



Solar photocatalytical treatment of carbofuran at lab and pilot scale: Effect of classical parameters, evaluation of the toxicity and analysis of organic by-products

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ABSTRACT

In this work the TiO₂ solar-photocatalytical degradation of the pesticide carbofuran (CBF) in water, at lab and pilot scale, was studied. At lab scale the evaluation of CBF concentration (14–282 μmol L⁻¹) showed that the system followed a Langmuir–Hinshelwood kinetics type. TiO₂ concentration (0.05–2 g L⁻¹) and initial pH (3–9) were also evaluated and optimized using the surface response methodology and the Pareto diagram. In the range of variables studied, initial pH 7.60 and 1.43 g L⁻¹ of TiO₂ favoured the efficiency of the process. Under optimal conditions the evolution of substrate, chemical oxygen demand, dissolved organic carbon, toxicity and organics by-products were evaluated. In the pilot scale tests, using direct sunlight, 55 mg L⁻¹ of CBF in a commercial formulation was eliminated after 420 min; while after 900 min of treatment 80% of toxicity (1/E₅₀ on *Vibrium Fischeri*), 80% of chemical oxygen demand and 60% of dissolved organic carbon were removed. The analysis and evolution of five CBF by-products, as well the evaluation of the treatment in the presence of isopropanol or using acetonitrile as a solvent suggest that the degradation is mainly carried out by •OH radical attack. Finally, a schema depicting the main degradation pathway is proposed.

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1. Introduction

Pesticide residues reach the aquatic environment through manufacturing plants, direct surface run-off, leaching, careless disposal of empty containers, equipment washings, etc. In the world, alarming levels of pesticides have been reported to be persistent, toxic, mutagenic, carcinogenic and tumorigenic. Due to their high toxicity, biological treatment of agro-industrial effluents is often perturbed and sometimes blocked.

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl-carbamate), a pesticide widely used in agriculture as an insecticide, is highly toxic (DL₅₀ 11 mg kg⁻¹ in mice) and an inhibitor of acetylcholinesterase, an enzyme vital to the functioning of the central nervous system [1]. Its implications as a potential endocrine disruptor have also been proved [2].

Carbofuran (CBF) has a high mobility in soils and is highly soluble in water (700 mg L⁻¹) [1]. Recently, the presence of this harmful chemical, in natural waters, has been reported [3]. There-

fore, the search of effective alternatives for CBF degradation is a need.

Physicochemical methods based on the production and use of hydroxyl radicals called advanced oxidation processes (AOPs) have been successfully tested for the elimination of organic compounds [4–7]. Because of its low cost and high effectiveness, heterogeneous photocatalysis is maybe the most promissory advanced oxidation processes and consequently, has been the subject of numerous studies [8,9]. This process uses UV light ($\lambda \leq 387$ nm) to excite the TiO₂ catalyst and to produce an electron–hole pair. Organic compounds may undergo oxidation directly at the hole. The hole can also undergo charge transfer with adsorbed water molecules or with hydroxide surface-bound species, forming •OH radicals,

Several papers have addressed the TiO₂ photocatalytical treatment of carbofuran. Kuo et al. [10] and Tennakone et al. [11], investigated the photocatalytical degradation of carbofuran using immobilized TiO₂. Kuo [12] and Mahalakshmi et al. [13], by using a medium-pressure mercury vapor lamp and a 254 nm UV lamp, respectively, in batch reactors, evaluated the effect of some classical parameters. These studies have confirmed the potentialities of the TiO₂ photocatalyst to obtain the complete mineralization of the pollutant. In recent years, the TiO₂ photocatalyst has gained interest because solar light can be used as a radiation source. It is a useful approach for regions with a high degree of sunlight radiation. However, few studies have tested the photocatalytical degradation

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of the pesticide under solar irradiation and, to our knowledge, no investigations at pilot scale have been carried out. Thus, to contribute to the actual application of this technology, the main goal of this work was to evaluate the photocatalytic degradation of carbofuran, under solar irradiation at lab and pilot scale. Additionally, the initial pH, TiO_2 concentration and pesticide concentration, under solar simulated radiation, were studied. In order to investigate the initial degradation pathway, experiments in the presence of isopropanol and acetonitrile, and an analysis of the generated by-products, were also investigated.

2. Experimental

2.1. Reagents

Titanium dioxide, with a surface area of $50 \text{ m}^2 \text{ g}^{-1}$ (size $\sim 20\text{--}30 \text{ nm}$), was purchased from Degussa AG. CBF (99.5%) was supplied by Ehrenstorfer GmbH, whereas the commercial grade Furadan, with a formulation of 330 g L^{-1} of CBF, was supplied by Bayer. Acetonitrile, dichloromethane, sodium hydroxide, sulphuric acid and ethyl acetate were supplied by Merck; while the potassium hydrogen phthalate was obtained from Carlo Erba. All chemicals were used without any further purification. Milli-Q water was used throughout for the preparation of aqueous solutions.

