

Removal of Pesticides by Electrochemical Oxidation using a Boron Doped Diamond Anode

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Received 20 Oct 2016,

Revised 1 Jan 2017,

Accepted 3 Jan 2017,

Keywords

- ✓ Pesticides removal,
- ✓ Organophosphate,
- ✓ Electrochemical oxidation,
- ✓ boron-doped diamond,
- ✓ depollution,
- ✓ wastewater treatment,
- ✓ electrochemical advanced oxidation process.

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Abstract

The direct or indirect discharges of the effluents of the agricultural practices constitute the important causes of degradation of the ecosystems. Particularly, the effluents of the agricultural practices (phytosanitary treatments, wash of the material and the rinsing of atomizers) circulate most of the time through the matrix of the ground and reach streams and even groundwaters. These practices establish a direct threat for the environment, the living beings and especially for the human health. Consequently, it needs to develop technics to detoxify the pesticide residues to reduce at least areas and contaminated matrix. In the present work, the treatment of synthetic and commercial solutions by electrolysis on BDD anode has been studied. The molecule model chosen was dimethoate that is an organophosphate insecticide and acaricide used against a broad range of insects and on a number of crops. It has been shown that the dimethoate has been removed completely by electro-oxidation and the kinetic follows a pseudo-first order reaction. The use of electrolytes containing chlorides must to be avoided because of the formation of undesired compounds such as perchlorate. The study of the influence of the applied current intensity revealed that the higher the current intensity, the faster the COD removal is.

Introduction

The safeguarding of the freshwater resources has become a major concern for many countries in the world, and protecting the environment is an economic and political issue, among the major sources of water pollution is noted organic contaminants especially pesticides or plant protection products introduced by farming to improve crop yields. It should be noted that the majority of pesticides used in the past contain the organochlorine molecules; the use of these later was prohibited because of their high toxicity. Actually the organochlorine compounds are replaced by organophosphorus molecules (OPPs) which are more selective and have a lower persistence [1-3]. Dimethoate is one of the most widely used organophosphorus insecticides in agricultural activities including olive cultivation in the Mediterranean region [4-5]. Dimethoate is an indirect acting OPP insecticide, it is converted in the body into the active metabolite, demithoxon [6], it is a real risk of adverse health effects following chronic cumulative exposure found in fruit, especially when the fresh fruit are consumed by children [7].

The use of physico-chemical and biological processes for the agricultural wastewater treatments are well known but their yields continue to decline by the presence of bio-refractory compounds such as pesticides and very often-secondary wastes are produced [8]. To overcome this problem, several processes have been developed, the AOPs (Advanced Oxidation Processes) that are based on generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) which have so high standard redox potential ($E^0(\cdot\text{OH}/\text{H}_2\text{O})=2.80\text{ V}$) and attack unselectively most of the organic molecules resulting in a partial or total decomposition [9-11].

Recently, many AOPs for OPP degradation were studied [8]. Ozonation and ozone-based AOPs such as O₃/H₂O₂, O₃/UV, and O₃/H₂O₂/UV, direct photolysis and various photochemical processes such as TiO₂/UV [12-15]. Meijers et al. demonstrated that dimethoate was readily degradable by ozonation at particular conditions but no further studies were reported on the kinetics, by-products, and pathway of this organophosphate insecticide degradation [16]. Solar photocatalysis employing titanium dioxide has been tested for dimethoate removal [13]. Although complete removal of the target molecule has been achieved, the detoxification of the solution was not reached whatever the operating conditions. Using the same process, Evgenidou et al. [14] showed that complete detoxification was reached only in the presence of photo-Fenton system with perchlorate addition. As well as the study of Badawy et al. [17], the combination of a homogeneous system of UV/H₂O₂/Fe²⁺, produced the highest photochemical elimination of many OPP pesticides. Whatever the AOP used, the treatment is not considered as complete and needs to be combined with biology to eliminate completely the organic matter [15].

Electrochemical Advanced Oxidation Processes (EAOPs) are environmental-friendly technologies which possess advantages over other techniques of easy implementation, no chemicals addition, and high efficiency [18-19]. Among EAOPs, one can cite Electro-Fenton oxidation H₂O₂/Fe²⁺ [18, 20] electrophoto-Fenton oxidation H₂O₂/Fe²⁺ with UV/Vis (solar) radiation [21] and Electro-Oxidation (EO).

