



Study of photo-assisted electrochemical degradation of carbaryl at dimensionally stable anodes (DSA[®])

G.R.P. Malpass^{c,*}, D.W. Miwa^a, A.C.P. Miwa^b, S.A.S. Machado^a, A.J. Motheo^{a,*}

^a Instituto de Química de São Carlos, P.O. Box 780, Universidade de São Paulo, São Carlos - SP, CEP, 13560-970, Brazil

^b Departamento de Hidráulica e Saneamento, P.O. Box 359, Universidade de São Paulo, São Carlos - SP, CEP, 13566-590, Brazil

^c Universidade Federal do ABC, Santo André - SP, CEP, 09.210-170, Brazil

ARTICLE INFO

Article history:

Received 5 September 2008

Received in revised form

24 November 2008

Accepted 22 December 2008

Available online 31 December 2008

Keywords:

Carbaryl

Electrochemical degradation

Pesticides

Photo-assisted electrochemical degradation

ABSTRACT

This paper presents the results concerning the degradation of the pesticide carbaryl comparing two methods: electrochemical (EC) and photo-assisted electrochemical (PAEC). The experimental variables of applied current density, electrolyte flow-rate and initial carbaryl concentration were investigated. The results demonstrate that the electrochemical degradation of carbaryl was greatly enhanced when simultaneous UV light was applied. The greatest difference between the PAEC and EC method was apparent when lower current densities were applied. The extent of COD removal was much enhanced for the combined method, independent of the applied current density. It should be noted that the complete removal of carbaryl was achieved with out the need to add NaCl to the reaction mixture, avoiding the risk of chlorinated organic species formation.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The increase in the world population has led to the need for increased agricultural production, and the reliance on pesticides for pest control on crops has grown proportionally. This has directly increased the extent of the problems associated with hazardous pesticide-containing wastes. One of the most worrying problems for developing nations is the manner in which used containers, contaminated materials, unusable/excess pesticide supplies are disposed of [1].

High temperature incineration in specialized hazardous-waste incinerators is the method recommended by the Food and Agricultural Organization (FAO) of the United Nations [2] for disposal of obsolete pesticides (and pharmaceuticals). However, such advanced incinerators do not necessarily exist in developing countries and, as a result, it is necessary to transport waste to a country where such facilities exist. It is estimated that for such treatment methods the cost of disposal ranges between US\$ 3000 and US\$ 4500 per ton [2].

In this light, the development of alternative methods that are cheaper and easily accessible to the pesticide user (for example, mobile systems) is important. In the last 15 years, the applica-

tion of electrochemical technology to the degradation/removal of organic pollutants has been an intense area of research [3]. Electrochemical treatment is an interesting alternative to conventional methods as it presents certain advantages [4]. For example, the catalyst/electrode is immobilized (separation of the catalyst from the reaction mixture is not required), the electrochemical variables (i.e. current, potential) are controllable and thus facilitate automation of a process [4]. It has also been stated that cost of the equipment is generally not that expensive [4]. However, it is only recently that investigation of the use of electrochemical technology has been applied to the degradation of pesticides. Electrochemical studies of pesticide degradation include atrazine [5,6], methylparathion, phosalone, azinphos-methyl, methidathion; demeton-s-methyl, metamidophos, fenthion, diazion [7–10].

For example, the work performed by Vlyssides and co-workers [7–10] is an interesting example of the electrochemical degradation of pesticides. The authors examined the use of brine solutions on the extent of pesticide degradation. Due to the presence of NaCl in the reaction mixture and its anodic conversion to Cl₂, the authors observed that efficient removal of both the pesticides and chemical oxidation demand (COD) was possible [7–10]. Interestingly, COD removal efficiency was observed to depend on the pesticide structure. For some pesticides removals of >65% (phosalone [9]) and >50% (diazinon [10]) were observed. On the other hand, it is possible to degrade methylparathion with COD removals of >80%.

In addition to Pt, Dimensionally Stable Anodes (DSA[®]) and related materials have attracted a great deal of interest as elec-

* Corresponding authors. Tel.: +55 16 3373 9733; fax: +55 16 3373 9952.
E-mail addresses: geoffmalpass@yahoo.com (G.R.P. Malpass), artur@iqsc.usp.br (A.J. Motheo).

