Fuel 198 (2017) 91–98

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Evaluation of a coupled system of electro-oxidation and ozonation to remove the pesticide Thiodan® 35 CE (endosulfan) in aqueous solution

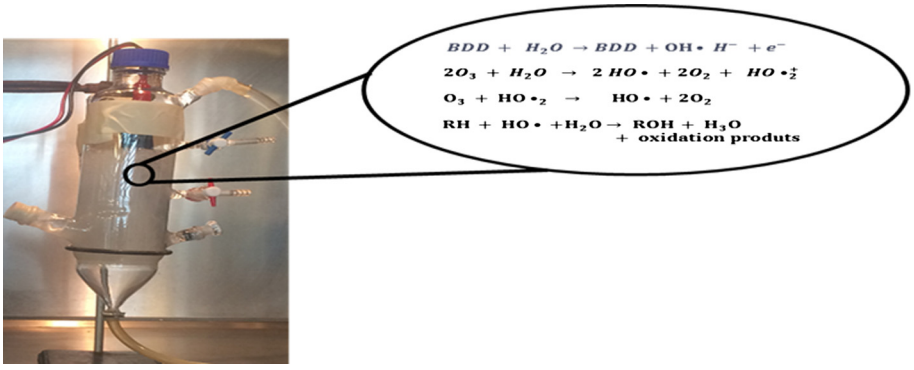
Claudia Rosales Landeros [a], Carlos E. Barrera Díaz [a,*], Araceli Amaya Cháves [b], Gabriela Roa Morales [a]

[a] Centro Conjunto de Investigación en Química Sustentable UAEM – UNAM, Carretera Toluca-Atlacomulco, km 14.5, Unidad El Rosedal, C.P. 50200 Toluca, Estado de México, Mexico
[b] Facultad de Química, UAEMex. Paseo Colón intersección Paseo Tollocan S/N, C.P. 50120 Toluca, Estado de México, Mexico

HIGHLIGHTS

- 60% less reaction time is required to remove endosulfan using a coupled process.
- The process synergy enhances the rate and extent of removal of COD, TOC and toxicity.
- The cyclic voltammograms indicate that an oxidation process takes place in reaction.
- A major advantage is that no chemicals are added in the process.
- This technology is sustainable since no sludge is produced as a reaction residue.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form 13 September 2016
Accepted 3 October 2016
Available online 6 October 2016

Keywords:
Electrooxidation
Ozonatio
Endosulfan
COD
TOC
Microtox

ABSTRACT

This research shows the results of the coupling of two advanced oxidation processes for the degradation of pesticide Thiodan® in water. Electrooxidation process with diamond electrodes doped with boron (BDD) alone removed 97% of COD in 100 min of reaction time. Furthermore, the process of ozonation only removed 77% removal of COD, in the same reaction time. However, when the processes are coupled, the % COD removal was achieved 95% with 40 min reaction time and the TOC decreased a 94%. With the coupled process practically the COD and TOC of the solution of Thiodan® was removed and MICROTOX® test showed that after 30 min of reaction the sample was not exhibit toxicity. The cyclic voltammograms obtained with the coupled process, indicate the oxidation of Thiodan®.

1. Introduction

Pesticides are chemical compounds which are used to eliminate pests in households and agriculture. Conversely, these chemical compounds are some of the most toxic, environmentally mobile and stable substances in the environment [1]. The mobility of pesticides in aquatic systems can easily reach the human population since conventional water treatment plants are unable to eliminate pesticides, due to their chemical stability [2,3]. Organochlorine pesticides have been extensively used over the last century; some of the common characteristics are: they have a cyclic structure, chlorine atoms are normally present, they are lipophilic, their volatility is low and are resistant to degradation [4–6]. Endosulfan

* Corresponding author.
E-mail address: cbd0044@gmail.com (C.E. Barrera Díaz).

http://dx.doi.org/10.1016/j.fuel.2016.10.031
0016-2361/

(6,7,8,9,10,10-hexachloro-1,5,5α, 6,9,9α-hexahydro-6,–9 methan o-2,3,4-benzo-dioxathiepin-3-oxide) is a cyclodiene organochloride insecticide, which is known by its broad spectrum of activity. The main use of this pesticide is in crops, such as: broccoli, cereals, coffee, cotton, ornamental flowers and oilseeds [7,8]. This pesticide is persistent in the environmental with an estimated half-life up to 6 years, such characteristic makes it persistent in the atmosphere, surface and ground water, sediment and food stuffs [9–11].

Two isomers (α and β) in the ratio 7:3 constitute the commercial endosulfan [12]. These isomers can be degraded via sulfur oxidation or by hydroxylation of the sulfite moiety to form endosulfan sulfate, which is as toxic and persistent as the original compound [13–15]. Some physico-chemical properties of α endosulfan, β endosulfan and endosulfan sulfate are shown in Table 1 [16,17].

