\mathrm{lim}}(t)}{j_{\mathrm{app}}} = \frac{\mathrm{COD}(t)}{\alpha\,\mathrm{COD}(0)} \tag{6}$$

where $j_{\mathrm{app}} = \alpha j_{\mathrm{lim}}(0)$.

From Fig. 3 we can see that COD values decreased almost exponentially. If we suppose that the anodic oxidation of organic matter by the electrogenerated hydroxyl radicals HO$^\bullet$ from water molecule discharge (Eq. (1)) is of a first-order relating to COD of the solution and the hydroxyl radicals concentration is constant during electrolysis, the oxidation rate (r) can be given by Eq. (7):

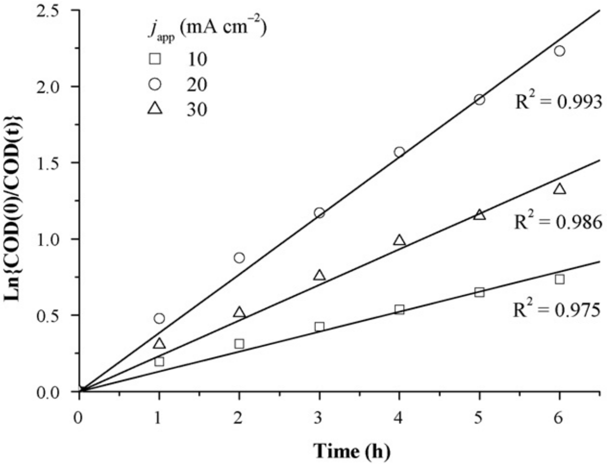

Fig. 4. Linear regression for COD removal with time during the electrochemical oxidation of chlorpyrifos (COD(0) = 450 mg L^{-1}) on the BDD anode for different current densities. pH = 2 and T = 50 °C.

$$r = -\frac{d\mathrm{COD}}{dt} = k[\mathrm{HO}^\bullet]^\beta\ \mathrm{COD}(t) = k_{\mathrm{app}}\,\mathrm{COD}(t) = \frac{Ak_{\mathrm{m}}}{V}\,\mathrm{COD}(t) \tag{7}$$

β is the reaction order related to the hydroxyl radicals, k is the real rate constant and k_{app} is the apparent rate constant of the COD elimination. k_{m} is the average mass transfer coefficient in the electrochemical cell (m s^{-1}), A is the electrode area (m^2) and V is the volume of the treated solution (m^3).

Integration of this equation subject to the initial condition COD(t) = COD(0) at t = 0 leads to the following equation [34,35]:

$$\mathrm{COD}(t) = \mathrm{COD}(0)\ \exp\left(-\frac{Ak_{\mathrm{m}}}{V}t\right) \tag{8}$$

k_{m} could be calculated from the slope value of the plot of Ln{COD(0)/COD(t)} versus t (Fig. 4). The straight lines obtained in these plots were in agreement with a pseudo first-order COD removal. $j_{\mathrm{lim}}(0)$ values, given in Table 1, are lower than j_{app} which means that the electrochemical process occurs under diffusion control. This is in accord with all ICE values which were below 100%.

This result can be explained by the fact that at high applied current, side reactions such as oxygen evolution (Eq. (9)) and/or electrolyte decomposition (Eq. (10)) occur at the diamond surface [17,33,36–37]:

$$2\mathrm{H_2O} \rightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \tag{9}$$

$$2\mathrm{SO_4}^{2-} \rightarrow \mathrm{S_2O_8}^{2-} + 2\mathrm{e^-} \tag{10}$$

According to results in Fig. 3, when the applied current increased from 10 to 20 mA cm^{-2}, Eq. (9) is more favored than Eq. (10). Thus, the mass transport can be significantly increased due to the formation and detachment of O$_2$ bubbles. This phenomena was also explained by several authors [2,4,38–40]. So, increasing the applied current density increases the diffusion flux of organic matter towards the anode surface. It results a decrease in the diffusion layer thickness and consequently an increase of k_{m} values (k_{m} increased from 1.01×10^{-5} to 2.66×10^{-5} m s^{-1} when j_{app} increased from 10 to 20 mA cm^{-2} (Table 1)). However, when the