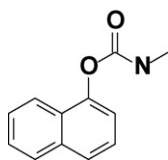


Fig. 1. Structure of carbaryl (1-naphthyl methylcarbamate).

trodes for organic degradation. This is due partly to the fact that DSA[®] materials present elevated stability under extreme electrolysis conditions and, depending on the material used, are capable of producing hydroxyl radicals [11]. According to the proposed mechanism [11] the oxidation of organics at Ti/Ru_{0.3}Ti_{0.7}O₂ DSA-type electrodes occurs simultaneously with the oxygen evolution reaction (OER) and begins with the initial decomposition of water at the electrode surface to form elevated oxidation states [11]:



where MO_{x+1} is considered the active species at RuO₂-containing electrodes and can either react with the organic (R) in solution:



or form O₂ in the OER:



In a recent study performed in this laboratory we investigated the removal of carbaryl [12] and atrazine using DSA[®]-type electrodes and demonstrated that efficient removal is only possible when degradation is attempted in the presence of NaCl due to the electroformation of oxidizing species at the anode. It should be noted that addition of organic-containing solutions may result in the formation of undesired disinfection by-products (DBPs), which can be more harmful than the original substance in question.

For some time it has been known that the simultaneous application of an external anodic bias to an irradiated semiconductor catalyst (e.g. TiO₂) can increase the rate of organic mineralization [13]. Recently, a number of studies have shown that DSA[®] electrodes of composition Ti/Ru_{0.3}Ti_{0.7}O₂ can also be utilized in photo-assisted electrochemical degradation processes [14–16]. For example, studies performed in this laboratory demonstrate that complex chemical species molecules such as humic acid [14], dyes [15] and atrazine [16] can be degraded with considerable increases in efficiency using photo-assisted electrochemical methods.

Carbaryl (1-naphthol *N*-methylcarbamate, Fig. 1) is a broad spectrum carbamate insecticide which is used in a variety of agricultural and public health pest control applications, which include cockroaches, ants, ticks and mosquitoes amongst others [17]. In the environment the levels of carbaryl encountered are generally considered to sub-hazardous [18], however, the toxicity of carbaryl towards certain species of amphibians can increase up to 46 times in the presence of predators [18]. In this light it is important that carbaryl, present in pesticide formulations be efficiently removed before release into water systems.

This paper presents the study of the photo-assisted electrochemical degradation of the pesticide carbaryl in a flow-cell. The effect of several experimental variables (applied current, electrolyte flow-rate and initial concentration) is investigated and the results discussed in terms of the rate of removal of carbaryl, chemical oxygen demand as well as energy required.

2. Experimental

2.1. Electrodes and reactor

A single-compartment filter-press cell was used with a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ DSA[®] plate (De Nora, Brazil), which had a geometric area exposed to the solution of 14 cm², and a Ti-mesh cathode. The reactor was mounted by positioning the electrodes between Viton[®] and Teflon[®] spacers of varying thickness. A quartz glass window was placed between the Ti-mesh cathode and the last spacer. The spacers were open in the middle in such a manner that UV–vis radiation was able to pass through both the quartz glass and the Ti-mesh cathode and reach the exposed surface of the Ti/Ru_{0.3}Ti_{0.7}O₂ electrode. The system functioned in recirculation (batch) mode with the electrolyte being pumped through the cell by an electric pump at a flow velocity of between 32 and 425 cm³ min⁻¹, depending on the experiment to be performed. The UV radiation was provided by a 250 W high pressure mercury lamp (Philips) with a fluency rate of 0.417 W cm⁻² (at λ = 254 nm). The distance between the lamp and the electrode was 7 cm and the fluency rate of the light incident on the DSA[®] plate (after passing through the quartz glass and counter electrode) was 0.113 W cm⁻². The entire set-up was placed in a closed box, which was equipped with an exhaust fan in order to dissipate the heat produced by the UV radiation source. Readers are directed to Malpass et al. [16] for more details of the experimental set-up.

A membrane (IONAC), which was open in the same manner as the spacers, with a strip positioned in an electrolyte bath of concentrated sodium sulfate, was used not to separate the cell compartments but to provide an “*in situ*” probe connected to the reference electrode. All potentials are referred to the reversible hydrogen electrode (RHE).

2.2. Materials and equipment

All electrochemical measurements were performed using a potentiostat/galvanostat (Autolab, model SPGSTAT). The HPLC determinations of Carbaryl were performed using a Shimadzu apparatus (LC-10AD VP) and UV detector (SPD-10A VP). The chemical oxygen demand was determined using Digester (HACH DRB 200) and a colorimeter (HACH DR 890).

2.3. Analysis

Analysis of carbaryl was performed by HPLC with a reverse phase column (LC-18, supelcol, see ref. [12]). The eluente was acetonitrile/water (1:1, v/v) at a flow-rate of 1 cm³ min⁻¹, under which conditions carbaryl presented a retention time of 3.05 min. The concentration of carbaryl was monitored using an ultraviolet detector at λ = 220 nm.

The extent of degradation was accompanied by determination of the chemical oxygen demand according to the standard methods [19]. Na₂SO₄ (>99.99%) was obtained from Malinkrodt and used without purification. The sample of carbaryl (99.26%) was obtained from Bayer Crop Science Ltd. and also used without further purification.