In order to degrade and remove pesticides from water various innovative technologies have been proposed, these technologies has showed good results, but it is important to consider the operation conditions for obtain high efficiencies, minimum cost and to prevent the formation of more hazardous products. Among these technologies, the Advanced Oxidation Processes (AOP) constitutes an emergent method for the degradation of pesticides. The advantages of electrochemical technologies rely on the use of a clean reagent, "the electron". The process can be carried out under conditions of ambient temperature and atmospheric pressure, they are very useful for refractory contaminants that resist other treatment methods and they are used to treat contaminants at very low concentration (eg ppb). However, some of the limitations are that these processes are at the lab-scale stage and for the technology to be scaled up, many improvements are required to make them cost-effective but they can become dominant in the near future, especially for the abatement of refractory substances [18–20,38].

AOP rely on the hydroxyl radical formation which reacts rapidly and usually indiscriminately with most organic compounds.

HO· radicals reactions takes place by different ways: (i) double bonds attack, (ii) by H-atom abstraction, which yields carbon centred radicals and (iii) HO· radical gets an electron from an organic substituent. Carbon centred radicals can react with oxygen to form organic peroxyl radicals. Peroxyl radicals reacts among themselves and lead to ketones or aldehydes and/or carbon dioxide [21].

In this study the electrochemical and ozone methods were used to produce HO· radicals. In the case of electrochemical process the HO· radicals production takes place on the surface of electrodes. Boron doped diamond (BDD) electrodes have high anodic stability, a wide working potential window, and low stable voltammetric background current in aqueous media, which make them ideal for electrooxidation processes [22–25].

Certain parameters must be considered to have a successful process, among them the pH, current density, and the temperature. However, a previous study reported that an increase in temperature does not increase the rate of oxidation and the formation of oxidizing species different to HO· [20] was not observed.

On the other hand ozone has a high oxidation standard potential (E° 2.1 V) and a major advantage is that it does not produce secondary pollution, since it decomposes into oxygen. Ozone is unstable in water and undergoes reactions with some water matrix components. However, the unique feature of ozone is its decomposition into HO· radicals [26]. The ozonation process involves the direct reaction with organic and dissolved inorganic substances at low pH, but can also react indirectly due to radical decomposition HO· (primarily at high pH), which react immediately with solutes [27].

Nevertheless, the main drawback of this technology is the mass transfer limitations from pollutants contained in wastewater to the anode surface. In order to overcome this limitation, new research is required to improve the efficiencies attain by single treatment. In this way, the ozone provide HO· radicals in solution for the removal of organics. This technology combined with electrochemical treatment allows generating higher concentrations of free radicals in the system. Thus, the main aim of the study is to present the optimal conditions, in terms of aqueous pH and current density for Thiodan® removal when an integrated electrooxidation using BDD electrodes and ozone process are used. This process is an attractive alternative since HO· radicals are produced in high concentrations in water, thus maximizing reaction rate and eliminating sludge production.

2. Materials and methods

2.1. Chemicals

Endosulfan formulation is commercially available as Thiodan®, which contains not less than 33% of endosulfan (equivalent to 350 g/L Endosulfan) and not more than 67% of excipients, it was purchased from Bayer Crop Science.

Thiodan® solution was prepared to have an endoulfan initial concentration of 20 mg L^{-1}.

In most studies of pesticides degradation using this technology, a solution is prepared with a higher concentration than that found in surface or groundwater, although the mass transfer can be a limitation, it has been observed that the degradation of an organic compound with different concentrations presents the same trends over four ranges of concentration, without significant variations, indeed, Rodrigo and co-workers concluded that this behavior takes place and can be extrapolated from high to low concentrations [18].

All chemicals used in the experiments were analytical pure grade and used without further purification. pH of the solutions were adjusted by adding small amounts of diluted NaOH and H_2SO_4 solutions. Na_2SO_4 0.1 M was used as support electrolyte, it was purchased from Reasol.

2.2. Electrooxidation reactor

A batch cylindrical electrochemical reactor was set up for the electrochemical process. The reactor cell contains a pair of BDD

Table 1
Physico-chemical properties of α endosulfan, β endosulfan and endosulfan sulfate.

Properties	α-endosulfan	β-endosulfan	Endosulfan sulfate
Water solubility pH 5, 25 °C, mg/L	0.33	0.32	0.22
Henry constant atm m^3/mol. 25 °C	1×10^{-5}	1.91×10^{-5}	2.61×10^{-5}
Vapor pressure at 25 ° C mm Hg	1×10^{-5}	1×10^{-5}	1.0×10^{-11}
Log. octanol-water partition coefficient (Kow) pH 5.1	3.83	3.62	3.66
Log. octanol-air partition coefficient (Koa)	10.29	10.29	5.18
Log. octanol-carbon partition coefficient (Koc)	3.5	4.1	No data
Dissociation constant	No determined (without acid protons)	No determined (without acid protons)	No determined (without acid protons)
$T_{1/2}$ water (days)	25 y 128		123–391
LD_{50} rats (mg/kg)	76	240	160

electrodes (BDD film supported on a niobium substrate), each electrode was 20.0 cm by 2.5 cm with a surface area of 50 cm^2 and an electrodes gap of 1 cm [28–31]. Batch volumes of 0.750 L were treated in the 1.00 L reactor. A direct-current power source supplied the system with current densities of 20, 40 and 60 mA/cm^2. The process was evaluated at different pH values of 3, 5 and 7. Thiodan® solution was prepared to have an endoulfan initial concentration of 20 mg L^{-1}. All tests were conducted by triplicate.