Table 1
Average mass transfer coefficient (k_{m}) and initial limiting current density $j_{\mathrm{lim}}(0)$ as a function of the applied current density (j_{app}).

j_{app} (mA cm^{-2})	10	20	30
k_{m} ($\times 10^5$ m s^{-1})	1.01	2.66	1.61
$j_{\mathrm{lim}}(0)$ (mA cm^{-2})	5.48	14.43	8.74

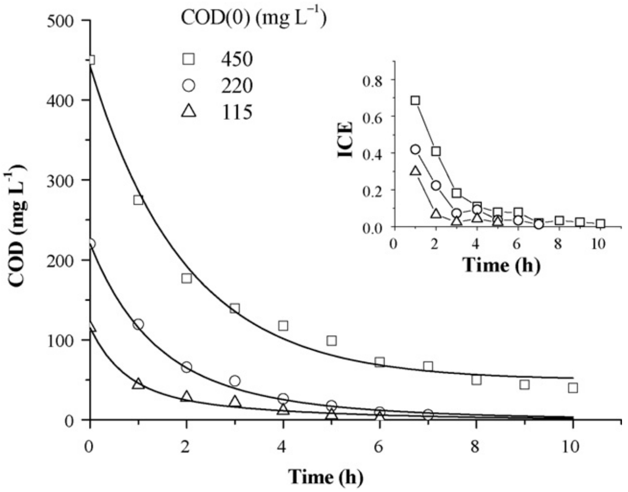

Fig. 5. Influence of the initial COD on the trends of COD and ICE during electrolysis on the BDD anode. j_{app} = 20 mA cm^{-2}; pH = 2 and T = 50 °C.

current exceeds a certain value of current (in this case 20 mA cm^{-2}), a greater amount of gas will be produced at the electrode surface and thus minimizes the number of active site of the electrode. It results a decrease in k_m values (k_m decreased from 2.66 × 10^{-5} to 1.61 × 10^{-5} m s^{-1} when j_{app} increased from 20 to 30 mA cm^{-2} (Table 1)).

3.2. Effect of the initial chlorpyrifos concentration

The initial concentration of pollutants is always an important parameter in wastewater treatment. Fig. 5 shows the effect of the initial concentration of chlorpyrifos (COD(0) = 115, 220 and 450 mg L^{-1}) on the COD removal during electrolysis at pH 2, temperature of 50 °C and using a current density of 20 mA cm^{-2}. For low concentrations (COD(0) = 115 and 220 mg L^{-1}), the COD decreased to zero after about 6 h, meaning complete degradation of chlorpyrifos. However, for higher concentrations, the total degradation requires longer time of electrolysis as shown in the trend of the curve (COD(0) = 450 mg L^{-1}) in Fig. 5. k_{app} values (Table 2) calculated from the straight lines, considering a first-order reaction (Fig. 6), decreased when the initial concentration of chlorpyrifos increased. However, overall mass transfer rates (k_mCOD(t)) increased with the increase of the initial COD (in Table 2, we showed the initial overall mass transfer rate), which explains the fact that the degradation rate was found increasing with the increase of the initial COD. This process can be interpreted in term of an increase in the organic matter diffusion flux caused by the increase of its initial concentration and secondly by a decrease of the oxygen formation rate when the initial COD increases.

On the other hand, it can be seen from the inset of Fig. 5, that the maximum efficiencies were obtained at the initial stages of the electrolysis (high COD concentrations), thereafter, ICE values undergo a dramatic decay when initial COD decreases. This outcome is in agreement with the data reported by Panizza and Cerisola [41,42]. This is usually explained in terms of mass transfer limitations assuming that both direct oxidation and mediated oxidation on the BDD surface by hydroxyl radicals and other electrogenerated oxidants ($S_2O_8{}^{2-}$ from the supporting electrolyte H_2SO_4) contribute in the electrochemical process. Several authors have shown that $S_2O_8{}^{2-}$ formed at the diamond surface (Eq. (10)) participates in the oxidation of the carboxylic acids, in the proximity of the electrode surface and/or in the bulk of the solution [36,43–46].