All analyses were performed in duplicate and when experimental error was >5% a triplicate sample was tested.

2.4. Experimental procedure

Two different degradation techniques were applied: (a) electrochemical (application of a constant current) abbreviated as EC and (b) photo-assisted electrochemical (simultaneous application of a constant current and irradiation of the electrode surface with UV light) abbreviated as PAEC. As a control step, to validate

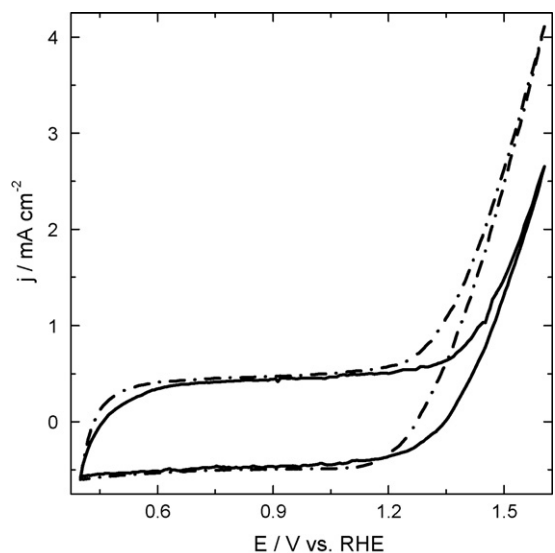


Fig. 2. Cyclic voltammogram of $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ in: (solid line) $0.033 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and (dash-dot) $0.033 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4 + h\nu + 20 \text{ mg L}^{-1} \text{ carbaryl}$.

the combined process (PAEC), a photocatalytic degradation assay (interaction of UV radiation and electrode surface) was performed and is abbreviated as PC. All electrolyses were performed using a solution volume of 0.25 L of $0.033 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4 + 20 \text{ mg L}^{-1} \text{ carbaryl}$, at a flow-rate of $425 \text{ cm}^3 \text{ min}^{-1}$. Any deviation from this procedure is reported at the appropriate point in the text.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 2 presents the cyclic voltammetric profile of the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode in sodium sulfate ($0.033 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$) in the absence and presence of carbaryl (20 mg L^{-1}). In the absence of carbaryl the electrode presents typical behavior for this kind of electrocatalytic material in the electrolyte used. When the electrode is simultaneously submitted to UV-vis radiation, an appreciable increase in both the current and potential associated with the oxygen evolution reaction (OER [20]) can be observed. This phenomenon has previously been reported [16] and it is apparent from reactions 3 and 4 (introduction) that the species responsible for the

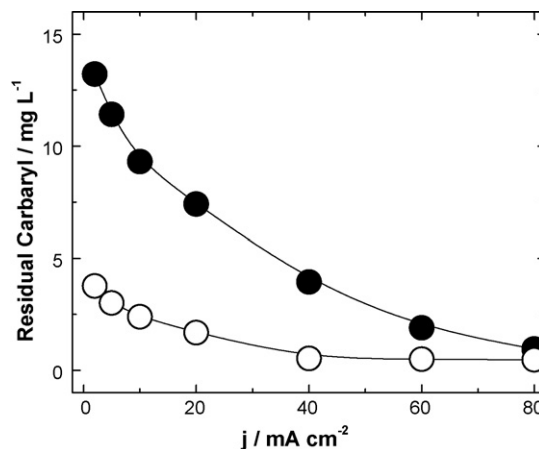


Fig. 4. Residual Carbaryl as a function of current density after electrolysis of 2 h. Starting concentration of carbaryl = 20 mg L^{-1} . Flow-rate = $425 \text{ cm}^3 \text{ min}^{-1}$.

formation of O_2 are also responsible for the oxidation of organic species in solution, i.e. O_2 evolution occurs simultaneously with organic oxidation [11]. In this light, it is evident that the reduction of the potential of the OER would result in a decrease in the energy necessary for organic oxidation to occur. When carbaryl is added to the solution almost no alteration in the voltametric profile is observed, in agreement with previous studies performed in this laboratory [12].

3.2. Degradation of carbaryl: effect of current density

The effect of current density on the rate of removal of carbaryl for electrochemical (EC) and photo-assisted electrochemical (PAEC) degradation was studied by varying the current density from 2 to 80 mA cm^{-2} . As a comparison the purely photochemical (UV irradiation of electrode) degradation was also analyzed.

