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# On-line photo-assisted catalytic degradation of carbofuran

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## Abstract

An on-line photo-assisted catalyzed degradation procedure has been developed for the detoxification of waters polluted with carbofuran. The system involves the use of an UV lamp and a $TiO_2$ slurry, employed as photocatalyst, for the on-line water treatment. Different experimental variables, such as pesticide and catalyst concentrations, irradiation time and pH, were evaluated by studying their effect on the degradation of carbofuran. Under the best photodegradation conditions, 15 mg $L^{-1}$ carbofuran can be totally mineralized in less than 2.5 minutes in the presence of 0.4 mg $mL^{-1}$ $TiO_2$.

**Key words:** Carbofuran; photo-assisted catalytic degradation; pH; $TiO_2$.

# Degradación en línea de carbofuran mediante fotocatálisis

## Resumen

Se ha desarrollado un procedimiento de degradación fotocatalítica en línea para la detoxificación de aguas contaminadas con carbofuran. El sistema emplea una lámpara de UV y una suspensión de TiO2, empleado como fotocatalizador, para el tratamiento en línea del agua. Se han estudiado las diferentes variables experimentales, tales como concentración de pesticida y catalizador, tiempo de irradiación y pH, evaluando su efecto sobre la degradación del carbofuran. Bajo las mejores condiciones de fotodegradación, 15 mg $L^{-1}$ de carbofuran pueden ser mineralizados completamente en menos de 2,5 minutos en presencia de 0.4 mg $mL^{-1}$ de $TiO_2$.

**Palabras clave:** Carbofuran; degradación fotocatalítica; pH; $TiO_2$.

## Introduction

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methyl-carbamate), is a dangerous carbamate pesticide for the environment. Carbofuran is widely used in agriculture as acaricide, nematicide and insecticide. Also it is used in rice culture, where it is applied in the form of granule (1). The accute oral dose $LD_{50}$ of carbofuran is 8 to 14 mg $Kg^{-1}$ for rats and the maximum permissible dose is fixed at 0.5 $mgKg^{-1}$ (2).

Most of the reported studies on carbofuran have been focused on the detection

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and determination of this carbamate in different matrices. Carbofuran can be determined by chromatography (3), fluorimetry (4) or spectrophotometry (5). The limits of detection in peppermint oil are 0.05 and 0.1 ppm by gas chromatography (6), 0.0012 ppm in tomatoes by HPLC (7) and 5 ng-mL$^{-1}$ in water by derivative spectrometry (5). Discussions on the cytotoxicity of carbofuran were also published (8,9).

The presence of carbofuran in water deteriorates its hygienic toxicological properties and the removal of this carbamate from water can present considerable difficulties. The most used processes (chemical, thermal, photochemical and microbiological treatments) require long periods of time.

The photo-assisted catalytic degradation of organic molecules in the presence of semiconductors is an interesting alternative for the fast decomposition of pesticides in water (10,11). In this system, the absorption of irradiation light of a wavelength shorter than the band-gap of the semiconductor induces the formation of electron/hole pairs and subsequently electron reactions occur across the semiconductor/liquid interface providing the formation of oxidizing radicals and molecules which destroy the pollutant (12). Among several semiconductors used (such as ZnO, CdS, $WO_3$, $SnO_2$) $TiO_2$, in its anatase form, has shown the best results. Recently our studies demonstrated that using $TiO_2$ slurries the catalytic photo-assisted degradation of organic pollutants in waters can be carried out on-line using flow systems (13-15).

The main objective of this research has been the developement of a fast and effective procedure for the removal of carbofuran from polluted waters by using a photodecomposition process involving UV irradiation and $TiO_2$ catalysis and to study the effect of the different experimental variables of this process.

## Materials and Methods

### Apparatus

A Hewlett Packard (Waldbronn, Germany) Model 8452 A diode-array spectrophotometer, equipped with an HP 89530 A MS-DOS UV-Visible software, with a response time of 0.1 s, was used to control the degradation of carbofuran by means its spectrophotometric determination off-line using a cell of 1 cm pathlength.