Table 2
Extent of COD removal (after 6 h), overall mass transfer coefficient (k_m) and overall mass transfer rate (k_m × COD(0)) as a function of initial COD of the solution.

COD(0) (mg L^{-1})	115	220	450
COD removal (%)	82	96	98
k_{app} (h^{-1})	0.62	0.52	0.38
k_m (×10^5 m s^{-1})	4.31	3.63	2.67
k_mCOD(0) (×10^3 g m^{-2} s^{-1})	4.96	7.98	12.01

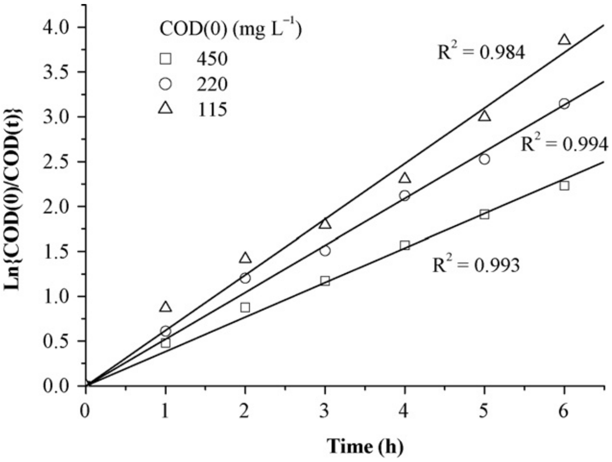

Fig. 6. Linear regression for COD removal with time during the electrochemical oxidation of chlorpyrifos on the BDD anode for different concentrations. j_{app} = 20 mA cm^{-2}; pH = 2 and T = 50 °C.

3.3. Effect of the temperature

Electrolyses of chlorpyrifos solutions (COD(0) = 450 mg L^{-1} and pH = 2) on BDD at an applied anodic current density of 20 mA cm^{-2} were carried out at different temperatures in the range 30–70 °C. Increasing the temperature considerably reduces the time necessary for the complete elimination of organic matter from the solution (Fig. 7). After 6 h time of electrolysis, the COD percent removal increased from 73 to approximately 100% when the temperature increased from 30 to 70 °C. This result is probably due to the increase in the indirect oxidation reaction of organics with $S_2O_8{}^{2-}$. This powerful oxidizing agent can oxidize organic matter by chemical reaction whose rate increases with temperature leading to an increase in COD removal rate. These results are in agreement with those obtained by other authors [43,44].

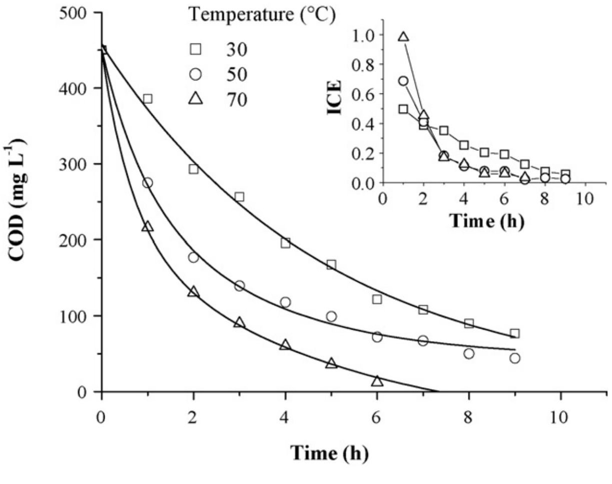

Fig. 7. Influence of the temperature on the trends of COD and ICE during the electrochemical oxidation of chlorpyrifos (COD(0) = 450 mg L^{-1}) on the BDD anode. j_{app} = 20 mA cm^{-2} and pH = 2.