2.2. Experimental design

In order to evaluate and optimize the initial pH (3–9) and the catalyst concentration ($0.05\text{--}2 \text{ g L}^{-1}$), multivariate analysis and factorial design were carried out using the Statgraphics Plus 5.1 software, thereby obtaining the polynomial associated with the reaction, the response surface and the Pareto diagram.

The study was performed with a confidence level of 95%. The degradation percentage of the CBF after 60 min of irradiation was chosen as the response factor.

2.3. Photolytic and photocatalytic systems

Preliminary experiments performed until 24 h under constant magnetic stirring indicated that under all the conditions tested, equilibrium was reached after 20 min. Thus, after adjusting the solution of CBF from pH 5.6 (natural pH) to the desired initial pH condition, the photocatalyst was added at the appropriate concentration and the resulting mixture was stirred in the dark for 20 min in order to reach the adsorption–desorption equilibrium between the substrate and catalyst.

Laboratory scale tests were carried out under constant magnetic stirring in a beaker containing 50 mL of CBF solution. The beaker containing the solution was introduced into a suntest CPS + reactor, and irradiated from the top using a xenon lamp (350 W m^{-2}) to simulate solar radiation. Degradation testing of commercial CBF was carried out at pilot scale in a solar collector of three modules, each with 8 Pyrex glass tubes joined together with PVC connections. Each module, with a working volume of 18 L, was fed from a storage tank with a total volume of 127 L. Water with the pesticide and TiO_2 was recirculated (at 1.6 L s^{-1}) through the glass tubes using a pump (Siemens). The average radiation intensity during the day of the experiment was 390 W m^{-2} . Additional details of the solar collector used were reported previously [14].

2.4. Analysis

During the photocatalytic treatment, aliquots were taken at specific time intervals and analyzed after filtration with filters of $0.45 \text{ }\mu\text{m}$ PVDF Millipore Millex[®]-HV to remove TiO_2 particles.

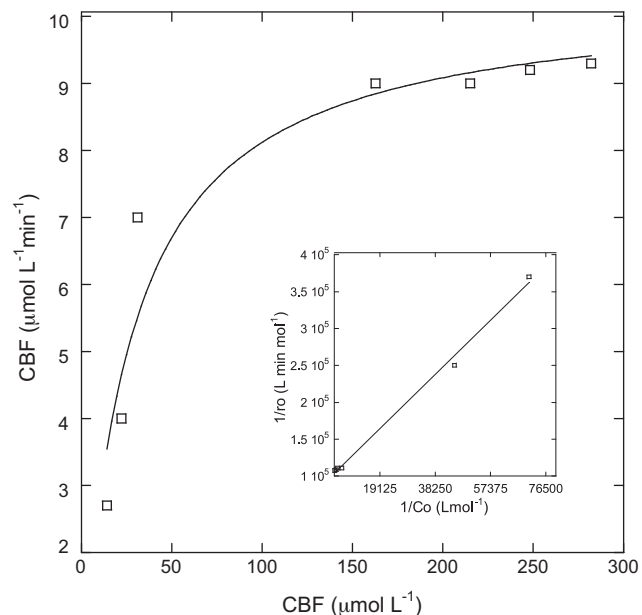


Fig. 1. Effect of initial concentration of carbofuran on the photocatalytic process after 10 min of treatment at initial pH 7.60 and 1.43 g L^{-1} of TiO_2 . The inset indicates the data adjusted to the Langmuir kinetics type.

The evolution of CBF concentration was performed by liquid chromatography (HPLC) in an Agilent 1100 Series instrument. A Zorbax SB C18 column and a diode array UV detector set at 220 nm were used. The mobil phase, 40/60 acetonitrile/water, was run in isocratic mode at 1 mL min^{-1} .

CBF by-products were concentrated by liquid–liquid extraction and subsequently analyzed by GC-MS in an Agilent 7890 coupled with a 5975C mass detector. A Zebtron column and helium as the carrier gas were used. The oven temperature was programmed as follows: after 80°C for 5 min, it was increased from 80 to 210°C at $10^\circ \text{C min}^{-1}$, then increased from 210 to 310°C at a speed of $30^\circ \text{C min}^{-1}$ and finally kept at 310°C for 5 min. The injector temperature and the interface were maintained at 220 and 250°C , respectively. The mass spectrum was obtained by electron impact at 70 eV using the full-scan mode.

