

# Photocatalytic degradation of carbamate insecticides: effect of different parameters

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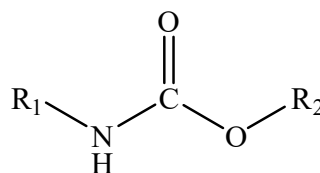
## SUMMARY

Photocatalytic degradation of a model compound of the carbamate insecticide carbofuran in water was studied using polychromatic light and ZnO and TiO<sub>2</sub> catalysts. The influence of operational parameters, such as reaction time and initial carbofuran concentration, on photocatalytic degradation was studied. A pseudo-first-order kinetic model was established and an almost complete removal of 88.4 mg L<sup>-1</sup> of carbofuran occurred within 2 h under optimized conditions. The reactions were examined by UV spectroscopy and high performance liquid chromatography (HPLC). In addition, the photocatalytic efficiencies of ZnO and TiO<sub>2</sub> were compared under the same reaction conditions.

**Keywords:** carbofuran model compound; photocatalysis; zinc oxide; titan dioxide; kinetics

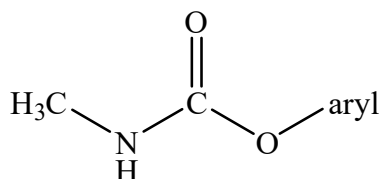
## INTRODUCTION

Carbamates were developed into commercial pesticides in the 1950s. It is a very huge family whose members are effective as insecticides, herbicides and fungicides, but they are most commonly used as insecticides. More than 50 carbamates are known (Tomašević & Gašić, 2012a). Carbamates are N-substituted esters of carbamic acid and their general formula is:



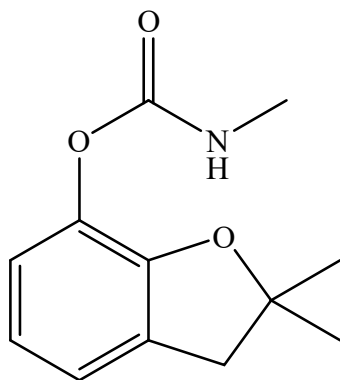
**Figure 1.** General carbamate structure, where R<sub>2</sub> is an aromatic or aliphatic moiety; if R<sub>1</sub> is a methyl group it is a carbamate insecticide, if R<sub>1</sub> is an aromatic moiety it is a carbamate herbicide, and if R<sub>1</sub> is a benzimidazole moiety it is a carbamate fungicide (WHO, 1986)

The most common carbamate insecticides (Figure 2) are: aldoxycarb, allyxycarb, aminocarb, BPMC, bendiocarb, bufencarb, butacarb, carbanolate, carbaryl, carbofuran, cloethocarb, dimetilan, dioxacarb, ethiofencarb, formetanate, hoppcide, isoprocarb, trimethacarb, MPMC, methiocarb, metolcarb, mexacarbate, pirimicab, promacyl, promecarb, propoxur, MTMC and XMC (WHO, 1986).



**Figure 2.** Structure of carbamate insecticides

The model carbofuran compound (Figure 3), 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate ( $C_{12}H_{15}NO_3$ ), was introduced in 1965 but it is currently only used in Asia and Africa (Benicha et al., 2013; Chowdhury et al., 2012). It is a highly toxic compound used as insecticide, acaricide and nematocide (Benicha et al., 2013; Chowdhury et al., 2012; Tomašević & Gašić, 2012b; MacBean, 2012). Carbofuran is highly soluble in water (at 20 °C, 0.320 g L<sup>-1</sup>, and at 25 °C 0.351 g L<sup>-1</sup>) (MacBean, 2012) and, due to its chemical stability, it can be detected in surface and waste waters. It is usually used for foliar treatments of plants or directly of soil (Tomašević & Gašić, 2012b). Carbofuran is stable in acidic media and hydrolysis occurs in basic water. The half-life of its hydrolysis may be from several hours up to 28 days. Bioaccumulation of carbofuran, as well as of its metabolites and degradation products, is low (EPA, 2006).



**Figure 3.** Carbofuran structure

The use of heterogeneous photocatalysis (Advanced Oxidation Processes-AOPs) in treatment of organic pollutants is characterized by their total mineralization (Tomašević et al., 2010). Various catalysts can be used, such as ZnO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnS or CdS, and TiO<sub>2</sub> has been found as the most effective (Daneshvar et al, 2003, 2004). Beside TiO<sub>2</sub>, ZnO has also been frequently used (Behnajady et al., 2006). Comparing the ZnO and TiO<sub>2</sub> absorption in the UV spectrum, it should be noted that ZnO absorbs over a larger fraction than TiO<sub>2</sub>. The threshold wavelength for ZnO is 440 nm according to Malato et al. (2009) or 425 nm according to Behnajady et al. (2006).