The manifold depicted in Figure 1 was employed to carry out the photo-assisted degradation of carbofuran. It is a double channel assembly with a Gilson Minipuls 2 peristaltic pump (Villiers Lebel, France), and Y-shaped merging zone. Both, aqueous solution containing carbofuran and an aque-

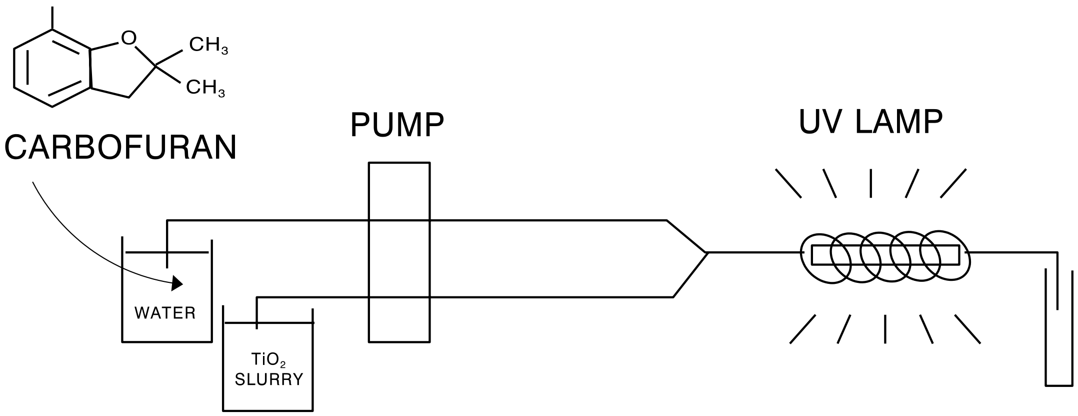


Figure 1. Manifold employed for the photo-assisted degradation of carbofuran.

ous $TiO_2$ slurry, were merged and introduced simultaneously into a PTFE coil of 6 m length and 0.8 mm internal diameter, rolled around an UV lamp Philips TL 29 D 16/09N (Germany) operated at 220 volts and 50 Hertz.

A Medifuge Heraeus sepatech centrifuge (Berlin, Germany) with a rotary speed of 3000 revolutions per minute was employed to separate the $TiO_2$ after the carbofuran photo-assisted degradation.

### Reagents

$TiO_2$ (Anatasa P25), obtained from Degussa A.G. (Frankfurt, Germany), was used as catalyst and different stock slurries of $TiO_2$ were prepared by weighting known amounts of $TiO_2$ which are suspended with deionized water.

Carbofuran (99%, $C_{12}H_{15}NO_3$) was provided by Chem Service (WestChester, USA) and working solutions containing from 5 to 50 mg $L^{-1}$ were prepared by dissolving carbofuran in deionized water.

Buffer solutions of pH: 3.4, 5, 6, 6.2, 7, 8, 9.2 and 10.2 were prepared from the appropriate analytical grade reagents acetic acid, sodium acetate, $NaH_2PO_4$, $Na_2HPO_4$, ammonium chloride and ammonia from Probus (Barcelona, Spain).

### General procedure

Water solutions and $TiO_2$ slurries were continuously merged, by using a Y-shaped Teflon piece and then passed through a Teflon coil wond around the UV lamp, in which the photo-assisted catalytic degradation of the pesticide takes place. After that, solutions were centrifuged and degradation yield controlled by UV absorbance measurements at 278 nm using a diode array spectrophotometer.

The influence of experimental variables, which affect the photodegradation of carbofuran as irradiation time, pH, $TiO_2$ and carbofuran concentrations were studied.

## Results and discussion

### Effect of irradiation time

In the manifold described in Figure 1, the irradiation time is inversely proportional to the total carrier flow, for a fixed volume of the reaction coil, and so, this parameter can be studied by modifying the flow of the peristaltic pump as can be seen in Figure 2.

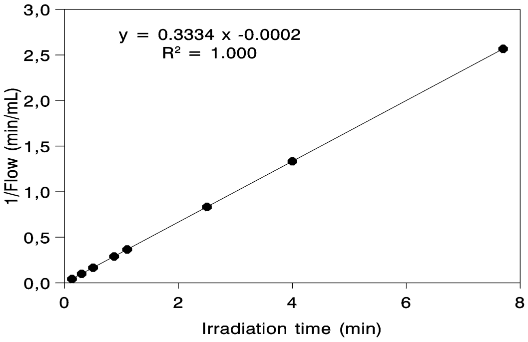
For a fixed concentration of 7.5 mg $L^{-1}$ of carbofuran the presence of a slurry of 0.2 mg $mL^{-1}$ $TiO_2$ produces a decreasing of the degradation yield of carbofuran when increasing the carrier flow and, considering the irradiation time inside the PTFE coil, it is clear that an irradiation time longer than 4 minutes is required to obtain a maximum degradation of around 60% in the aforementioned conditions.