Because the oxidation of refractory compounds occurs at very high overpotential, the choice of the anode material represents the key point. It is well known that electrochemical oxidation using a Boron-Doped Diamond (BDD) anode represents a promising technique for the elimination of persistent organics [22-25]. Indeed, the strong oxidation ability of the BDD is due to the electrogeneration of hydroxyl radical ([•]OH) from the water discharge (Eq. 1).



On BDD anode, the hydroxyl radicals are quasi-free on the surface and can react massively close to the anode with organics.

The aim of this work is to study the electrochemical oxidation of dimethoate in synthetic and commercial solutions. The rate of mineralization has been estimated by the measurement of global parameters such as total organic carbon and chemical oxygen demand. The influence of operating conditions such as current intensities, nature of electrolytes has been studied on the efficiency of dimethoate removal.

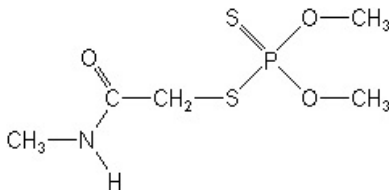
2. Experimental

2.1. Chemicals and solutions

2.1.1 Synthetic solutions

The dimethoate (DIM) (≥98.5% purity) was purchased from Dr. Ehrenstorfer GmbH Company. All synthetic solutions were prepared with ultrapure water (ρ = 18.2 MΩ cm). The structure of DIM is reported in Table 1. Sodium sulfate (≥99% purity), potassium nitrate (≥99.8% purity), potassium chloride (≥99% purity) were analytical grade and supplied by Sigma Aldrich and Prolabo (VWR International). Other chemicals, organics or solvents were HPLC or analytical grade.

Table 1 Structure of the target molecule

| | Dimethoate (DIM) |
|---|--|
| Formula | C ₅ H ₁₂ NO ₃ PS ₂ |
| Molecular weight (g mol ⁻¹) | 229.26 |
| Structure |  |

2.1.2. Wastewater source

Danadim Progress, the commercial solution used by the farmers, was purchased from Cheminova. It contains dimethoate 400g/L, cyclohexanone (43% weight), xylene (13% weight) and emulsifier (5 % weight).

2.2. Analytical techniques

Concentrations of salts in synthetic solution and wastewater were measured by ionic chromatography with an ICS 3000 system (Dionex, France). The injection volume was 25 μL and the column temperature was set at

30 °C. The concentrations of anions and cations were analyzed with two columns (Thermo Scientific, *Dionex*): IonPac™ AS19, (the mobile phase consisted of a gradient with 5 mM NaOH and 100 mM NaOH), IonPac™ CS12A (mobile phase: CH₄O₃SO₃ 20 mM), respectively. Analytical errors for anions and cations ranged from 1.5 % for K⁺ to 6 % for SO₄²⁻. In this mobile phase, all phosphate species (H₃PO₄, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻) were reported as PO₄³⁻. Table 2 reports the obtained retention times for each anion.

Table 2 : Retention times for anions

| Anions | SO ₄ ²⁻ | PO ₄ ³⁻ | NO ₃ ⁻ | NO ₂ ⁻ | ClO ₃ ⁻ | ClO ₄ ⁻ |
|----------------------|-------------------------------|-------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|
| Retention time (min) | 15.37 | 17.90 | 12.41 | 7.50 | 8.24 | 18.60 |

DIM concentration was measured by high performance liquid chromatography connected with an ultraviolet-visible spectrometry detector (HPLC-UV). The analyses were conducted on Agilent 1200 Series HPLC systems (Agilent Technologies, USA). A VYDAC C18 reverse phase 250 x 4.6 mm x 5µm from Fisher Scientific was used. The detection UV wavelength was set to 200 nm. The mobile phase of HPLC is the mixture of ultrapure water /methanol (≥99.8% purity) with a ratio: 1/1 and the column temperature was set to 30 °C. The flow rate was 0.5 mL min⁻¹ and the volume of injection was 10 µL. The detection limit of dimethoate is 0.3 mg L⁻¹ and the quantification limit is 1.1 mg L⁻¹ in Na₂SO₄ solution. The analytical errors range is 5.6% for 2 ppm in Na₂SO₄ solution.

TOC and inorganic carbon (HCO₃⁻) were measured with a TOC-VCSN instrument (Shimadzu). The concentration of inorganic carbon was measured after acidification and degassing, performed automatically. TOC was calculated from the difference between the total carbon and inorganic carbon. COD was determined by photometry using disposable test tubes (HI93754H-25 LR from HANNA Instruments) and a HACH DR/2400 photometer. Test tubes were heated at 160°C for 2 hours and left to cool down at room temperature before measurement. The analytic errors for TOC and COD were estimated to 5%.