We are presenting the results of a comparison of photocatalytic efficiency of ZnO and TiO<sub>2</sub> catalysts in photodegradation of the model compound of carbofuran under polychromatic light source. The first part of the study presents the effect of reaction time, as well as initial carbofuran concentration. The reactions were examined by UV spectroscopy and high performance liquid chromatography (HPLC). The second part of the study focused on studying and comparing the influence of different catalysts on the photodegradation process.

## MATERIALS AND METHODS

### Reagents

Analytical-grade model compound carbofuran (99.5%) was granted by FMC, USA. The photocatalysts were: commercial ZnO with surface area 10 m<sup>2</sup> g<sup>-1</sup> and particle size 0.1-4.0 μm, obtained from Merck; TiO<sub>2</sub> P-25 (Degussa) having 70% anatase and 30% rutile, surface area 50 m<sup>2</sup> g<sup>-1</sup> and particle size 25 nm; TiO<sub>2</sub> Merck (anatase) with surface area 10 m<sup>2</sup> g<sup>-1</sup>; TiO<sub>2</sub> Merck Eusolex<sup>®</sup> T (anatase modification), and TiO<sub>2</sub> Merck R-706 (rutile modification). All catalysts were used as received. HPLC grade acetonitrile for HPLC analysis was provided by Fluka. Millipore Waters deionized water (18.2 MΩ cm<sup>-1</sup> at 25 °C) was used for preparation of pesticide solutions.

### Photodegradation procedure

Initial pesticide solutions were prepared by dissolving carbofuran in deionized water and providing additional sonification in ultrasonic water bath, and agitation for 60 min. Photocatalytic degradation experiments were performed at 20 °C in a glass batch thermostated reactor

(500.0 mL) with an Osram Ultra-Vitalux® lamp (300 W, 315–400 nm) (UV-A:UV-B=13.6:3), light intensity  $75 \text{ mW cm}^{-2}$  (Amaprobe SOLAR-100 Meter). The lamp was placed at 300 mm distance from the reaction mixture. Generally, pesticide solutions (250.0 mL) with  $2.0 \text{ g L}^{-1}$  of each catalyst were first agitated at 500 rpm in the dark for 60 min to analyze the extent of adsorption, while further photocatalytic degradation experiments were performed under illumination. Solution aliquots were taken at certain time intervals. Each catalyst was precipitated by centrifugation and filtration through a  $0.20 \mu\text{m}$  Sartorius regenerated cellulose filter.

### UV spectroscopy, HPLC analysis, and optical characterization of $\text{TiO}_2$ and $\text{ZnO}$ catalysts

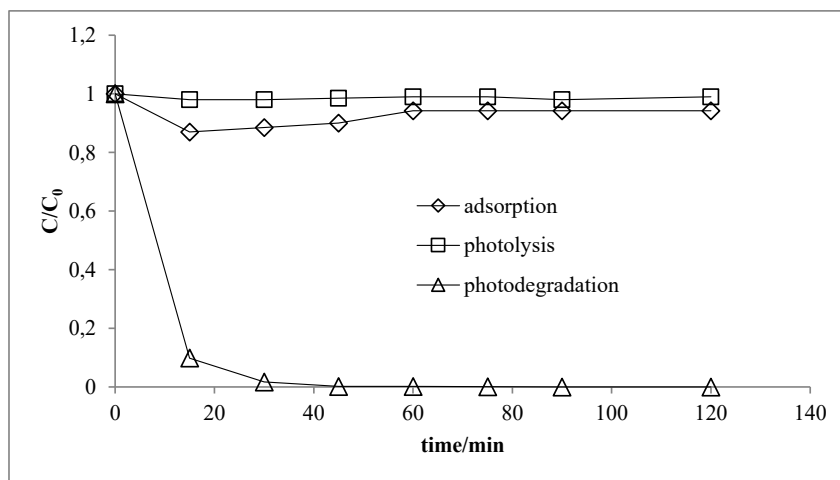
Photocatalytic degradation of the model compound was examined using UV spectroscopy (Noor et al. 2014) and HPLC (Martijn & Dobrat 1988). A sample of 5.0 mL of irradiated solution was withdrawn and filtered, and the spectrum was recorded using a Shimadzu 1700 UV-VIS spectrophotometer in a range from 200 to 400 nm. Linear dependence between the initial carbofuran concentration and the appropriate absorption at 275 nm allowed the monitoring of degradation kinetics at this wavelength. For the HPLC analysis, all solutions were filtered through Sartorius  $0.20 \mu\text{m}$  syringe filters and analyzed using the UV detector at 280 nm and ambient temperature ( $25 \text{ }^\circ\text{C}$ ). Hewlett Packard HP 1050 liquid chromatograph with a UV-Vis detector,