Fig. 3 presents the concentration–time profiles for the degradation of carbaryl at 2 (**Fig. 3a**) and 80 mA cm^{-2} (**Fig. 3b**). It is interesting to note that at the lower current density there is a distinct difference between the EC and PAEC methods with the PAEC method resulting in much greater removal rates. However, as the current density is increased there is a steady increase in the extent of carbaryl removed by the EC method and this is better exemplified in **Fig. 4** where the level of residual carbaryl at the end of each degradation assay is presented. At all current densities the

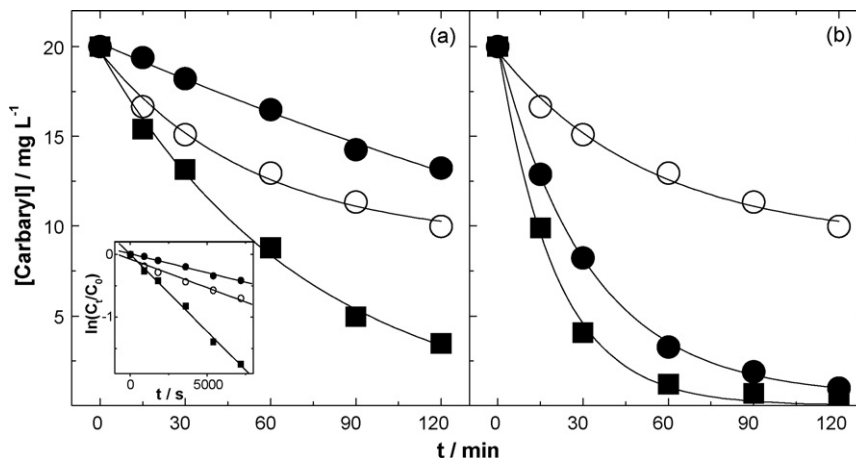


Fig. 3. Variation of carbaryl concentration during electrolysis at (a) 2 and (b) 80 mA cm^{-2} : (●) EC; (○) PC; (■) PAEC. Starting concentration of carbaryl = 20 mg L^{-1} . Flow-rate = $425 \text{ cm}^3 \text{ min}^{-1}$. Inset: pseudo 1st order plot for degradation of carbaryl at 2 mA cm^{-2} (symbols as for main figure). C_0 and C_t = initial concentration and concentration after a time, t , respectively.

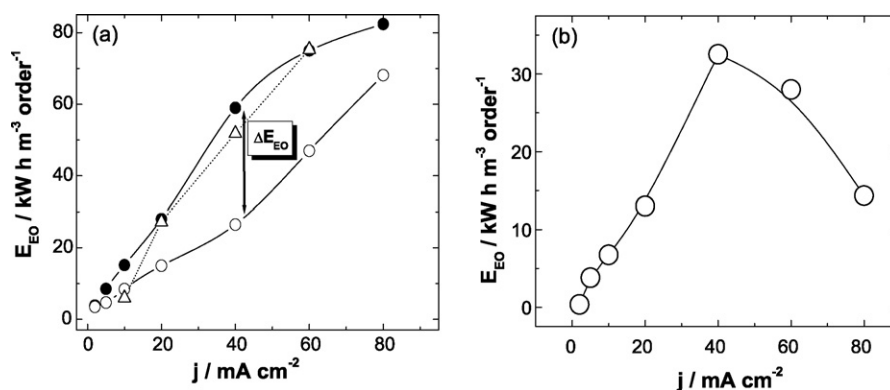


Fig. 5. (a) Variation of the energy per order (E_{EO}) as a function of current density for degradation by (●) EC; (○) PAEC methods and (Δ) represents data extracted from Miwa et al. [10] for EC degradation. (b) Difference between E_{EO} for EC and PAEC methods (ΔE_{EO}). Starting concentration of carbaryl = 20 mg L^{-1} . Flow-rate = 425 $\text{cm}^3 \text{min}^{-1}$.

removal of carbaryl can be seen to follow pseudo 1st order kinetics, as shown in Fig. 3a (inset), and this is important when deciding which measure of the energy consumption can be applied [21].

From Fig. 4 it can be seen that the level of residual carbaryl for the PAEC method varies from $\sim 4 \text{ mg L}^{-1}$ at 2 mA cm^{-2} to $\sim 0 \text{ mg L}^{-1}$ at 80 mA cm^{-2} , whereas for the EC method it varies respectively from ~ 13 to $\sim 0 \text{ mg L}^{-1}$. The increase in the current density represents, in simple terms, an increase in the quantity of electrical energy being injected into the system. As a result, the rate of Eqs. (1)–(4) is proportionally increased, increasing the rate of organic degradation. These results demonstrate that the degradation of carbaryl is increased at higher current densities due to the increased rate of formation of the electro-active species formed at the electrode surface (Eqs. (1)–(3)). This result is in agreement with previous studies in this laboratory with carbaryl [12] in which an increase in the applied current results in a corresponding increase in the degradation rate. On the other hand, the degradation of atrazine [6] does not increase with current density and these results indicate that there is some kind of interaction with the electrode surface in the case of carbaryl. Previous studies in this laboratory [22] and in the literature [23] indicate that, during the use of $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrodes, the organic species can actually replace the H_2O molecule in Eq. (1) and form an $\text{MO}(\text{Carbaryl})$ species which would then mediate a direct electron transfer and this would increase with applied current. In the case of atrazine, it is probable that there is no direct interaction of the molecule with the electrode surface.