2.3. Ozonation reactor

The ozone experiments were conducted in a 1.0 L up flow glass bubble column reactor and the treated reaction volume was 0.750 L. Ozone was supplied by a Pacific Ozone Technology generator. The ozone was fed into the reactor through a gas diffuser at the bottom of the reactor. The ozone was fed at a rate of 0.05 L min^{-1} using a gas diffuser of 0.2 mm pore size situated at the reactor bottom. The quantification of the ozone liquid phase was performed by indigo spectrophotometric method [32]. In acidic solution, ozone rapidly discolours indigo. The decrease in absorbance is proportional to the increased concentration and the proportionality constant is at 600 nm is 0.42 ± 0.01/cm/mg/L ($\Delta\varepsilon$ = 20000 μcm compared to the UV absorption of pure ozone ε = 2.90 μcm 258 nm). For determining the ozone to the ozone generator output, the calibration curve was constructed by preparing a stock solution with 770 mg of potassium thiosulfonate indigo and 1 mL of concentrated phosphoric acid and graduated to 1 L. An indigo reagent was prepared with 100 mL stock solution, 10 g NaH_2PO_4 and 7 ml of phosphoric acid to 1 L of solution. An ozonation process of deionized water was performed and samples were taken at specific time intervals. The concentration was calculated as shown in Eq. (1)

$$O_3 \text{ mg L}^{-1} = \frac{100\Delta A}{f \times b \times V} \quad (1)$$

where

ΔA: Absorbance t_0 - Absorbance t_1;
b: light path cuvette (1 cm);
V: Sample volume (9 mL);
f: factor (0.42).

It was found that the average amount of produced ozone was 5 mg L^{-1}.

The ozone that not reacts in the liquid phase gas conducted in tube pipe at the top of the reactor and decomposed by an ozone destructor Model No. d41202. The process was evaluated to different pH values 3, 5 and 7. Thiodan® solution was prepared to have an endoulfan initial concentration of 20 mg L^{-1}. All test were conducted by triplicate.

2.4. O_3-electrochemical coupled process

For the combined system the pair of BDD electrodes from the electrooxidation reactor was installed in the ozone reactor (Fig. 1). Thiodan® solution was prepared to have an endoulfan initial concentration of 20 mg L^{-1} in the supporting electrolyte, current density applied was 60 mA cm^{-2}, pH initial was 3, the volume was 0.750 L and the ozone concentration was 5 ± 0.5 mg L^{-1}. Treated samples were taken at the same intervals of time and were analyzed in the same way that the individual treatments. All test were conducted by triplicate.

2.5. Methods of analysis

Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) were determined using the American Publish Health Association [32], standard procedures, using a Hach DR 5000 and TOC-L Shimadzu Total Organic Carbon analyzer, respectively.