equipped with a reverse-phase column type Zorbax Eclipse XDB-C18  $150 \times 4.6 \text{ mm}$  (*i.d.*)  $\times 5 \mu\text{m}$ , was used for HPLC analysis. The mobile phase (flow rate  $1.5 \text{ mL min}^{-1}$ ) was a mixture of methanol and water (70:30, v/v), and both samples and standards were diluted with methanol. The data presented in this work were obtained from three determinations (as mean values). A Shimadzu UV-Visible UV-2600 spectrophotometer (Japan) was used for diffuse reflection spectra measurements. The spectrophotometer was equipped with an integrated sphere (ISR-2600 Plus [for UV-2600]). The spectra were obtained in the range from 220 to 900 nm with 1 nm resolution.

## RESULTS AND DISCUSSION

### Effect of reaction time on photocatalytic degradation of carbofuran

Processes of adsorption, photolysis and photocatalytic degradation of the model compound are presented in Figure 4 using the relation  $C/C_0$  versus  $t$ , where  $C/C_0$  is a normalized concentration ( $C$  is the concentration of pesticide at irradiation time  $t$  and  $C_0$  is the initial concentration of pesticide). A negligible change in pesticide concentration in the presence of light was observed, while pesticide adsorption in the presence of  $\text{ZnO}$  without illumination was about 5.8%. The degradation observed in the presence of  $\text{ZnO}$  under irradiation confirmed that the process takes place in a photocatalytic regime.



**Figure 4.** Effects of different experimental conditions on carbofuran degradation rate ( $C_0(\text{carbofuran}) = 88.4 \text{ mg L}^{-1}$ ,  $c(\text{ZnO}) = 2.0 \text{ g L}^{-1}$ ,  $\text{pH} = 5.9$ )

The highest photocatalytic degradation rate of carbofuran in our earlier investigation (Tomašević et al., 2007) was obtained for 2 g L<sup>-1</sup> of ZnO. Therefore, 2 g L<sup>-1</sup> of photocatalyst was chosen as the concentration in all photocatalytic degradation experiments performed in this study. The kinetics of carbofuran photocatalytic degradation was examined using the UV spectrophotometric method, and the results were consistent with those of the HPLC analysis (Figure 5). The reaction was practically completed within 60 minutes. The initial concentration of model compound decreased from 88.4 to 8.7 mg L<sup>-1</sup>, within 15 min, while 98.3% of the pesticide content was degraded after 30 min and the model compound was not detected in reaction solution after 2 h of illumination.

The kinetics of photocatalytic degradation rates can be described using the pseudo-first kinetic order (Konstantinou & Albanis, 2003), and presented by eqs. (1) and (2):

$$\ln(C_0 / C) = k \cdot t \quad (1)$$

$$C = C_0 \cdot e^{-k \cdot t} \quad (2)$$

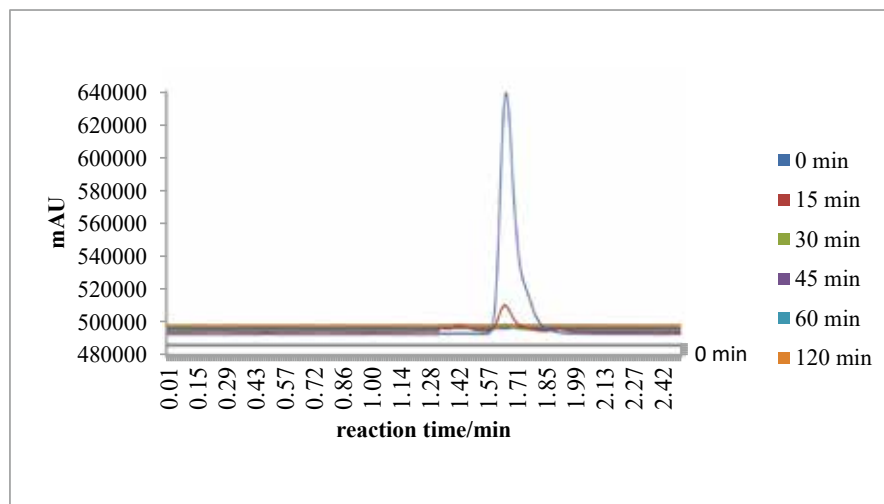
where  $C_0$  and  $C$  are concentrations at  $t = 0$  min and at appropriate reaction time  $t$ , respectively, and  $k$  is the pseudo-first order rate constant. For reactions of pseudo-first order, the reaction half time can be calculated according to eq. (3):