### Effect of $TiO_2$ concentration

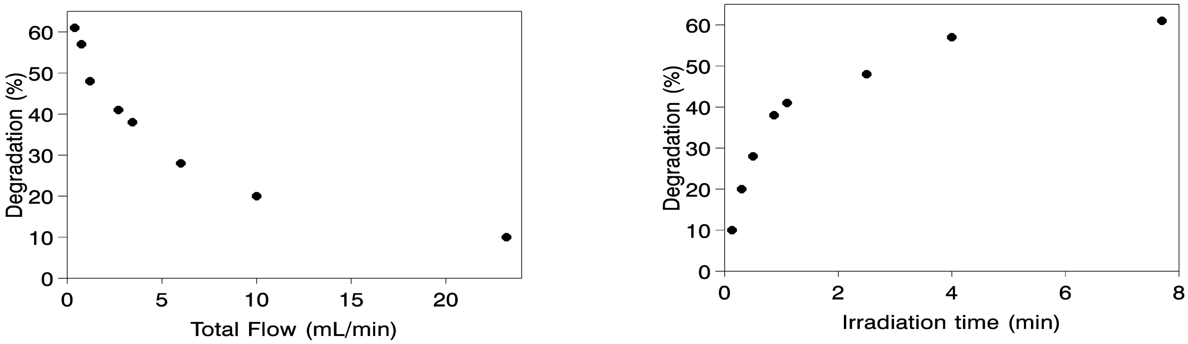
The degradation of carbofuran depends on the irradiation by UV light but also on the amount of catalyzer and, as can be seen in Figure 3, the use of increasing concentrations of $TiO_2$ improves the degradation of a fixed concentration of 7.5 $mgL^{-1}$ carbofuran. This figure shows that the increase of the $TiO_2$ concentration increases the degradation rate and also increases the maximum degradation yield, being possible to obtain a complete detoxification of a 7.5 mg $L^{-1}$ carbofuran solution in less than 4 minutes in the presence of 1.2 mg $mL^{-1}$ $TiO_2$. In the absence of $TiO_2$ the degradation of carbofuran is very low for an irradiation time of 1 minute and can reach a maximum decomposition of 30% after 2 minutes.

### Effect of carbofuran concentration

It has been studied the effect of carbofuran concentration, from 5 to 50 mg $L^{-1}$ on its photodegradation yield, using a fixed $TiO_2$ concentration of 0.8 mg $mL^{-1}$. Data obtained in these experiments are summarized in Figure 4 and show that the increase of carbofuran concentration decreases the maximum degradation attainable.



a) Relation between irradiation time and 1/flow



b) Relation between flow and degradation yield

c) Influence of irradiation time on the degradation of carbofuran

Figure 2. Effect of irradiation time on the degradation of carbofuran. $TiO_2$ concentration 0.2 mg $mL^{-1}$. Carbofuran concentration 7.5 mg $L^{-1}$.

## Effect of pH on the degradation of carbofuran

The pH can affect the surface properties of semiconductors, as well as the chemical form of substrates. A study concerning the influence of pH on the catalytic photodegradation of carbofuran, was carried out using the manifold previously described.

To carry out these experiments, differents buffer solutions of acetic acid/acetate, $NaH_2PO_4/Na_2HPO_4$ and $NH_4^+/NH_3$ were tested and 15 mg $L^{-1}$ solution of carbofuran and 0.8 mg $mL^{-1}$ $TiO_2$ slurry were employed.

Results obtained after 2.5 minutes irradiation are shown in Table 1. It can be seen, that the degradation yield increases until to reach a maximum value with total degradation at pH 7, probably due to the deprotonation of carbofuran and its interaction on the surface of $TiO_2$. However, for a pH higher than 10.2 a strong reduction of the degradation yield takes place; probably due to a change of the $TiO_2$ surface which inhibits the interaction with the anionic form or carbofuran.

## Conclusions

Results of studies carried out show that the photo-assisted degradation of carbofuran is an interesting way for the detoxification of polluted waters, which can be carried out very fastly in the presence of $TiO_2$, employed as photocatalyst. The degradation yield of carbofuran is a function of its concentration and the increase of the pesticide concentration decreases the speed of degradation.