As the treatment process used here employs electrical energy it is important to have a measure of the efficiency of its use. In many electrochemical degradation studies, the current efficiency (electrical charge used to degrade organics vs. total electrical charge passed) is employed (for example see Malpass et al. [24]). However, it is interesting to have a unit that can be compared with other studies that use other energy sources (e.g. photochemical). In this light, IUPAC recommends the use of the energy per order ($E_{EO}/\text{kWh m}^{-3} \text{order}^{-1}$) for advanced oxidation processes where 1st order kinetics are observed [21]. The E_{EO} is defined as the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant C by one order of magnitude in 1 m^3 (1000L) of contaminated water or air. The E_{EO} is given by:

$$E_{EO} = \frac{P \cdot t \cdot 1000}{V \cdot \log(c_i/c_f)} \quad (5)$$

where P is the rated power (kW), t the time (h), V the volume (m^3) treated, c_i and c_f the initial and final concentrations of the organic species of interest.

The analysis of the degradation profiles demonstrates that the variation of the concentration of carbaryl with time obeys pseudo 1st order kinetics (Fig. 3a (inset)) and as a result the

energy per order ($E_{EO}/\text{kWh m}^{-3} \text{order}^{-1}$) can be applied [20] (Fig. 5a). In the present study, the highest efficiency (lowest E_{EO}) for both treatment methods can be found at lower current densities, with the PAEC method always providing the greater efficiency. For example, at 2 mA cm^{-2} , the E_{EO} values are 3.51 (PAEC) and 3.86 (EC) $\text{kWh m}^{-3} \text{order}^{-1}$ and at 80 mA cm^{-2} , the values are 82.41 (PAEC) and 68.10 (EC) $\text{kWh m}^{-3} \text{order}^{-1}$. Shown in Fig. 5b is the value of ΔE_{EO} ($E_{EO}(\text{EC}) - E_{EO}(\text{PAEC})$) and it can be seen that the greatest difference is observed at 40 mA cm^{-2} with $\Delta E_{EO} = 32.50 \text{ kWh m}^{-3} \text{order}^{-1}$. When previous studies carried out in a stationary cell [12] are compared together with the results obtained in the present study (Fig. 5a) it can be seen that the E_{EO} for EC carbaryl removal is practically the same at the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode at the same current densities used for both studies. So, the PAEC method presents a substantial improvement in efficiency of carbaryl degradation at the electrode used in this study. However, the development of reactors is required, which both improves the rate of carbaryl degradation and its efficiency, before any large application can be considered. The fact that the PAEC method consumes more than the electrochemical method in the presence of NaCl, is due to the formation of Cl_2 in the presence of NaCl. Cl_2 is a powerful oxidizing agent and is formed efficiently at the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode [20] and thus promotes the increase in degradation efficiency. The great advantage of not using NaCl as the electrolyte in the PAEC method is that organo-chlorine species are unlikely to form.

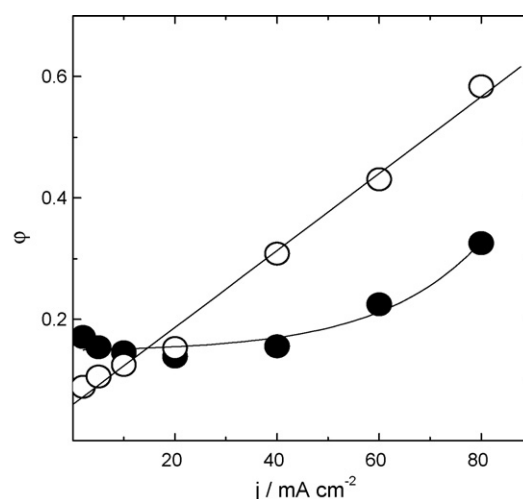


Fig. 6. Variation of ϕ with current density for (●) EC and (○) PAEC methods. Starting concentration of carbaryl = 20 mg L^{-1} . Flow-rate = 425 $\text{cm}^3 \text{min}^{-1}$.