$$t_{1/2} = \ln 2 / k \quad (3)$$

Calculation of the pseudo-first order rate constant for the ZnO catalyst ( $C_0 = 88.4$  mg L<sup>-1</sup>) gave a  $k$  value of 0.1072 min<sup>-1</sup>, which is similar to the one found by Konstantinou and Albanis (2003). This result is typical for heterogeneous photocatalysis and low initial concentrations of pollutants.

### Effects of initial pesticide concentrations

The influence of initial pesticide concentration on photocatalytic degradation rate was tested using solutions in a concentration range from 22.1 to 88.4 mg L<sup>-1</sup>. Decrease in the rate constant was observed with increasing  $C_0$ , and a 3.75 times lower rate constant was found for higher initial carbofuran concentrations (Table 1). The increased  $C_0$  implies an increased competition between pesticide molecules and consequently a lower probability to be attacked by •OH radicals. Due to the heterogeneity of the system, different mass transfer processes at appropriate periods of photodegradation processes could be of different contribution and a controlling factor of overall mass transport. At higher solute concentration there is a higher probability (i.e. higher diffusion flux across the bulk liquid and liquid film at adsorbent exterior surface) of solute transport in the pores and/or along the pore walls to be adsorbed at adsorbent active sites. Hence, a higher coverage of the ZnO surface is achieved in solutions with higher pesticide concentrations, affecting the inhibition of photocatalytic degradation reaction with holes or hydroxyl radicals (Daneshvar et al., 2008).



**Figure 5.** HPLC chromatogram of carbofuran photocatalytic degradation solutions at different time intervals ( $C_0$ (carbofuran) = 88.4 mg L<sup>-1</sup>,  $c$ (ZnO) = 2.0 g L<sup>-1</sup>, pH 5.9)

**Table 1.** Effect of initial carbofuran concentrations on initial photocatalytic degradation rate constant ( $k$  (ZnO) = 2.0 g L<sup>-1</sup>, pH 5.9)

$C_0$ (mg L <sup>-1</sup> )	$k$ (min <sup>-1</sup> )	$t_{1/2}$ (min)	$R$
88.4	0.1072	6.47	0.9836
66.3	0.1624	4.27	0.9822
44.2	0.2340	2.96	0.9975
22.1	0.4020	1.72	0.9997

**Table 2.** Kinetics of carbofuran degradation with 2 g L<sup>-1</sup> of catalysts ( $C_0$  (carbofuran) = 88.4 mg L<sup>-1</sup>, pH 5.9)

Catalyst	$k$ (min <sup>-1</sup> )	$t_{1/2}$ (min)	$R$
ZnO Merck	0.1072	6.47	0.9836
TiO <sub>2</sub> Degussa P-25	0.0822	8.43	0.9824
TiO <sub>2</sub> Merck Eusolex® T	0.0268	25.86	0.9836
TiO <sub>2</sub> Merck anatase	0.0179	38.72	0.9784
TiO <sub>2</sub> Merck R-706 rutile	0.0143	48.47	0.9786

### Comparison of photocatalytic performance of catalysts

Comparisons of photocatalytic performances of catalysts of different origin have given us valuable information for their possible applications, revealing the relationship between photocatalyst properties/performance of the studied materials, and expanding the knowledge necessary for synthesizing new improved materials. The mechanism/efficiency of photocatalytic degradation of pollutants is known to be a complex process, which depends on several parameters: type and intensity of irradiation, structure and concentration of a pollutant (pesticide), temperature, pH, the duration of pollutant exposure to a light source, the type and concentration of an applied catalyst, crystallinity, surface area, surface properties, doping, etc. Evaluation of the most influential factors is a difficult task which requires careful and detailed analysis of the studied system. As a result, the influence of different types of TiO<sub>2</sub> photocatalysts (Degussa P-25, Merck anatase, Merck Eusolex® T anatase, and Merck R-706 rutile) on carbofuran degradation was investigated and compared with ZnO Merck (Table 2) in order to get a deeper insight into the relation of catalyst properties/photocatalytic efficiency.