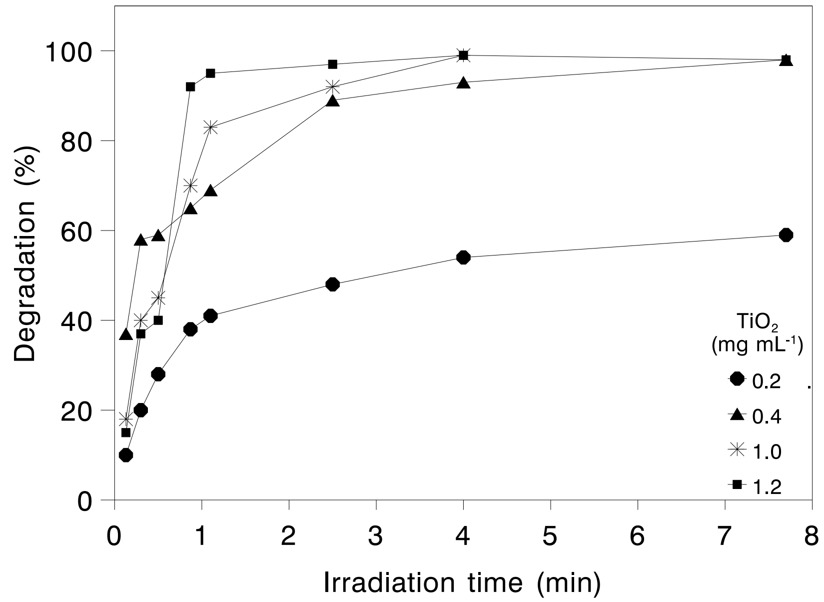


Figure 3. Effect of $TiO_2$ concentration on the degradation of 7.5 mg $L^{-1}$ carbofuran.

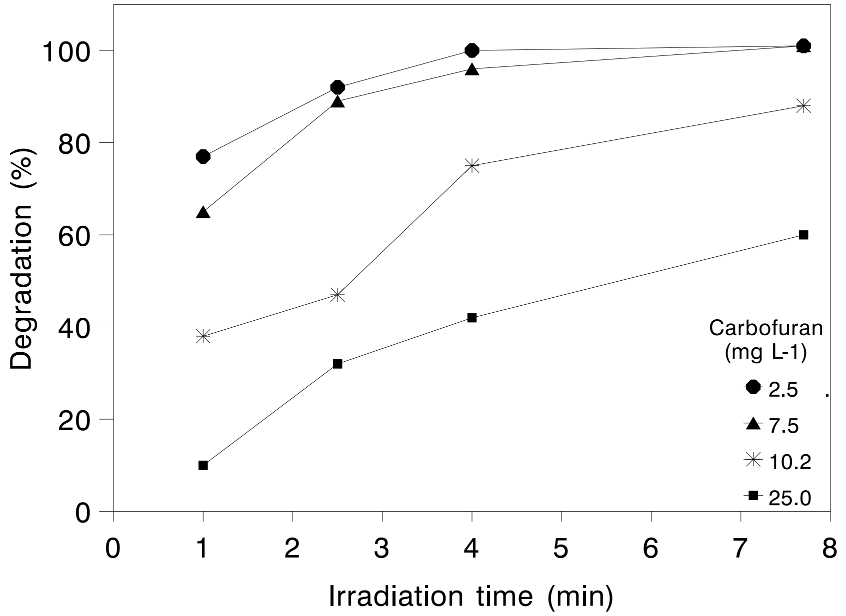


Figure 4. Variation of the degradation yield of carbofuran as a function of its concentration and the irradiation time. $TiO_2$ concentration 0.4 mg $mL^{-1}$.

The photodecomposition of carbofuran also depends on the irradiation time which allows us to obtain a complete degradation in 2.5 minutes for carbofuran concentrations lower than 15 mg $L^{-1}$. The process is also affected by pH, being pH 7 the most favorable.

In short, the studies carried out evidence the possibilities to do the on-line detoxification of waters polluted with trace amounts of carbofuran until to reach a total mineralization of this compound after a relatively short period of time and using small

Table 1
Effect of pH on the photo-assisted degradation of carbofuran

| Buffer | pH | Degradation (%) |
|---|---|---|
| HOAc/AcO$^-$ | 3.4 | 6 ± 1 |
| Ibid | 5 | 8 ± 1 |
| $NaH_2PO_4/Na_2HPO_4$ | 6 | 60 ± 5 |
| Unbuffered aqueous solution | 6.2 | 88.0 ± 0.6 |
| $NaH_2PO_4/Na_2HPO_4$ | 7 | 100 |
| $NaH_2PO_4/Na_2HPO_4$ | 8 | 87 ± 1 |
| $NH_4^+/NH_3$ | 9.2 | 71 ± 4 |
| $NH_4^+/NH_3$ | 10.2 | 3.7 ± 0.9 |

Irradiation time: 2.5 minutes. Concentration of $TiO_2$: 0.4 mg mL$^{-1}$.

amounts of $TiO_2$ which can be reutilized, being this process a good alternative for the development of clean analytical methods of analysis, including an on-line degradation step after measurement and also an appropriate strategy for detoxification of polluted industrial or agricultural wastes.

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