To confirm mineralization, i.e. the transformation of organic matter into CO_2 , H_2O and inorganic ions, the dissolved organic carbon (DOC) was quantified in a COT1010 OI-Analytical instrument. A solution of potassium phthalate was used as the calibration standard. Chemical oxygen demand (COD) measurements were carried out according to the closed reflux titrimetric method [15] in a Nanocolor 500D instrument.

The toxicity of the treated solutions was determined by measuring the EC_{50} on *Vibrio Fisheri* with a Biofix[®] Lumi-10 instrument.

3. Results and discussion

3.1. Effect of the initial carbofuran concentration in the photocatalytic reaction

Fig. 1 shows the initial photocatalytic decomposition rate of CBF in the suntest reactor during the first 10 min of treatment at various concentrations ranging between 14 and $282 \text{ }\mu\text{mol L}^{-1}$. The curve indicates that the higher the substrate concentration, the higher the initial decomposition rate. CBF at 22 and $31 \text{ }\mu\text{mol L}^{-1}$ was degraded at 4.0 and $7.0 \text{ }\mu\text{mol L}^{-1} \text{ min}^{-1}$, respectively. In spite of this, there is not much difference observed in the degradation rate of CBF when increasing the concentrations from 215 to $282 \text{ }\mu\text{mol L}^{-1}$ (degradation rates 9.0 and $9.3 \text{ }\mu\text{mol L}^{-1} \text{ min}^{-1}$

Table 1

Experimental design for carbofuran degradation by TiO₂ photocatalysis and comparison between experimental data and calculated from the reduced model.

Test	Initial pH	TiO ₂	CBF experimental (%)	CBF calculated (%)
1	3.00	0.050	29.06	37.99
2	9.00	0.050	70.88	62.71
3	3.00	2.000	66.21	68.64
4	9.00	2.000	82.96	93.36
5	3.00	1.025	70.00	70.08
6	6.00	0.050	51.18	50.35
7	6.00	2.000	93.93	81.00
8	6.00	1.025	86.11	82.44
9	6.00	1.025	83.98	82.44
10	6.00	1.025	86.60	82.44
11	9.00	1.025	85.66	94.80

respectively). Thus, a linear relationship is not observed as expected for a first order kinetic law. Several reports have established that the TiO₂ photocatalysis degradation rate fits well to the classic Langmuir–Hinshelwood (L–H) mechanism [16–18]. The linearized L–H equation can be represented as follow:

$$\frac{1}{r_0} = \frac{1}{(k_{LH}K_L C_0)} + \frac{1}{k_{LH}} \quad (1)$$

In the L–H model (Eq. (1)), k_{LH} represents the apparent L–H rate, K_L is the adsorption/desorption equilibrium constant and C_0 is the initial concentration in equilibrium [19]. The linearized results shown in the inset of Fig. 1, indicate a very good correlation with the kinetic model ($r^2 > 0.99$). The values of k_{LH} and K_L obtained were $1.1 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$ and $2.4 \times 10^4 \text{ L mol}^{-1}$ respectively, which are in accordance with previous values reported for photocatalytic degradation of organic pollutants [20,21]. In spite of the good correlation achieved, several studies are against the use of the L–H model as it is still a subject of debate [20]. Such LH constants have very little, if any, physical meaning, and consequently, the simple LH kinetic model that theoretically describes very nicely the kinetic data (reaction rates) of surface processes in a heterogeneous system can be a deceptive, delusory model [18]. Thus, the degradation percentage was preferred and considered in this work as the response variable to evaluate the effect of the catalyst concentration and initial pH during the photocatalytic treatment of CBF.

3.2. Effect of catalyst concentration and initial pH during the photocatalytic degradation of carbofuran

The initial pH of the solution and the catalyst concentration are two of the most important parameters in the evaluation of photocatalytic reactions [22,23]. In order to evaluate the influence of these two parameters on the photocatalytic degradation of carbofuran, a factorial design was implemented using the Statgraphics Plus 5.1 software. Factorial design has become an important tool for obtaining valuable and statistically significant models of a phenomenon by doing a minimum set of well chosen experiments. With a determined number of assays, information can be obtained regarding the importance of each variable and their interaction effects [24,25]. Table 1 shows the matrix design obtained by the computer program. The table shows the conditions and the response factor for each experiment, defined as the percentage of degradation after 60 min of treatment. Experiments were carried out by using $250 \mu\text{mol L}^{-1}$ (55 mg L^{-1}) CBF aqueous solutions in order to maximize the degradation rate of the process (Fig. 1). It is important to indicate that during the experiments pH changes were practically insignificant. Fig. 2 shows the response surface diagram obtained. As shown in Fig. 2 and Table 1, the percentage of degradation initially increases by increasing the TiO₂ concentration. This behavior is explained by the increase in the number of active sites as