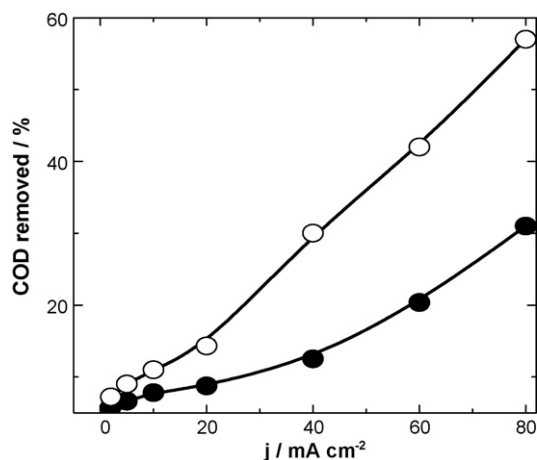


Fig. 7. Removal of COD as a function of current density for (●) EC and (○) PAEC methods. Starting concentration of carbaryl = 20 mg L⁻¹. Flow-rate = 425 cm³ min⁻¹.

In the present study, the data given in Fig. 5a demonstrates that there is a converging of the E_{EO} values at higher current densities. It should be noted that the values obtained at lower current densities for the PAEC method, although lower than those obtained using the EC method, are still much higher than those obtained for atrazine (~0.8–1.4 kW h m⁻³ order⁻¹ for PAEC [16]) and carbaryl for purely EC in the presence of NaCl (~0.9–0.33 kW h m⁻³ order⁻¹ [12]).

The differences in the methods used can be better seen when the extent of the decrease of the chemical oxygen demand is considered. Fig. 6 presents the COD removal of as a function of current density and it can be noted that there is an almost linear relationship as the current increases for both the PAEC and EC methods. However, it is apparent that there is a large difference in the quantities removed when the methods are compared. At lower current densities there is almost no difference between the two methods, but as the current density increases there is an increasing difference which, at 80 mA cm⁻², reaches approximately double the EC removal for the PAEC method.

If the total oxidation index is considered [12], modifying the TOC removed to the COD, a dimensionless value (φ), which indicates the

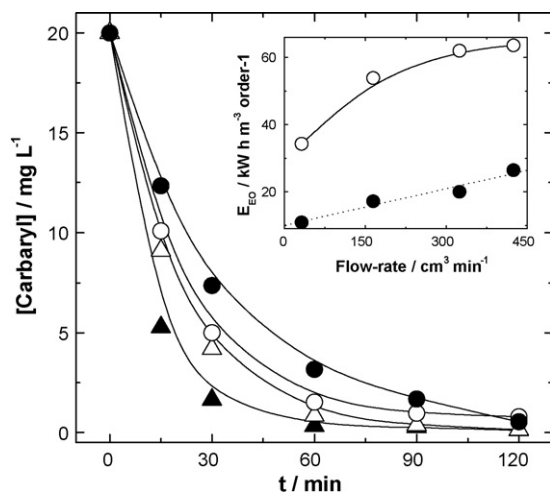


Fig. 8. Variation of carbaryl concentration during PAEC degradation at 40 mA cm⁻² at different flow-rates: (▲) 32; (△) 165; (○) 325 and (●) 425 cm³ min⁻¹. Starting concentration of carbaryl = 20 mg L⁻¹. Inset: Variation of E_{EO} with flow-rate for (○) EC and (●) PAEC methods.

Table 1

Extent of COD removal (after 2 h) as a function of flow-rate at 40 mA cm⁻² for both the EC and PAEC methods.

Flow-rate/cm ³ min ⁻¹	COD removal (%)	
	EC	PAEC
32	13.00	31.5
165	12.90	31.0
325	12.38	30.5
425	12.50	30.0

level of total combustion/removal, is obtained.

$$\frac{\%[\text{COD}]_{\text{removed}}}{\%[\text{Carbaryl}]_{\text{removed}}} = \varphi \quad (6)$$

If φ tends towards 1, then almost all the carbaryl removed is subsequently mineralised to CO₂. It can be observed in Fig. 7 that the values of φ reach a maximum of 0.58 for the PAEC method. This value is greater than that obtained for the same electrode using purely EC methods in previous studies [12]. Considering the results obtained, it is probable that the PAEC method is more efficient at breaking down the intermediates formed after the initial breakdown of the carbaryl molecule.

3.3. Degradation of carbaryl: effect of electrolyte flow-rate

As the greatest difference in the efficiency of carbaryl removal was obtained at 40 mA cm⁻² all the subsequent experiments were performed at this current density value. Fig. 8 presents the effect of electrolyte flow-rate on the PAEC degradation of carbaryl (main figure) and the E_{EO} (inset) for the EC and PAEC methods. It can be observed that there is a distinct electrolyte flow-rate effect with lower flow-rates favoring a quicker removal of carbaryl. From the inset in Fig. 8 it can be seen that the energy per order is also much reduced at the lower electrolyte flow-rate studied (10.90 compared to 26.47 kW h m⁻³ order⁻¹ at 32 and 425 cm³ min⁻¹, respectively). This result would indicate that the degradation of carbaryl proceeds via some kind of initial electron transfer step or adsorption process, which is favored at lower flow-rates. The possible formation of an MO(Carbaryl) species (Section 3.2) would most probably be favored at lower electrolyte flow-rates (a slower refreshing of the electrolyte surface), thus resulting in greater carbaryl removal.