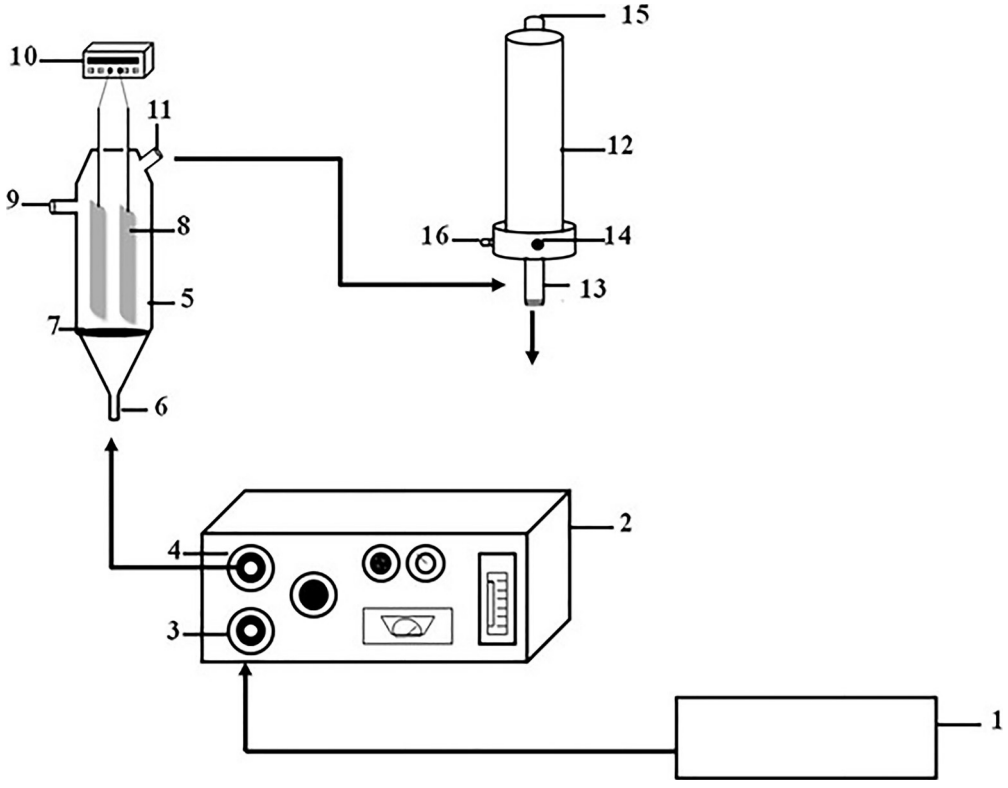


Fig. 1. Scheme of O_3-electrochemical coupled process. (1) Air generator, (2) ozone generator, (3) air input, (4) ozone generated output, (5) up-flow glass bubble reactor, (6) ozone input, (7) gas diffuser, (8) boron – doped diamond electrodes, (9) sample output, (10) power supply, (11) residual ozone output, (12) heated catalytic ozone destruct, (13) residual ozone input, (14) heater ON indicator light, (15) ozone destroyed output and (16) power connection.

Acute toxicity measurement was performed by MICROTOX®. This assay is a biosensor based on the luminescence inhibition of *Vibrio fischeri* (*Photobaterium phosphoreum*). The test were expressed as Effective Concentration 50% (EC_{50}) and were performed through standard MICROTOX® test (UNI EN ISO 11348-3), using a Model 500 analyzer and MicrotoxOmni software [33–35]. The Toxicity Unit (TU) was recommended and it was calculated as shown in Eq. (2)

$$TU = \left(\frac{1}{EC_{50}}\right)100\% \quad (2)$$

TU is unitless and it is relative toxicity classified into four categories: TU < 1 (non toxic), TU between 1 and 10 (toxic), TU between 10 and 100 (very toxic) and TU > 100 (extremely toxic) [36].

The cyclic voltammetry of Thiodan® solution at different times of coupled treatment were performed using a standard three-electrode cell. The wareforms were generated by Autolab AUT 83582, software GPES Manager version 4.9. A carbon paste electrode used as working electrode, the superface of electrode was renewed through light polishing after each potential scan. The scan rate was 100 mV s^{-1} with an Ag/AgCl reference electrode and platinum counter electrode. The cyclic voltammetry was obtained by starting the potential scan in the positive direction.

The COD removal efficiency (%) at the different processes was calculated as shown in Eq. (3).

$$E = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

where E is the COD removal efficiency (%), C_0 is the initial value of the COD (mg L^{-1}) in the Thiodan® solution and C_t is the value of COD (mg L^{-1}) at time *t* after the different processes.

3. Results and discussion

3.1. Electrooxidation treatment

3.1.1. Effect of pH

Fig. 2 shows the effect of pH on the initial electrodegradation of Thiodan®. As can be observed the initial pH in the aqueous solution has no significant effect on the amount of the COD removal. The COD decrease in 67%, 61% and 60% for pH 3, 5 and 7, respectively.

As a consequence of the high oxidation power of the BDD anode, commonly the mineralization process is independent of the nature of the organic species being degraded, in this way, contrasting our results with a previous report in which picloram was used, it was noticed that a similar independence of pH behavior is obtained, indeed they conclude that the pH of the solution had not significant effect on pollutant removal rate [37]. Brillas et al. demonstrated that is possible obtain the complete mineralization of compounds such as pesticides and drugs with the anodic oxidation with BDD. Their experiments demonstrated that the removal of pollutants is practically pH-independent, but depend on the pesticides concentration and current density. They reported that persistent organic compounds are mainly destroyed by reaction with HO· produced at BDD surface [38].

In the case of endosulfan molecule, it has not a pK_a value, in all pH interval, the same molecule is present. The pH effect was studied for evaluated the generation of OH·. The adsorbed OH· generated on the electrode surface by water oxidation of a high O_2-overvaltage at acid media, it describe in Eq. (4) [31,39]:

$$H_2O \rightarrow {\cdot}OH_{ads} + H^+ + e^- \quad (4)$$

or hydroxide ion at pH ⩾ 10, Eq. (5)

$$OH^- \rightarrow {\cdot}OH_{ads} + e^- \quad (5)$$

The results suggest that at pH values studied there is no variation in the generation of hydroxyl radicals.