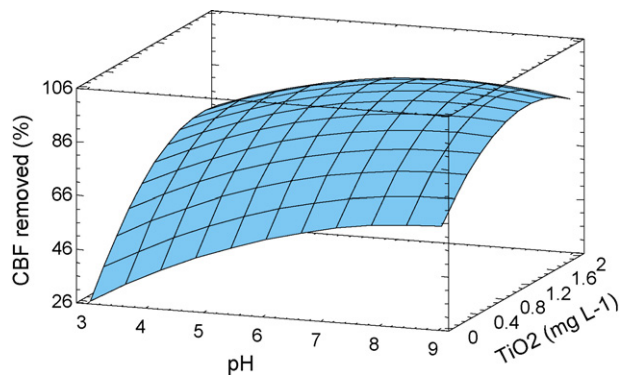


Fig. 2. Optimization of TiO₂ load and initial pH for photocatalytic degradation of CBF (55 mg L^{-1}) using a response surface diagram. Three-dimensional representation for the degradation percentage after 60 min of irradiation.

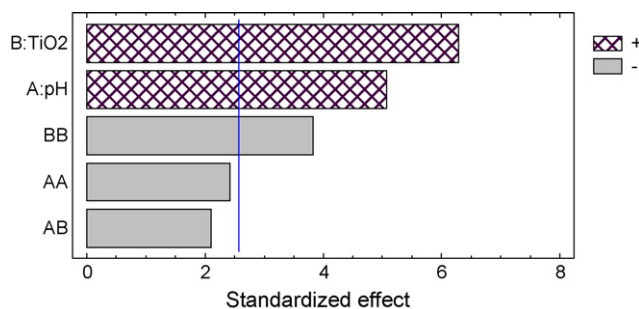


Fig. 3. Pareto diagram for the photocatalytic degradation of carbofuran with TiO₂. Figure obtained with the Statgraphics Plus 5.1 software according to the design of experiments presented in Table 1.

a result of an increasing dosage of catalyst [26]. However, when the catalyst concentration increases above 1.43 g L^{-1} , a negative effect is observed. This unfavorable effect could be due to light scattering and the reduction of light penetration at a relatively high catalyst loading [27,28].

Fig. 2 also indicates that the initial pH of the solution affects the efficiency of the process. At relatively low pH values, CBF might be protonated at the nitrogen or at the carbonyl oxygen of the carbamate group. Such protonation could provoke repulsion between the substrate and catalyst (pzc 6.8 [29]). Therefore, as the initial pH increases, from 3 to ~ 7.60 the CBF degradation also increases. Higher initial pH values produce a practical insignificant effect. Thus, the photocatalytic treatment can be successfully carried out under initial slightly basic pH values.

3.3. Optimization of the photocatalytic CBF degradation

To optimize the process, it is necessary to evaluate which variables, and interactions between these variables, significantly affect the photocatalytic process. The Pareto diagram (Fig. 3) represents a valuable tool to evaluate this. The Pareto diagram shows both the magnitude and the significance of effects (variables and interactions). On the Pareto chart there is a reference line (the solid vertical line), and any effect that surpasses this line is potentially important [25]. On the figure the signs “+” and “-” represent positive and negative effects of the variable (or interaction) on the degradation of carbofuran. A positive effect of a variable indicates that the CBF degradation increases to high values of the respective variable, while a negative effect indicates that the degradation of CBF increases at low values of the variable. Positive quadratic order polynomial coefficients indicate a synergistic effect, while negative coefficients indicate an antagonistic effect between or among