Table 1 presents the extent of COD removal as a function of flow-rate and it can be seen that there is a small increase in the amount of COD removed at lower electrolyte flow-rates indicating that the

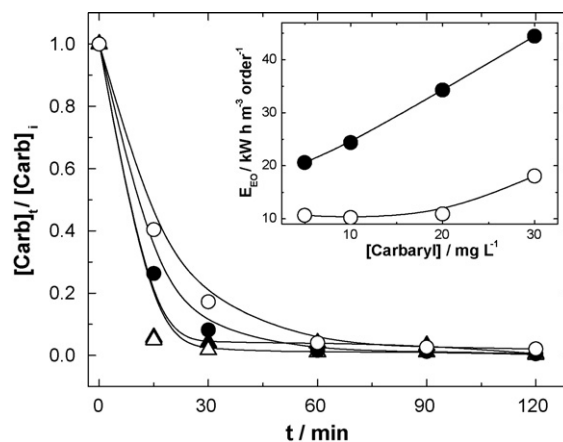


Fig. 9. Variation of normalized carbaryl concentration during PAEC degradation at 40 mA cm⁻² at different initial concentrations: (▲) 5; (△) 10; (●) 20 and (○) 30 mg L⁻¹. Inset: Variation of E_{EO} with carbaryl concentration for (○) EC and (●) PAEC methods. Flow-rate = 32 cm³ min⁻¹.

Table 2

Extent of COD removal (after 2 h) as a function of initial carbaryl concentration at 40 mA cm⁻² for both the EC and PAEC methods. Flow-rate = 32 cm³ min⁻¹.

[Carbaryl]/mg L ⁻¹	COD removal (%)	
	EC	PAEC
5	25.10	40.77
10	17.90	35.76
20	13.00	31.5
30	9.24	23.6

removal of COD does not depend strongly on the flow-rate, probably being more reliant on the initial removal of carbaryl.

3.4. Degradation of carbaryl: effect of initial concentration

With the aim of understanding the effect of concentration on the rate and efficiency of carbaryl degradation, it was decided to vary the concentration of carbaryl from 5 to 30 mg L⁻¹ (5, 10, 20 and 30 mg L⁻¹) whilst using the optimized flow-rate. Fig. 9 presents the variation of the normalized carbaryl concentration ($[\text{Carbaryl}]_t/[\text{Carbaryl}]_i$) as a function of electrolysis time for the different concentrations studied. It can be seen that the PAEC method is capable of removing almost completely all the carbaryl in solution, regardless of the initial starting concentration. This is also true of the EC method, but the rate is much slower and this is exemplified by the values of the E_{EO} (Fig. 9—inset). Whereas the E_{EO} values increase linearly for the EC method there is almost no variation for the PAEC method. The removal of COD is presented in Table 2 and it is evident that a lower percentage is removed as the concentration is increased.

4. Conclusions

The results demonstrate that the electrochemical degradation of carbaryl can be greatly enhanced when simultaneous UV light is applied. It is observed that the greater difference for the PAEC method compared to the EC one is when lower current densities are applied. For example at 10 mA cm⁻² the PAEC method gives a carbaryl removal of ~88%, whereas only ~55% is seen for the purely EC method. At 80 mA cm⁻², the extent of removal is practically the same at ~100%. It should also be noted that the extent of COD removal is much enhanced for the combined method, independently of the applied current density.

When the flow-rate is decreased the rate of carbaryl removal is increased, but the COD removal is practically unchanged. When the carbaryl concentration is varied, it can be observed that the PAEC method is capable of removing almost completely all the carbaryl in solution, regardless of the initial starting concentration.

It is important to stress that the complete removal of carbaryl was achieved without the need to add NaCl to the reaction mixture, avoiding the risk of possible organo-chloride formation. Future work in this lab will concentrate on the scale-up of this kind of technique, with special emphasis on the development of light-weight and easily transportable (mobile) systems to be used between multiple users. Currently, prototype reactors for PAEC degradation exist [REF.MARA], but field applications are still unavailable.

Concluding, the results obtained are promising and demonstrate the need for careful analyses to set the operational parameters (electrolyte flow-rate, electrolysis time, current density) in order to obtain satisfactory results. Such analyses would include (at the

laboratory scale) the evaluation of the toxicity of the treated effluents.

Acknowledgement

The authors wish to thank FAPESP, Brazil for the financial support.