In all cases, when both ZnO and TiO<sub>2</sub> photocatalysts were used, degradation of carbofuran followed a pseudo-first order kinetics, and a higher  $k$  value was obtained for ZnO Merck. It had been found earlier that TiO<sub>2</sub> Degussa P-25 was a better catalyst than ZnO Merck in photocatalytic degradation of carbofuran (Mahalakshmi et al., 2007), but our experimental results (Table 2) confirmed the superiority of Merck ZnO over TiO<sub>2</sub> photocatalysts. When ZnO Merck was used, the rate constant of carbofuran degradation was 1.3 times faster than in the presence of TiO<sub>2</sub> Degussa P-25, and 7.5 times faster than in the presence of TiO<sub>2</sub> Merck R-706 rutile.

There is also a widespread literature controversy about the efficiency of photocatalysts, ZnO *versus* TiO<sub>2</sub>, and a significant volume of published results claim higher photocatalytic degradation rate obtained by the ZnO catalyst. For example, it was shown that in photocatalytic degradation of the organophosphorous insecticide dichlorvos in water using TiO<sub>2</sub> and ZnO catalysts (Evgenidou et al., 2005), ZnO appeared as the more efficient catalyst, especially at high concentrations (above 0.2 g L<sup>-1</sup> of catalyst). At lower concentrations, TiO<sub>2</sub> was more effective probably due to its larger surface area, while at higher concentrations, light scattering, which is greater in TiO<sub>2</sub> suspension because of smaller particle size, reduced the efficiency of the TiO<sub>2</sub> catalysis. The opposite is true for ZnO, which absorbed more light at higher concentrations (Sakthivel et al., 2003). It was also found earlier that during photocatalytic degradation of the herbicide clopyralid in water, ZnO Merck was the better catalyst than TiO<sub>2</sub> P-25 (Degussa) and other commercial forms of TiO<sub>2</sub> (Berberidou et al., 2016). According to literature data, the beneficial properties of the ZnO catalyst could be attributed to similar band gap energy (3.2 eV) as TiO<sub>2</sub> (~ 3.1 eV), similar photocatalytic capacity and a wider absorption region in the UV spectrum than TiO<sub>2</sub> (Malato et al., 2009). Although the surface area of TiO<sub>2</sub> is several times higher than that of ZnO, some studies have indicated that the photocatalytic activity of ZnO powder depends on crystallinity rather than surface area (Li & Haneda, 2003]. The superiority of the ZnO catalyst was also attributed to its morphology and crystallinity (Jing et al., 2001). Thus, it was concluded that high surface reactivity of the ZnO catalyst is not necessarily in relation with a high surface area (Li & Haneda, 2003).

On the other hand, the efficiency of four commercial TiO<sub>2</sub> catalysts in carbofuran degradation under polychromatic light irradiation is a slower process in comparison with ZnO, and it increases in the

following order: Merck R-706 rutile < Merck anatase < Merck Eusolex® T anatase < Degussa P-25 (Table 2). Similar to ZnO, the crystal morphology of TiO<sub>2</sub> was proposed as one of the most critical properties related to photocatalytic efficiency (Nargiello & Herz, 1993). It is known that the anatase form of TiO<sub>2</sub> is more effective than the rutile (Huang et al., 1995). P-25 (Degussa) is highly efficient because of a synergistic effect of anatase and rutile (anatase is a carrier for rutile). Also, the small size of rutile particles in P-25 and their close proximity to anatase particles is very important for high photoactivity of Degussa P-25 TiO<sub>2</sub>. Hurum et al. (2005) reported that P-25 owes its catalytic reactivity to a slower recombination between electrons and holes.

### Optical characterization (band gap determination) of TiO<sub>2</sub> and ZnO catalysts

Light absorption capability is another very significant characteristic of all catalysts and the parameter was characterized by ultraviolet-visible diffuse reflectance spectroscopy. In this work, optical properties such as the band gap of TiO<sub>2</sub> and ZnO catalysts were also studied. The band gap ( $E_g$ ) was determined according to Dolić et al. (2018) and Antić et al. (2017).