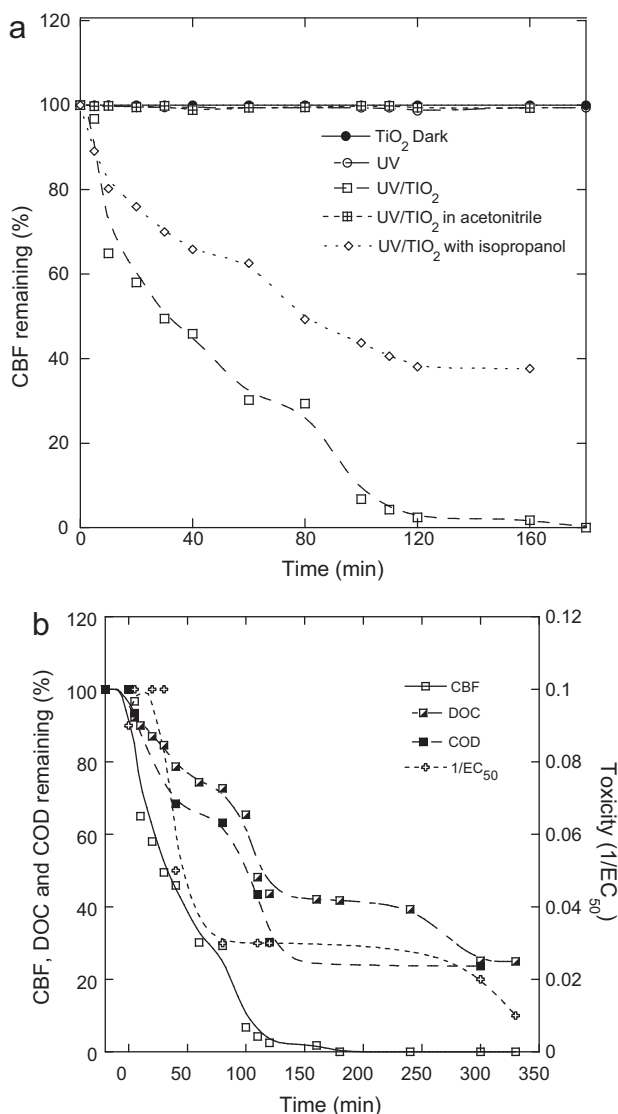


Fig. 4. Photocatalytic treatment of carbofuran (55 mg L^{-1}) at initial pH 7.60 and 1.43 g L^{-1} of TiO_2 . (a) Profile of carbofuran as a function of time under the action of UV light, TiO_2 , UV/ TiO_2 , UV/ TiO_2 in acetonitrile and UV/ TiO_2 with isopropanol (25 mmol L^{-1}). (b) Evolution of substrate, dissolved organic carbon, chemical oxygen demand and toxicity during the photocatalytic treatment.

the variables. Thus, Fig. 3 shows that the variables and interactions that can be considered particularly important for treatment are the concentration of the catalyst (B), initial pH (A), and the square of the concentration of the catalyst (BB). Additionally, the Pareto diagram shows that while the TiO_2 concentration and initial pH have a positive effect on the photocatalytic process, the quadratic term of catalyst load has a negative effect, thereby confirming the results shown in Fig. 2.

The experimental design methodology leads to obtaining a reduced model that directly relates the influential variables and interactions with the response factor (% degradation), thereby facilitating the study of the pollutant degradation.

After multiple regressions using the statistical software the following reduced model, where Y (%) represents the degradation percentage of CBF, was obtained:

$$Y(\%) = 23.08 + 51.88 [\text{TiO}_2] + 4.12 [\text{pH}] - 17.64 [\text{TiO}_2]^2 \quad (2)$$

The negative quadratic factor of the catalyst load in the polynomial expression corroborates the fact that the optimal catalyst concentration is an intermediate value (around 1.4 g L^{-1}). Very high

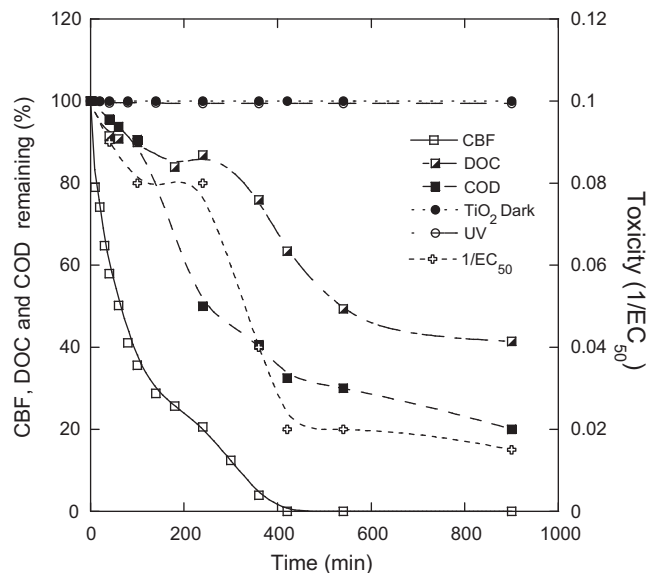


Fig. 5. Photocatalytic treatment of a commercial formulation of carbofuran (Furadan) in the solar collector. Initial pH 7.60, 1.43 g L^{-1} of TiO_2 and 55 mg L^{-1} of CBF.

or very low values of TiO_2 concentration are detrimental to the CBF degradation. Similar dependence of catalyst load has been reported for the photocatalytic degradation of antibiotics in water [20,33]. Table 1 shows the comparison between experimental results and those predicted by the model (Eq. (2)). As shown in Table 1, the proposed model predicts the experimental results quite accurately. Additionally, R^2 , the fraction of the response variation explained by the model, was 85%. These results verify the validity of the model.