3.1.2. Effect of current density

Different current densities were applied to investigate this effect on the electrochemical degradation of Thiodan® (endosulfan 20 mg L^{-1}) in Na_2SO_4 0.1 M. Fig. 3 shows that the COD removal increases as a function of electrolysis time and the removal rate increased when the applied current density is raised. The COD removal after 100 min of electrolysis was 67%, 92% and 97% for 20 mA cm^{-2}, 40 mA cm^{-2} and 60 mA cm^{-2}, respectively. The results indicated that current density is a key parameter on the COD removal.

The same effect was observed by Solano et al., they reported the degradation of organic material from real textil industrial effluent by electrooxidation BDD at the same current densities used in this study (20, 40 and 60 mA cm^{-2}), they noticed that the color removal efficiency significantly increased as a function of current density [40].

Panniza and co-workers reported that increasing the current density increases the removal rate. They mention that the current density is an important parameter because the BDD can oxidize organic compounds in the potential region of water discharge, in this zone the hydroxyl radicals are generated. At a potential lower than the water discharge, it is produced a deactivation of anode surface with a deposition of a polymeric film. In their study they

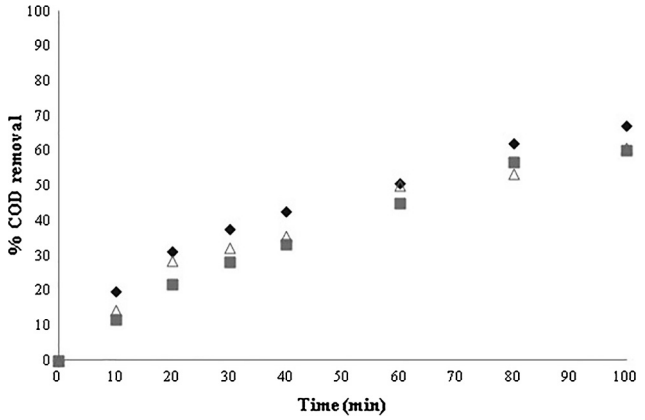


Fig. 2. Effect of pH (◆) pH 3, (■) pH 5 and (Δ) pH 7 on the % COD removal as a function of electrolysis time (min). Electrolysis conditions: 20 mA cm^{-2}, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M.

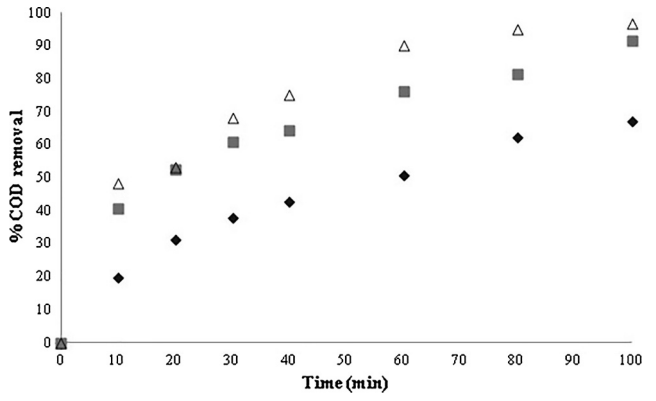


Fig. 3. Effect of current density (◆) 20 mA cm^{-2}, (■) 40 mA cm^{-2} and (Δ) 60 mA cm^{-2} on the % COD removal as a function of electrolysis time (min). Electrolysis conditions: pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M.

observed that increasing the current density increases the removal rate, due to higher generation of hydroxyl radicals [41].

3.1.3. Kinetics of degradation

The COD removal rate of pesticides can be represented by the following linear- pseudo - first – order Eq. (6) as described by Errami et al. [23]

$$\frac{d[COD_0]}{d[COD_t]} = kt \tag{6}$$

The integrated form is Eq. (7):

$$Ln\frac{COD_0}{COD_t} = kt \tag{7}$$

where COD_0 and COD_t are the COD of the solution at the beginning and at time t respectively, and k is the observed pseudo first-order rate constant. Rate constants can be determined by plotting the Ln (COD_0/COD_t) against time at different applied current density as shown in Fig. 4.

The electrodegradation rate depends on the current density, this suggests a greater oxidation ability of BDD anode increasing the current density applied due to the production of more electro-generated active oxidant ·OH [39].

In the oxidative process at BDD several series/parallel steps may be involved, the first process takes place at the electrode surface when organic compounds are oxidized directly, the second process occurs at the same time, with the generation of hydroxyl radicals by decomposition of water molecules, which are able to oxidize the organic compounds, this process can occur in either one stage or multiple stages, and it proceeds until the final oxidation product is generated (usually carbon dioxide). The third process due to hydroxyl radicals is not stable, the formation of other oxidants (ozone, hydrogen peroxide, peroxodisulphate, chlorine, etc.) is possible, which can in turn react chemically with the organic matter through mediated oxidation processes or, alternatively, can promote the formation of oxygen. If these oxidant compounds reach the bulk zone, it is necessary to take into account their mass transfer process and the oxidation of the organics in the bulk zone [20,42].

Table 2 shows the effect of the current density on the values of the rate constant for COD removal.

It is interesting to note that the process can be faster (three times) when the current density used is 60 mA cm^{-2}.