2.3 Electrochemical set-up

The experimental solution was stored in a 1-liter thermoregulated glass reservoir and circulated through the electrochemical cell using a centrifugal pump. The flow rate was 360 L h⁻¹. Electrolyses were conducted at 30 °C in a one-compartment flow filterpress reactor under galvanostatic conditions. Electrodes were two discs of 69 cm² of active surface. The BDD anode from Adamant (Switzerland) was elaborated by chemical vapor deposition on a conductive substrate of silicium. The cathode was a 1 mm thick disc of zirconium. The current was supplied by an ELCAL 924 power supply. The mass transfer coefficient can be determined by Eq. 2 at 30 °C [26]:

$$k_d \times 10^5 = 0.0051\Phi + 0.4367 \quad (2)$$

where, k_d is the mass transfer coefficient (m s⁻¹), Φ is the flow rate in L h⁻¹

In the present study, the mass transfer coefficient corresponding to the flow rate of 360 L h⁻¹ equals 2.30 × 10⁻⁵ m s⁻¹. Before each electrolysis, the working electrodes were anodically pretreated (40 mA cm⁻² for 30 min in 0.1M H₂SO₄) to clean their surfaces of any possible adsorbed impurities. Then, the system was rinsed by ultrapure water. Samples were taken at regular intervals in the tank. The global volume of samples was less than 10 % of the total volume.

According to the properties of the BDD anode, the limiting current density can be defined by using a global parameter, the COD [27].

$$i_{lim} = 4Fk_dCOD \quad (3)$$

where i_{lim} is the limiting current density for the mineralization of organics (A m⁻²), F is the Faraday constant (C mol⁻¹) and COD is in mol O₂ m⁻³. In our experimental conditions for 0.1mM of DIM, the limiting current intensity is 90 mA.

Depending on the value of the current density (i), two different kinetic regimes can be defined: (1) $i < i_{lim}$: the kinetics of the reaction is charge controlled; (2) $i > i_{lim}$: the kinetics of the reaction is controlled by mass transfer. In this paper, the oxidation was under mass transfer control ($i > i_{lim}$), thus the evolution of COD with time can be expressed by equation (4):

$$COD(t) = COD^0 \exp\left(-\frac{Ak_d t}{V}\right) \quad (4)$$

where V and A are the volume of the solution (m^3) and the electrode surface (m^2), respectively.

3. Results and discussion

3.1. Synthetic solutions

Fig. 1 shows the variation of DIM concentration in 0.5 M Na_2SO_4 during electrolysis on BDD anode at $30^\circ C$. The inset panel highlights that the DIM degradation follows a pseudo-first order reaction. The quasi-complete degradation of DIM, 92%, has been reached after 120 min of electrolysis. At the same time the removal of COD and TOC reached only 54% and 51%, respectively. This results show that intermediates are generated during electrolysis which have high COT and COD. According to the theoretical model of Eq. 4, 90% of COD removal is reached after 11 hours of electrolysis. This comparison evidences that an electrical consumption of 0.18 Ah/L is required to degrade the target molecule while 1 Ah/L is necessary for a complete mineralization.

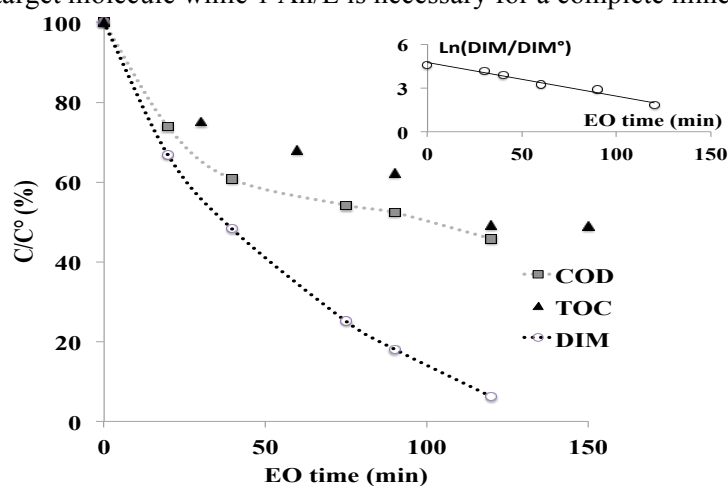


Figure 1. Variation of TOC, COD and [DIM] during electrolysis in 1L of Na_2SO_4 0.1 M. Inset panel: pseudo-first order plot for DIM degradation. Operating conditions: $[DIM]^0 = 0.1mM$, Flow rate = $366 L h^{-1}$, $T = 30^\circ C$, $V = 1 L$, $i = 1.28 mA cm^{-2}$