According to the response surface diagram (Fig. 2) and Eq. (2), under the work conditions, initial pH 7.60 and 1.43 g L^{-1} of TiO_2 are the optimal values for the photocatalytic degradation of the pesticide CBF.

3.4. Characteristics of photocatalytic degradation of carbofuran under optimal conditions

In a new set of experiments, the photocatalytic degradation of CBF (55 mg L^{-1}) was conducted under optimal conditions (1.43 g L^{-1} of TiO_2 and initial pH 7.60). The degradation profile of CBF is shown in Fig. 4a. From this figure it is possible to see that

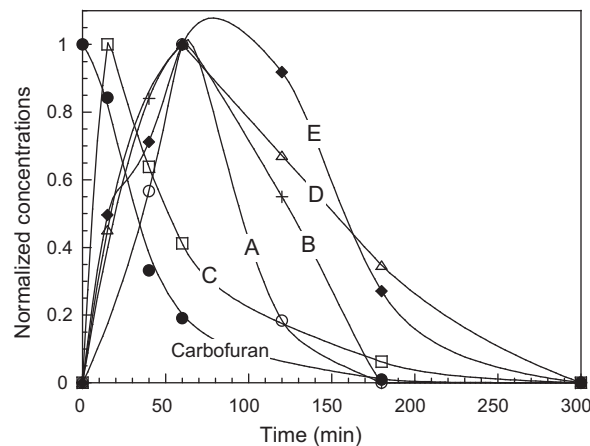
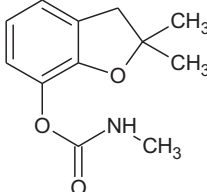
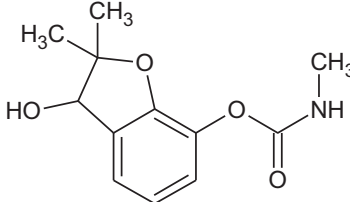
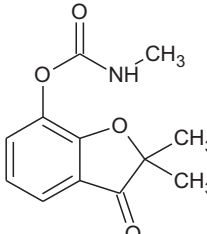
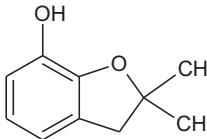
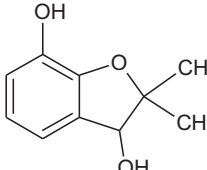
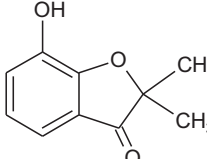


Fig. 6. Evolution of normalized concentrations of carbofuran by-products during the TiO_2 photocatalysis under optimized conditions in the sunstest reactor: initial pH 7.60 and 1.43 g L^{-1} .

Table 2
Main carbofuran intermediates formed by TiO₂ photocatalysis and identified by GC–MS.

Compound	Structure	Molecular weight (m/z)	Retention time (min)
CBF		221	17.60
A		237	18.98
B		235	18.46
C		164	11.82
D		180	13.10
E		178	14.08

the adsorption of pesticide on the catalyst surface, under dark conditions, is almost negligible (~1%). Furthermore, the CBF shows a marked stability under solar radiation. However, as noted previously, the combined action of radiation and the catalyst (UV/TiO₂ system) leads to the elimination of the pesticide. After 180 min of treatment, practically 100% of CBF was removed.

The poor adsorption of CBF onto the catalyst surface suggests that the •OH radical attack is the main degradation pathway in the process. To analyze the role of radicals and holes and determine the main route of degradation, additional tests were conducted in the presence of isopropanol and acetonitrile. Due to its high rate constant ($1.9 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$) isopropanol is well known as an excellent scavenger of hydroxyl radicals [30], and it has been widely used in photocatalysis in order to discriminate the direct oxidation of substrates by holes or by •OH radicals [31,32]. In Fig. 4a, it can be

seen that in presence of isopropanol, in a concentration 100 times greater than the analyte, carbofuran degradation is significantly reduced.

The use of a non-aqueous solution as a reaction media could also help to discern the role that hydroxyl radicals play in the reaction mechanism. A non-aqueous reaction medium rules out the participation of hydroxyl radicals, generated by water getting trapped in the hole, in the oxidation process [33]. Experiments carried out using acetonitrile as solvent showed a total inhibition of the degradation of CBF. These results suggest that, as anticipated, the elimination of the CBF by the photocatalytic process is mainly carried out via •OH radical attack.