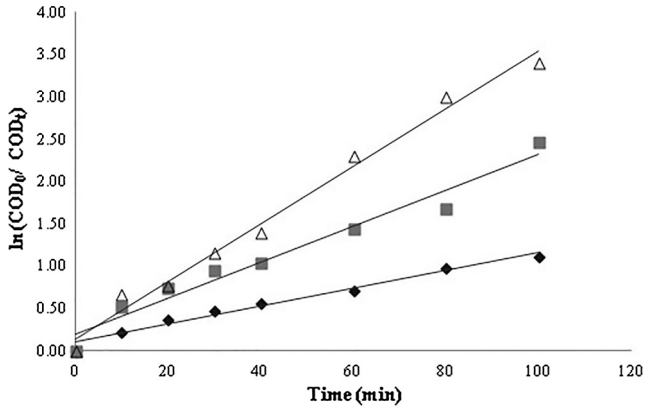


Fig. 4. Kinetic of % COD removal of Thiodan® solution at different applied current density (◆) 20 mA cm^{-2}, (■) 40 mA cm^{-2} and (Δ) 60 mA cm^{-2}. Electrolysis conditions: pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M.

Table 2
Rate constant for COD removal at different applied currents density.

pH	Current density (mA cm^{-2})	Rate constant (min^{-1})	R^2
3	20	0.0106	0.9781
	40	0.0212	0.9636
	60	0.0341	0.9880

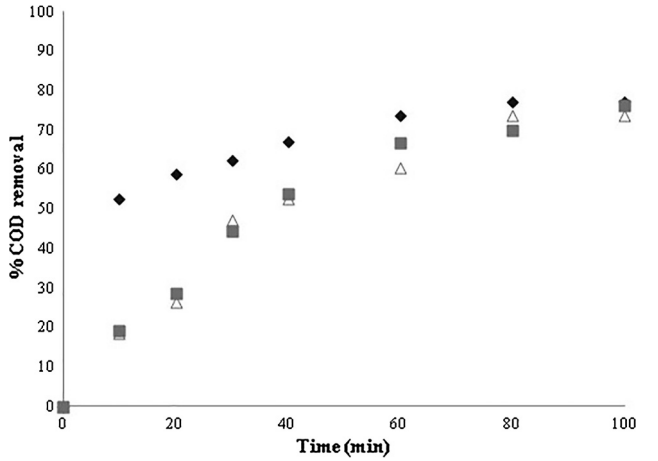


Fig. 5. Effect of pH (◆) pH 3, (■) pH 5 and (Δ) pH 7 on the % COD removal from the solution as a function of ozonation time (min). Ozonation conditions: ozone concentration 5 ± 0.5 mg L^{-1}, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.750 L.

3.2. Ozonation treatment

During the ozonation treatment of the endosulfan solution, the COD was monitored as a function of treatment time. As shown in Fig. 5 COD reduction was 77%, 76% and 74% for pH 3, 5 and 7, respectively after 100 min of treatment time. Note that, no significant difference between pH 3, 5 and 7 is observed.

A previous study, reported that, during the degradation of aqueous solution of alpha endosulfan by ozonation there are not significant differences between pH 4–7 and the highest oxidation rate (94% removal) was obtained at pH 4 [43]. Conversely, in a study conducted by Begum and Gautam [44] the effect of initial pH was studied, they found that a 99% degradation of endosulfan was observed at pH 12.

As earlier discussed, the pH reaction plays an important role in the degradation of pollutants using ozonation. At low pH, the predominant reaction mechanism is the direct electrophilic attack by molecular ozone. At high pH, ozone decomposes in water to form HO· radicals which are stronger oxidizing agents than molecular ozone, thus inducing the so-called indirect ozonation. Indirect ozone oxidation is non-selective, faster and is favored under alkaline conditions. Both reaction mechanisms lead either to mineralization or to transformation of organics by formation of products with higher oxygen content [45].

With data obtained in this study from the degradation of Thiodan® by ozonation at pH 7 and lower values, it can be concluded that the oxidation of Thiodan® is conducted mainly by direct reaction of ozone.

3.2.1. Kinetics of degradation

Fig. 6 shows the COD removal rate of pesticides which can be represented by the following linear- pseudo - first – order (Eq. (7)).

The observed rate constant values for the set of kinetics performed indicating that the highest rate constant was observed at pH 7. Table 3 shows the effect of the pH value on the rate constant for COD removal.