A careful attention should be given to the interactions between salts with hydroxyl radicals generated at the anode surface. Therefore, different electrolytes were tested for the DIM removal by electrochemical oxidation. Fig. 2 shows the normalized DIM concentration during electrolysis on BDD using three electrolytes : KNO_3 , Na_2SO_4 and KCl .

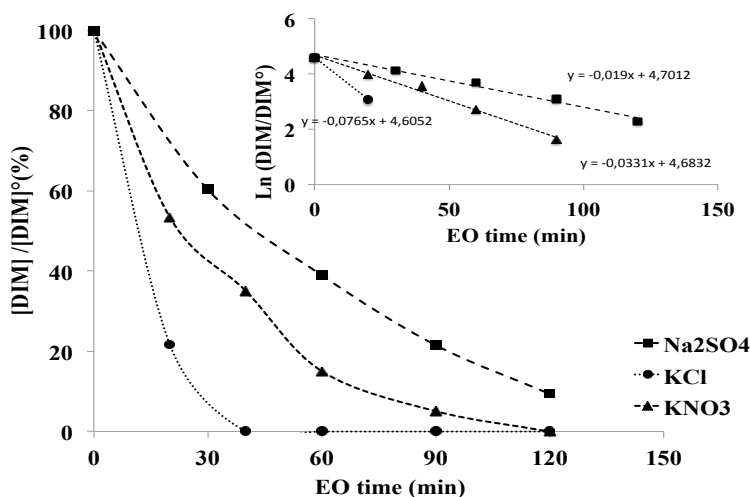
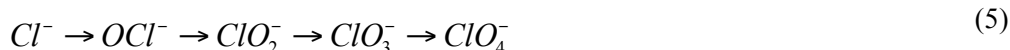


Figure 2. Temporal variation of DIM concentration during electrolysis using different electrolytes: $[Na_2SO_4] = 0.05 M$, $[KCl] = 0.05 M$ or $[KNO_3] = 0.05 M$. Inset panel: pseudo-first order plot of DIM removal for the three electrolytes. Operating conditions: $[DIM]^0 = 0.1mM$, $T = 30^\circ C$, Flow rate = $366 L h^{-1}$, $V = 1L$, $i = 1.28 mA cm^{-2}$.

The inset panel shows that the rate of removal of DIM is higher in presence of KCl then KNO_3 and Na_2SO_4 . The presence of chloride ions allows increasing the efficiency of the DIM degradation, while at the same time, chlorate (17 ppm) and perchlorate (12 ppm) were detected by ionic chromatography after 1.5 Ah/L of

electrolysis in KCl. Since these compounds pose a serious hazard for drinking water and aquatic ecosystems [28-29] and are resistant to further oxidation, it is extremely important to minimize the formation of these compounds during water treatment.

Previous works have investigated that ClO_4^- is generated via a multistep oxidation pathway from chloride, as shown in reaction (5) [28].



Using a BDD anode, besides the chemical reactions between organics and hydroxyl radicals, the electro-oxidation pathway of Cl^- also includes the chemical oxidation reactions with hydroxyl radicals [30-33]. Moreover, one can note that after 10 Ah/L, 26% of TOC are remained. In this case, reactions of addition and substitution between the organics and the active chlorine species (e.g. Cl_2 , OCl^- , HOCl) or chlorine radicals (Cl^\cdot , $\text{Cl}_2^{\cdot-}$) are mainly responsible for the formation of undesired halogenated organic compounds [28]. Therefore sodium sulfate has been chosen as electrolyte for the electrochemical wastewater treatment.

3.2. Real effluent

To investigate first the electrochemical oxidation of the commercial solution (Danadim), the concentration of the target molecule, DIM, has been followed and compared with the electrolysis of a synthetic solution containing only DIM and Na_2SO_4 . Fig. 3 shows that the degradation speed of DIM in both solutions is the same, there is no competition between DIM and the other compounds for the chemical reaction with hydroxyl radicals, these compounds (cyclohexanone, xylene and emulsifier) present in Danadim represent 14% and 74 % of the total COD and TOC, respectively.