It is well known that pollutant removal is not sufficient evidence to prove the effectiveness of the technology. Some previous reports have shown that in some cases, advanced oxidation processes can

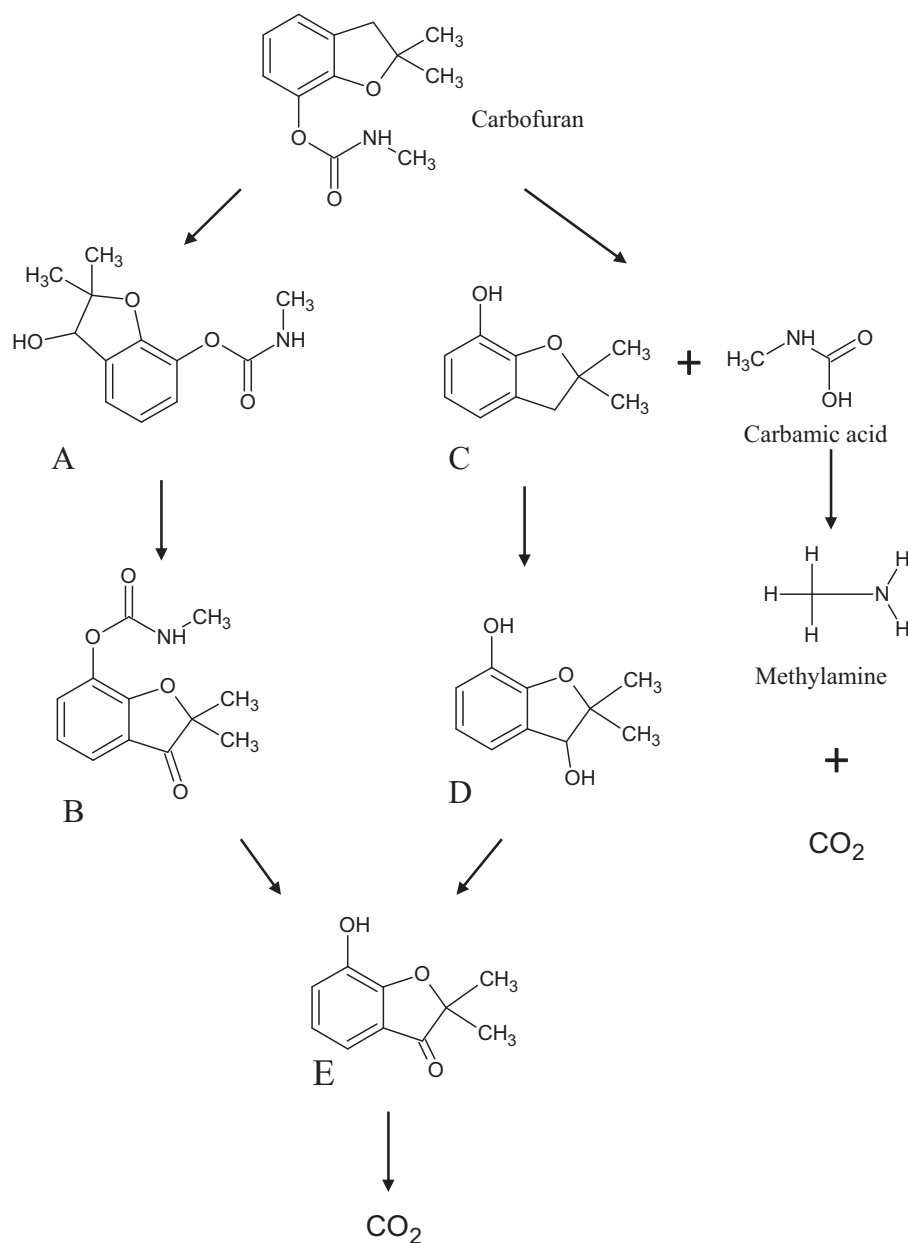


Fig. 7. Main TiO_2 photocatalytical degradation pathways of carbofuran.

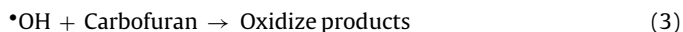
transform the initial substrate into more dangerous contaminants [34,35]. Therefore, the evolution of COD, DOC and the toxicity of the photo-treated solutions were also evaluated and are presented in Fig. 4b. As shown in the figure, after 120 min, the time in which the CBF was almost completely eliminated, the toxicity ($1/\text{EC}_{50}$) of the initial solution was considerably reduced ($\sim 65\%$), while after 330 min, $\sim 86\%$ of this parameter was eliminated. The measurement of the COD, which indicates the oxidation degree of the substrate, showed that ($\sim 70\%$), of this parameter was removed after 120 min, while at 300 min, 77% of the initial COD was eliminated. In addition, the evaluation of the DOC, which expresses the degree of mineralization of the substance during treatment, showed that after 120 min, $\sim 56\%$ of DOC was removed. At the end of the process (330 min), 75% of the initial DOC was removed. The findings suggest that via $\bullet\text{OH}$ radical attack the photocatalytic system is able to considerably oxidize and mineralize the pesticide CBF and thereby reduce significantly the toxicity of the solution.