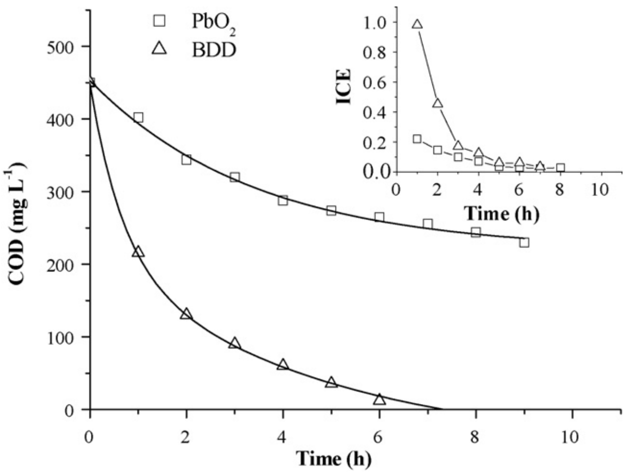

Fig. 8. Comparison of the trend of COD and ICE during the electrochemical oxidation of chlorpyrifos (COD(0) = 450 mg L^{-1}) on the BDD and PbO_2 anodes. j_{app} = 20 mA cm^{-2}, pH = 2 and T = 70 °C.

Moreover, the decrease of the medium viscosity with the increase of the temperature increases the diffusion rate of organic matter to the anode surface and consequently participates on the increase of COD removal rate. This explanation was also suggested by Rodriguez et al. [37].

3.4. Comparison between BDD and PbO_2 anode

Fig. 8 and its inset show the trend of COD and the current efficiency during the oxidation of chlorpyrifos (COD(0) = 450 mg L^{-1}) using BDD and Nb/PbO_2 anodes. As can be seen, BDD anode provided an oxidation rate and current efficiency higher than PbO_2 for the same operating conditions (j_{app} = 20 mA cm^{-2}, pH = 2 and at 70 °C). At 6 h of treatment on a BDD anode COD removal was very close to 100%, while under the same conditions a PbO_2 anode hardly achieved 41%. This behaviour is also found by many authors like Sirés et al. [14] when they compared the electrochemical incineration of the herbicide mecoprop in aqueous solutions using BDD and PbO_2 anodes, Weiss et al. [47] when they tested the electrochemical degradation of phenol on these two anodes.

The large difference in COD removal rate can be explained by the different nature of the physisorbed $HO^{\bullet}$ generated on both anodes (Eq. (1)). These radicals have a lower enthalpy of adsorption on the BDD surface [14,17,18,48], so they are more active and effective because they react very rapidly with all organics arriving at the surface and even in the vicinity of the anode. However, hydroxyl radicals are strongly adsorbed on the surface of PbO_2 electrode and consequently less reactive [42]. Therefore, all the factors that contribute to accelerate the diffusion of organic matter towards the BDD cause an extraordinary improvement of the treatment, which is more significative than with PbO_2 because this one does not produce so much reactive hydroxyl radicals.

Today PbO_2 is a material commercially available, while BDD, not yet accessible at large scale, can be a good candidate for electrochemical treatment of waste waters polluted by organics.

4. Conclusion

Electrochemical oxidation using a BDD anode has been successfully applied to treat aqueous solutions containing chlorpyrifos. The experimental results showed that:

- The process was under mass transport control within the range studied, regardless of the experimental conditions, due to the extraordinary high activity of hydroxyl radicals from the water discharge and the removal of COD was well described by a pseudo first-order kinetic.
- The removal rate of COD increases with applied current density until 20 mA cm^{-2} due to the increase of the mass transport caused by oxygen evolution reaction, but decreases for higher values due to the improvement of this reaction.
- The increase in temperature significantly improved the percentage of COD removal; from 73 to approximately 100% when the temperature increased from 30 to 70 °C at 6 h of treatment.
- The best obtained conditions for COD removal on the BDD anode to degrade chlorpyrifos solutions (COD(0) = 450 mg L^{-1}) include operating at 20 mA cm^{-2} and 70 °C. This arrangement allows to completely degrade the organic matter in just 6 h.
- For comparison, the degradation of chlorpyrifos on BDD anode provided an oxidation rate and current efficiency higher than PbO_2 for the same operating conditions. This preliminary study suggest that anodic oxidation with BDD electrode constitutes a viable method for the treatment effluents contaminated with chlorpyrifos and related pesticides.

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