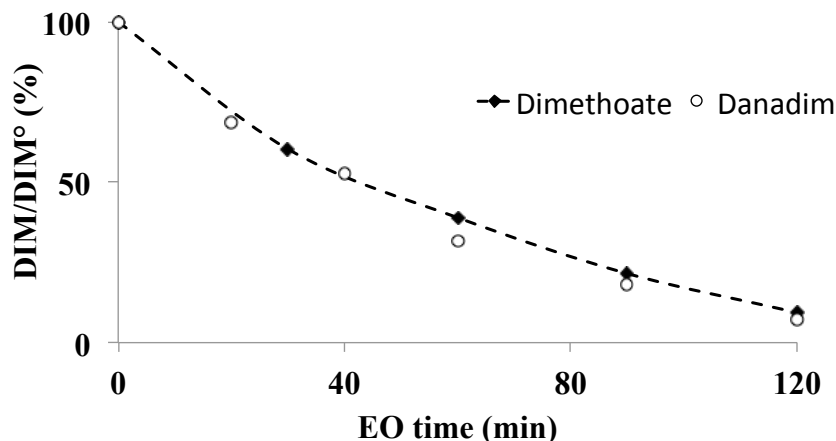


Figure 3. Comparison of DIM concentrations during the electrolysis of synthetic solution (full symbols) and Danadim effluent (empty symbols). Operating conditions: $[\text{DIM}]^0 = 0.1\text{mM}$, $[\text{Na}_2\text{SO}_4] = 0.05\text{ M}$, Flow rate = 366 L h^{-1} , $i = 1.28\text{ mA cm}^{-2}$, $V = 1\text{L}$, $T = 30\text{ }^\circ\text{C}$.

Fig. 4 compares the experimental COD variation during the electrolysis of Danadim at 0.1 A with the model represented by Eq. 4. A good agreement is obtained which confirms that Eq. 4 can be used for predicting the removal of COD during electrolysis. The results obtained in figures 3 and 4 confirm that the electrochemical oxidation on BDD anode is not selective, the electrogenerated hydroxyl radical is one of the most powerful oxidant, it can react with numerous refractory organics.

For an initial COD of 125 mg/L, the corresponding limiting current intensity is close to 0.09 A. Using current densities higher than the limiting current density, the process is controlled by the mass transfer. Different current intensities have been tested to measure the TOC and COD variations during electrolysis. Fig. 5 shows the TOC removal for three different current densities. One can observe that whatever the current intensity, the temporal variation of TOC is the same. This result confirms that when the electrochemical process is under mass transfer control, it doesn't depend on the value of the current intensity. Surprisingly, this tendency is not observed for the COD variation: Fig. 6 highlights that the temporal COD removal is higher with increasing applied current intensity. This phenomenon can be explained by the fact that the amount and nature of intermediates depend on the current intensity. Indeed, it seems that a higher current intensity produces a greater number of physisorbed hydroxyl radicals at the anode generating intermediates with a lower equivalent COD. This assumption needs to be confirmed by a further study.

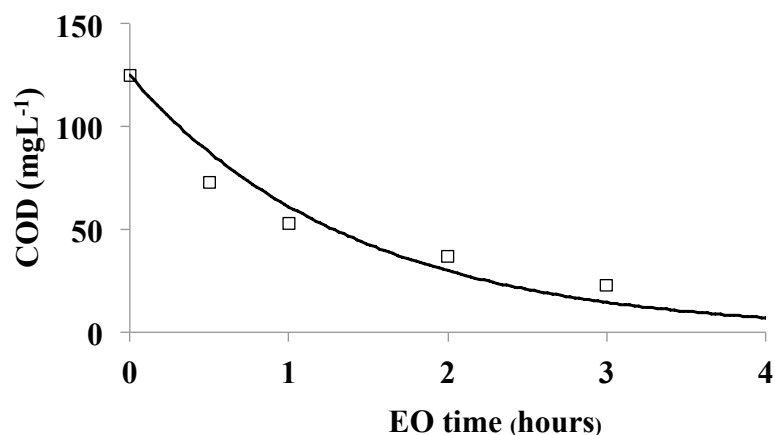


Figure 4. Comparison of experimental COD (symbols) with theoretical COD (line) during electrolysis in 1L of Na₂SO₄ 0.1M. Operating conditions: Solution of Danadim, [DIM]⁰ = 0.1mM, COD^o =125 mg/L, Flow rate = 366 L h⁻¹, T = 30 °C, V = 1 L, i = 1.28 mA cm⁻².