References

- [1] A.S. Felsot, K.D. Racke, D.J. Hamilton, Disposal and degradation of pesticide waste, *Rev. Environ. Contam. Toxicol.* 177 (2003) 123–200.
- [2] Food and Agricultural Organization of the United Nations (FAO), Guidelines on Disposal of Bulk Quantities of Pesticides in Developing Countries, 1996, FAO, Rome, Italy.
- [3] C.A. Martinez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- [4] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, *Electrochim. Acta* 45 (2000) 2575–2594.
- [5] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, Oxidation at boron doped diamond electrodes: an effective method to mineralise triazines, *Electrochim. Acta* 50 (2005) 1841–1847.
- [6] G.R.P. Malpass, D.W. Miwa, S.A.S. Machado, A.J. Motheo, Oxidation of the pesticide atrazine at DSA® electrodes, *J. Hazard. Mater.* 137 (2006) 565–572.
- [7] D. Arapoglou, A. Vlyssides, C. Israilides, A. Zorpas, P. Karlis, Detoxification of methyl-parathion pesticide in aqueous solutions by electrochemical oxidation, *J. Hazard. Mater.* B98 (2003) 191–199.
- [8] A. Vlyssides, E.M. Barampouti, S. Mai, D. Arapoglou, A. Kotronarou, Degradation of methyl-parathion in aqueous solution by electrochemical oxidation, *Environ. Sci. Technol.* 38 (2004) 6125–6131.
- [9] A. Vlyssides, D. Arapoglou, C. Israilides, P. Karlis, Electrochemical oxidation of three obsolete organophosphorus pesticides stocks, *J. Pestic. Sci.* 29 (2004) 105–109.
- [10] A. Vlyssides, D. Arapoglou, S. Mai, E.M. Barampouti, Electrochemical detoxification of four phosphorothioate obsolete pesticides stocks, *Chemosphere* 58 (2005) 439–447.
- [11] O. Simond, V. Schaller, Ch. Comminellis, Theoretical model for the anodic oxidation of organics on metal oxide electrodes, *Electrochim. Acta* 42 (1997) 2009–2012.
- [12] D.W. Miwa, G.R.P. Malpass, S.A.S. Machado, A.J. Motheo, Electrochemical degradation of carbaryl on oxide electrodes, *Water Res.* 40 (2006) 3281–3289.
- [13] K. Vinodgopal, P.V. Kamat, Combine electrochemistry with photocatalysis, *ChemTech* 26 (1996) 18–22.
- [14] L. Pinheiro, R. Pelegrini, R. Bertazzoli, A.J. Motheo, Photoelectrochemical degradation of humic acid on a (TiO₂)(0.7)(RuO₂)(0.3) dimensionally stable anode, *Appl. Catal. B-Environ.* 57 (2004) 75–81.
- [15] M. Catanho, G.R.P. Malpass, A.J. Motheo, Photoelectrochemical treatment of the dye reactive red 198 using DSA® electrodes, *Appl. Catal. B-Environ.* 62 (2005) 193–200.
- [16] G.R.P. Malpass, D.W. Miwa, A.C.P. Miwa, S.A.S. Machado, A.J. Motheo, Photo-assisted electrochemical oxidation of atrazine on a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ DSA® electrode, *Environ. Sci. Technol.* 41 (2007) 7120–7125.
- [17] C.R. Worthing, *Pesticide Manual*, 8th ed., Thornton Heath, 1987.
- [18] R.A. Relyea, Predator cues and pesticides: a double dose of danger for amphibians, *Ecol. Appl.* 13 (2003) 1515–1521.
- [19] APHA, Standard Methods for the Examination of Water and Wastewater, 18th, Washington, APHA - AWWA - WPCF, 1995.
- [20] S. Trasatti, Physical electrochemistry of ceramic oxides, *Electrochim. Acta* 36 (1991) 225–241.
- [21] R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems - (IUPAC Technical Report), *Pure Appl. Chem.* 73 (2001) 627–637.
- [22] G.R.P. Malpass, A.J. Motheo, Screening process for activity determination of conductive oxide electrodes for organic oxidation, *J. Braz. Chem. Soc.* 19 (2008) 672–678.
- [23] C.L.P.S. Zanta, A.R. de Andrade, J.F.C. Boodts, Solvent and support electrolyte effects on the catalytic activity of Ti/RuO₂ and Ti/IrO₂ electrodes: oxidation of isosafrole as a probe model, *Electrochim. Acta* 44 (1999) 3333–3340.
- [24] G.R.P. Malpass, R.S. Neves, A.J. Motheo, A comparative study of commercial and laboratory-made Ti/Ru_{0.3}Ti_{0.7}O₂ DSA® electrodes: “in situ” and “ex situ” surface characterisation and organic oxidation activity, *Electrochim. Acta* 52 (2006) 936–944.