3.5. Evaluation of photocatalytic treatment of a commercial sample of the pesticide carbofuran on a pilot scale

Several tests were conducted at pilot scale, using direct sunlight, in order to test the effectiveness of TiO_2 photocatalysis to remove the pesticide CBF in conditions more similar to a water treatment plant. A solution prepared from the commercial pesticide formulation (Furadan) was used. The experiments were carried out under the same conditions outlined in the previous section: 55 mg L^{-1} CBF, initial pH 7.60 and 1.43 g L^{-1} catalyst. The results, presented in Fig. 5, indicate that even during long periods of irradiation (900 min) the sole sunlight action is not able to remove the initial contaminant.

Additionally, as observed in the laboratory-scale reactor, under dark conditions the substrate does not adsorb significantly onto the surface of TiO_2 or onto the walls of the solar reactor. Thus, the elimination of CBF can be explained by $\bullet\text{OH}$ radical attack on the

substrate (Eq. (3)).



The evolution of the DOC, the COD and toxicity were also followed during the photocatalytic treatment of the commercial CBF preparation (Fig. 5). At 380 min, when the CBF reached 96% degradation, only 25% of DOC was eliminated while 60% of COD was reduced. This indicates that during the first stage of treatment, the CBF is transformed into degradation intermediates with a higher oxidation state. After this time, degradation intermediates generated are in turn removed and in a large proportion converted into CO₂. At 900 min, approximately 60% of DOC and almost 80% of the COD were removed. In Fig. 5 it can be also observed that, with the elimination of CBF, the toxicity of the solution is considerably reduced, gaining a reduction greater than 80% of its initial value at the end of treatment.

3.6. Identification of primary by-products and proposed degradation pathway

In order to verify the main degradation pathway during the photocatalytic elimination of carbofuran, the identification of the primary by-products, using a GC–MS mass spectrometer, was achieved by electron impact at 70 eV using the full-scan mode. The study was carried out into the suntest reactor using 55 mg L⁻¹ of CBF, initial pH 7.60 and 1.43 g L⁻¹ catalyst. Five CBF by-products were identified: 3-hydroxy-2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate (A); 2,2-dimethyl-3-oxo-2,3-dihydro-1-benzofuran-7-yl methylcarbamate (B); 2,3-dihydro-2,2-dimethylbenzofuran-7-ol (C); 2,2-Dimethyl-2,3-dihydro-1-benzofuran-3,7-diol (D); 2,2-dimethyl-3-oxo-2,3-dihydro-1-benzofuran-7-ol (E). The chemical structure and the GC retention times for the detected by-products are indicated in Table 2. All the detected compounds were also found by Kuo et al. [10] during the photocatalytic treatment of CBF. By-products C, D and E were also found Katsumata et al. [36] during CBF degradation by Fe (III) aquacomplex. Compound C was also reported to appear in hydrolysis [37] and photolysis [38]. D and E were also detected during CBF elimination by anodic Fenton treatment [39]. The apparition of the detected by-products in other AOPs confirms that photocatalytic CBF degradation is mainly carried out by •OH radical attack.

The time evolution of intermediates and substrate during the treatment is shown in Fig. 6. As suggested in Fig. 6 and presented in Fig. 7, in the first step the •OH radical attacks the C–O bond in the carbamate group to yield compound C and carbamic acid [38]. Carbamic acid is unstable [40], and is rapidly transformed into methylamine and carbon dioxide [13]. To a lesser extent, the hydroxylation of CBF, by replacing a hydroxyl group for one on the H atoms at C-3 position of the furan ring, leads to the formation of compound A, which is further oxidised to compound B, by substituting another H atom at C-3 position. Successive attack of •OH radicals on compound C produces the respective hydroxylated intermediated D, which is then oxidised to compound E. Compound E can be also formed from further oxidation of compound B. Although some of these CBF by-products can be harmful to the environment, all of them were eliminated after 300 min of treatment (Fig. 6). The strong DOC removal (more than 70%), which can be observed in Fig. 4b, indicates that further oxidation of compound E leads to ring opening and subsequent mineralization to carbon dioxide, water and inorganic ions.

4. Conclusions

Under our work conditions, the best CBF degradation was obtained at initial pH 7.60 and 1.43 g L⁻¹ of TiO₂. Analysis of the

evolution of five CBF by-products, as well as of the reaction in acetonitrile media or in the presence of isopropanol suggests that the oxidative process is carried out via •OH radical attack. The results at lab and pilot scale indicated that TiO₂ photocatalysis using direct sunlight is able to completely degrade the pesticide and thereby considerably reduce the toxicity of the initially contaminated solution.

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