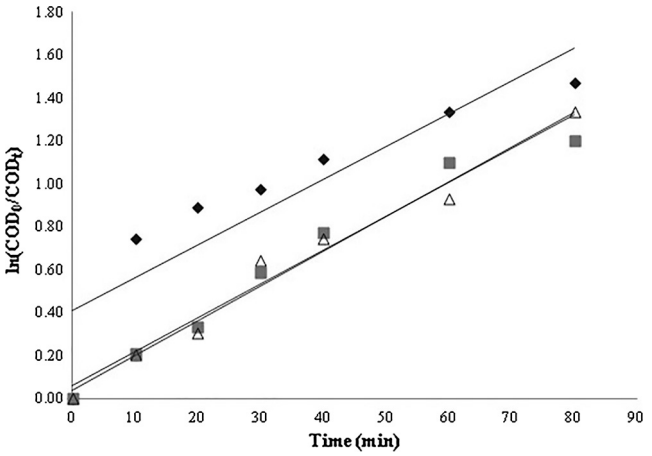


Fig. 6. Kinetic of COD removal of Thiodan® solution (endosulfan) at (◆) pH 3, (■) pH 5 and (Δ) pH 7 at ozonation treatment. Ozonation conditions: ozone concentration 5 ± 0.5 mg L^{-1}, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.750 L.

Table 3
Rate constant for COD removal at different pH values.

O_3 concentration	pH	Rate constant k (min^{-1})	R^2
5 ± 0.5 mg L^{-1}	3	0.0153	0.801
	5	0.0157	0.968
	7	0.0162	0.978

Enjarlis et al. showed that pesticides degradation by ozonation followed a pseudo first order kinetic, with similar values as reported in Table 2 [46]. As a selective oxidant, O_3 reacts rapidly with organic compounds containing electron rich functional groups, such as phenols, amines, olefins, activated aromatic compounds and sulfur containing compounds. Therefore, micropollutants containing can be eliminated efficiently during ozonation [47,48].

3.3. Electrochemical - O_3 coupled process

Fig. 7 shows the effect of coupling electrooxidation and ozonation processes in the COD and TOC reduction as a function of treatment time for Thiodan® aqueous solution. After 40 min of treatment, the % COD removal was 89% and % TOC removal was 94%. The results suggest that the coupled process not only reduces to Thiodan®, also mineralizes it.

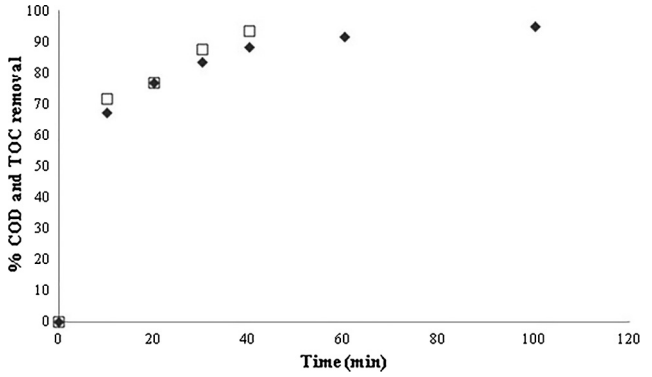


Fig. 7. % COD (◆) and % TOC removal (□) as a function of coupled treatment time. Electrolysis conditions: pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M and Ozonation conditions: ozone concentration 5 ± 0.5 mg L^{-1}, 20 mg L^{-1} of endosulfan solution (Thiodan®).

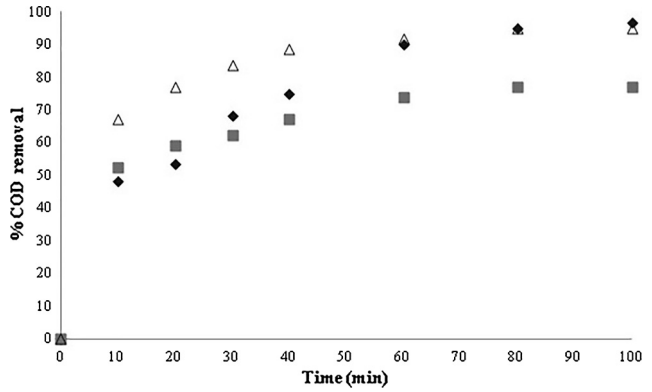


Fig. 8. % Removal of COD treatment function of time for three different processes (◆) Electrooxidation, Electrolysis conditions: pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M and 60 mA cm^{-2}, (■) Ozonation, Ozonation conditions: ozone concentration 5 ± 0.5 mg L^{-1}, 20 mg L^{-1} of endosulfan solution (Thiodan®), and (Δ) Coupled, Electrolysis conditions: pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M and 60 mA cm^{-2}, Ozonation, Ozonation conditions: ozone concentration 5 ± 0.5 mg L^{-1}, 20 mg L^{-1} of endosulfan solution (Thiodan®).

Fig. 8 shows a comparative graph of % COD removal as a function of treatment time for three treatments. After 100 min of reaction, a 95% of COD is achieved when the coupled process is used. Similar removal, about 97%, can be achieved when the electrochemical process is used, but 50% more process time is required. For ozonation process the maximum reduction is only about 77%. These results show that the coupled process degrades faster the Thiodan® present in aqueous solution.

3.4. MICROTOX® analysis

The use of the Microtox® test has many advantages, such as: rapid exposure (15 min), only requires a small volume of sample, various sample types and testing matrices and it is accepted worldwide as an effective toxicity test.