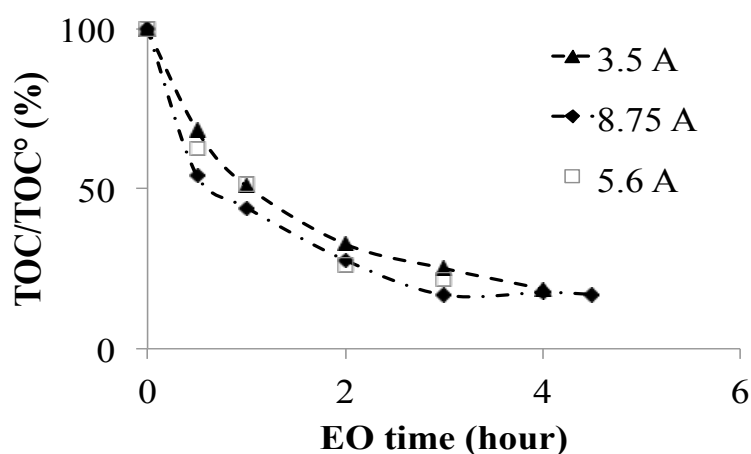


Figure 5. Variation of TOC during electrolysis of Danadim solution at different current intensities. Operating conditions: [DIM]⁰ = 0.1mM, [Na₂SO₄] = 0.1M, S = 69 cm², V= 1 L, Flow rate = 366 L h⁻¹, T = 30 °C.

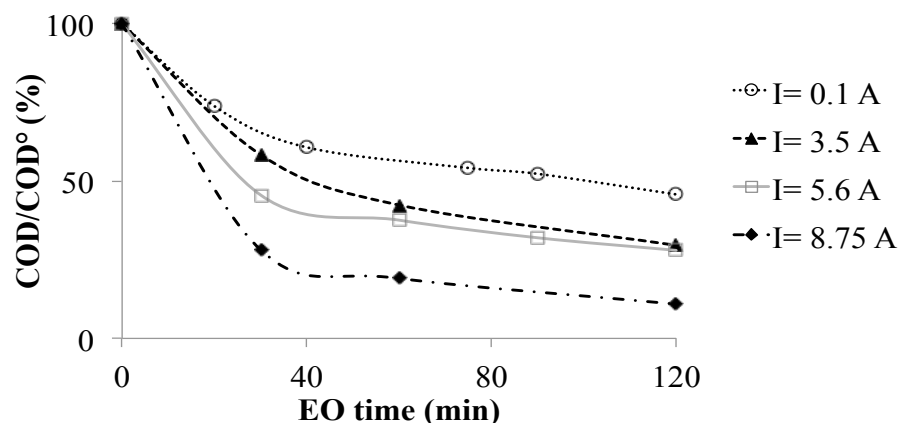


Figure 6. Variation of COD during electrolysis of Danadim solution at different current intensities. Operating conditions: [DIM]⁰ = 0.1mM, [Na₂SO₄] = 0.1M, S = 69 cm², V= 1 L, Flow rate = 366 L h⁻¹, T = 30 °C.

Conclusions

The electrochemical oxidation of dimethoate (DIM), an organophosphorous pesticide has been studied using a boron-doped diamond anode. The degradation of the pesticide follows pseudo-first order kinetics. Its removal is quasi complete after 0.2 Ah/L of electrolysis for a 0.1mM initial concentration whereas only 50% is mineralized. It has been shown that the rate of DIM removal can be accelerated using chlorides as electrolytes. The reaction of these anions with hydroxyl radicals generates active chlorine species. However, the use of Cl⁻ is not recommended in the process because chlorate and perchlorate have been detected and organochlorides can

be generated. The presence of these undesired products enhances the toxicity of the solution. It has been evidenced that the applied current intensity plays an important role on the mineralization rate: in the regime of diffusion control (when $i > i_{lim}^{\circ}$), the TOC removal is not affected by the value of the current density while the COD removal increases with a higher current intensity. This phenomenon can be explained by the fact that the amount and nature of intermediates depend on the current intensity. Indeed, a higher current intensity may produce a greater number of physisorbed hydroxyl radicals at the anode generating intermediates with a lower equivalent COD. This assumption needs to be confirmed by a further study of identification of the main intermediates.

Acknowledgments - The authors would like to thank the Partenariat Hubert Curien Program for the financial support.

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(2017) ; <http://www.jmaterenvirosci.com>