Optical band gap determination for TiO<sub>2</sub> rutile is presented in Figure 6. The values of TiO<sub>2</sub> Degussa P-25 and ZnO Merck band gaps had been determined earlier (Tomašević et al., 2020, in press). The band gap of TiO<sub>2</sub> Degussa (3.3 eV) was found to be higher than reported (3.2 eV) (Hanaor et al., 2011). The band gap of ZnO Merck, also determined earlier (Tomašević et

al., 2020, in press) (3.2 eV), was found to be lower or similar to earlier reported data (Panigrahi et al., 2012; Davis et al., 2019). In addition, the band gap of TiO<sub>2</sub> rutile was determined to be 2.96 eV, which is similar to a literature value of around 3 eV (Luttrell et al., 2014). It is known that the band gap of semiconductors should have strong influence on the activity of certain photocatalysts. Although, the TiO<sub>2</sub> used in the present experiment has a higher energy gap than ZnO, it was found that the photocatalytic activity of ZnO was the highest. So the degradation effectiveness of the studied catalysts is not solely correlated to their optical band gaps. According to literature sources, properties other than energy gap should also be concerned, such as the oxidation “power” of electrons, charge transport, surface properties, etc. (Luttrell et al., 2014).

### CONCLUSION

Photocatalytic degradation of the carbamate insecticide carbofuran as a model compound was studied using the ZnO and TiO<sub>2</sub> catalysts and polychromatic light. The results showed that carbofuran photodegradation was affected by the initial concentration of carbofuran. A decrease in carbofuran photodegradation with increasing initial concentration was observed. A pseudo-first-order kinetic model was established and almost complete removal of carbofuran occurred within 2 h. In addition, comparing the ZnO Merck and four commercial TiO<sub>2</sub> catalysts, it is evident that ZnO Merck was the best catalyst for 315–400 nm carbofuran oxidative degradation.

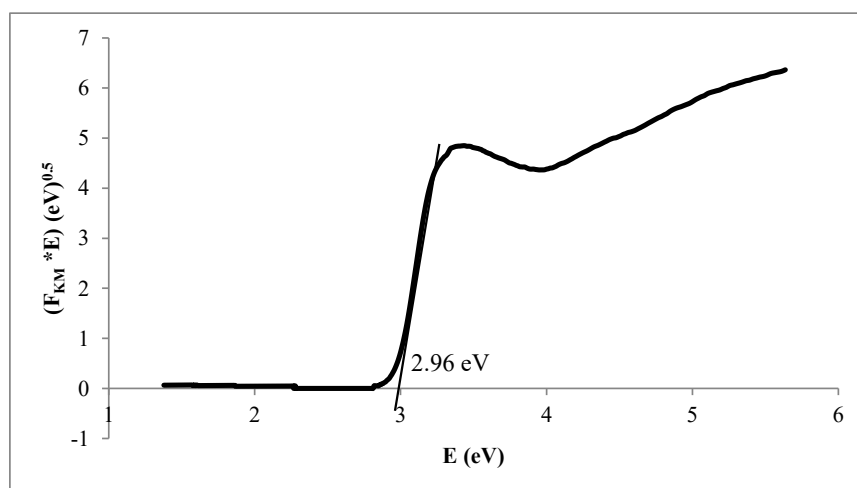


Figure 6. Determination of energy gap for TiO<sub>2</sub> rutile

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## Fotokatalitička degradacija karbamatnih insekticida: efekti različitih parametara

### REZIME

Proučavana je fotokatalitička degradacija model jedinjenja karbamatnog insekticida karbofurana u vodi, u prisustvu polihromatske svetlosti i katalizatora ZnO i TiO<sub>2</sub>. Ispitivan je uticaj reakcionih parametara, kao što su vreme reakcije i početna koncentracija karbofurana, na fotokatalitičku degradaciju. Ustanovljeno je da je reakcija bila pseudo-prvog reda i primenom optimalnih uslova skoro potpuno uklanjanje 88,4 mg L<sup>-1</sup> karbofurana dogodilo se u toku 2 sata. Reakcije su praćene primenom UV spektroskopije i tačne hromatografije visokih performansi (HPLC). Naknadno, upoređena je fotokatalitička efikasnost katalizatora ZnO i TiO<sub>2</sub> primenom identičnih reakcionih uslova.

**Ključne reči:** model jedinjenje karbofuran; fotokataliza; cink oksid; titan dioksid; kinetika