The Microtox® test was performed for sample of Thiodan® with an endosulfan concentration of 2.5 mg L^{-1} without treatment, the result of EC_{50} was 9.62% and TU was 10. This result indicates that the sample with a lower concentration that the concentration evaluated in each treatment, is toxic. For electrochemical process sample the EC_{50} could not be determined with dilutions established on regulation because after 30 min of reaction time, the sample showed a high toxic effect; conditions were the electrooxidation pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M and current density 60 mA cm^{-2}. On the other hand, ozonation process sample, the EC_{50} was 7.46% and TU was 13, in this case the sample was classified as very toxic, the ozonationation conditions were ozone concentration 5 ± 0.5 mg L^{-1}, pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), solution volume 0.75 L, However, when the coupled electrochemical - O_3 process sample was analyzed, it did not show toxicity, the conditions in the process were pH 3, 20 mg L^{-1} of endosulfan solution (Thiodan®), 0.75 L, Na_2SO_4 0.1 M, current density 60 mA cm^{-2} and ozone concentration 5 ± 0.5 mg L^{-1}. It is important to remember that the Thiodan® solution had an endosulfan concentration initial of 20 mg L^{-1} for each treatment. Thus, the combined process not only reduces COD and TOC, it also gives a toxicity free solution, which makes it a clean technology.

3.5. Cyclic voltammetry

Fig. 9 shows the voltammograms of Thiodan® solution prior and after the application of the coupled treatment. As can be observed,

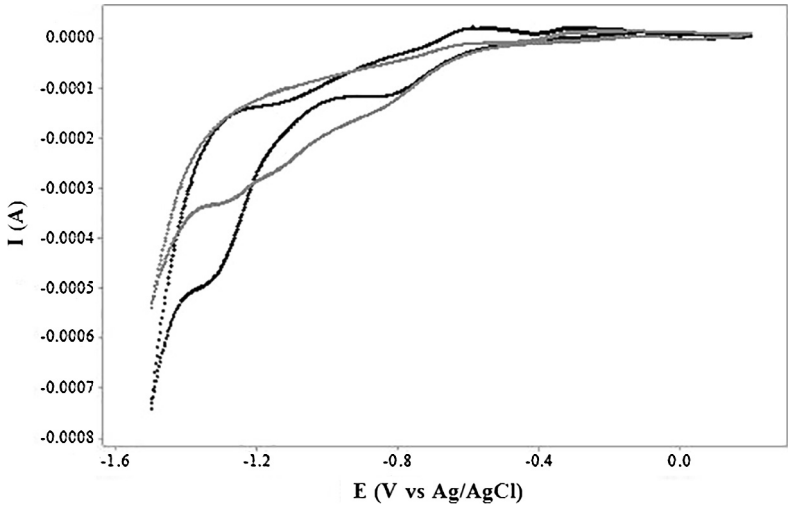


Fig. 9. Cyclic voltammograms of Thiodan® solution at a scan rate of 100 mV s^{-1} (•) before and (•) after coupled process.

these results show a peak oxidation in the Thiodan® solution without treatment. It should be noted after 30 min of reaction with the coupled treatment, the oxidation peak disappears.

Gurumalleshá Prabu et al. studied a determination of endosulfan by voltammetry, in conditions similar to those used in this study. They found than endosulfan shows an anodic plateau and the cyclic voltammogram is similar to that obtained by us [49].

4. Conclusions

The efficiency of an electrochemical, ozonation and couple system was tested on the Thiodan® oxidation reaction. Among the studied variables, it can be concluded that the initial pH of Thiodan® solution does not significantly affect the percentage of COD removal when either electrooxidation or ozonation process is applied. Nevertheless, in both cases the highest removal percentage was achieved at pH 3. The applied current density increases the COD removal rate in the electrochemical oxidation process. The highest removal percentage was achieved at 60 mA cm^{-2}. The coupled process Electrooxidation-O_3 increases the effectiveness in the removal of COD as compared with electrooxidation and ozonation treatments. In the case of TOC removal, the coupled process showed a considerable decrease after 40 min of treatment time. This result is consistent with the cyclic voltammogram obtained. Another advantage that showed the coupled process is that after 30 min of reaction the solution does not show toxicity, this is due to the mineralization of Thiodan® and possible degradation products generated during the coupled process as evidenced by the TOC. Finally, the comparison of the here reported results allows to conclude that the Electrooxidation - O_3 coupled process is advantageous compared with any single processes for Thiodan® degradation.

Acknowledgements

The authors wish to acknowledge the support given by the Centro Conjunto de Investigación en Química Sustentable, UAEM-UNAM, Centro Interamericano de Recursos del Agua UAEM, MCA Ana Elisa Alcántara Valladolid are gratefully acknowledged for granting access to apparatus needed of MICROTOX® test and financial support from the CONACYT through the project 153828 is greatly appreciated.

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