

ANĐELKA TOMAŠEVIĆ<sup>1</sup>  
JELENA ĐAJA<sup>2</sup>  
SLOBODAN PETROVIĆ<sup>2</sup>  
ERNŐ E. KISS<sup>3</sup>  
DUŠAN MIJIN<sup>2</sup>

<sup>1</sup>Institute of Pesticides and Environment Protection, Banatska 31b, 11080 Belgrade-Zemun, Serbia

<sup>2</sup>University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>3</sup>University of Novi Sad, Faculty of Technology, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia

SHORT COMMUNICATION

UDC 628.316:632.951

## A STUDY OF THE PHOTOCATALYTIC DEGRADATION OF METHOMYL BY UV LIGHT

*The photocatalytic degradation of insecticide methomyl in water, using TiO<sub>2</sub> and ZnO (Merck), under UV (366 nm) was studied. The influence of the catalyst concentration and pH was investigated. The optimal concentration of the catalyst was found to be 2.0 g/l. It was found that ZnO is a better catalyst than TiO<sub>2</sub> under the same reaction conditions. Also, the influence of NaCl was studied. The presence of Cl<sup>-</sup> significantly affects the photodegradation of the pollutant.*

*Key words: photocatalytic degradation; methomyl; titanium dioxide; zinc oxide.*

Methomyl (Figure 1) is a broad spectrum insecticide. It is a very toxic and hazardous compound and a pollutant of environmental concern because of its high solubility in water (57.9 g/l at 25 °C) [1]. Since the sorption affinity of methomyl to soils is rather low, it can easily cause contamination of both ground and surface water sources [2].

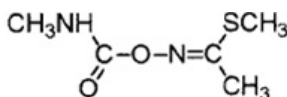


Figure 1. Structure of methomyl. IUPAC name: *S*-methyl *N*-(methylcarbamoyloxy) thioacetimidate.

Although biological processes are often most economical for a contaminated site cleanup and an industrial waste treatment, the advanced oxidation processes (AOPs) provide an effective means of rapidly treated compounds with the efficient process control [3].

Methomyl has also been photodegraded by using AOP. A different catalyst has been used, mostly TiO<sub>2</sub> [4–8]. Photo-Fenton reaction was also employed [9].

The aim of the present work is to study the photocatalytic degradation of insecticide methomyl in water using TiO<sub>2</sub> and ZnO (Merck) under UV light (366 nm). The influence of the catalyst concentration, pH and NaCl concentration was studied.

### EXPERIMENTAL

Hydrochloric acid, sodium chloride and sodium hydroxide (all p.a.) were obtained commercially. TiO<sub>2</sub>, Merck Eusolex<sup>®</sup> T (anatase modification), and ZnO (Merck) were used as received. Methomyl was obtained from DuPont (analytical grade, 99.8 %). Deionised water was obtained from a Milipore Waters Milli Q purification unit.

Irradiations under UV light (366 nm) were performed in an open flask made of a quartz glass (20 ml volume) with the UV lamp (2x8 W) placed 5 cm from the surface of the reaction mixture.

The photodegradation of methomyl was studied by preparing a solution containing 16.4 mg/l of methomyl and a certain amount of the catalyst. In a typical experiment, 15 ml of the solution was used. Then, the lamp was switched on and during the irradiation the agitation was applied, and after an appropriate time of irradiation the suspension was sampled. The reaction mixtures were kept at 20 °C. The concentration of methomyl was determined after the centrifugation of a sample by UV-Vis spectrophotometer (Shimadzu 1700)

Corresponding author: A. Tomašević, Center for Pesticides and Environment Protection, Banatska 31b, 11080 Belgrade-Zemun, Serbia

E-mail: academia@beotel.yu

Paper received: October 6, 2008.

Paper revised: October 30, 2008.

Paper accepted: October 31, 2008.

at  $\lambda_{\max} = 234$  nm, and by HPLC. The characteristics of the HPLC instrument are as follows: HPLC Instrument GBC, a pump LC 1120, a UV-Vis detector LC 1205, a manual injector RHEODYNE 7725i, a column ZORBAX Eclipse XDB-C8 (4.6×150 mm, 5 $\mu$ m), a mobile phase acetonitrile: water (25:75, flow rate 1.0 cm<sup>3</sup> min<sup>-1</sup>), wavelength 234 nm. pH of the samples was adjusted by adding a dilute NaOH and HCl and measured using a pH meter (PHM93 reference pH meter, Radiometer Copenhagen, Denmark).

## RESULTS AND DISCUSSION

### UV-Vis spectra changes

The changes in the absorption spectra of the methomyl solution during the photocatalytic degradation at different irradiation times are presented in Figure 2. The insecticide shows a band with a maximum absorption at 234 nm. The decrease of the absorption peak actually indicates a rapid degradation of the insecticide.

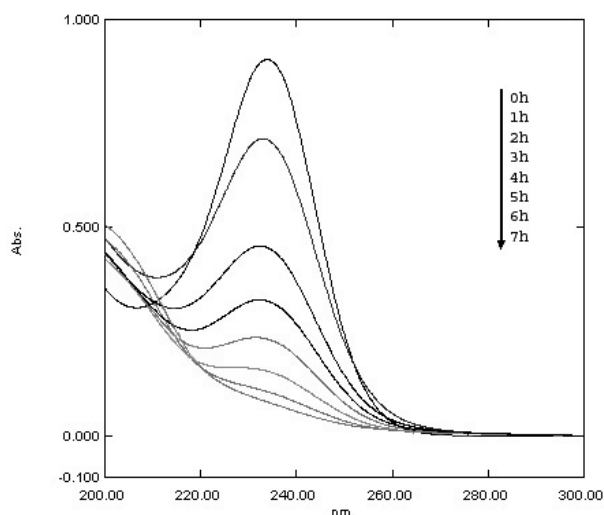


Figure 2. UV-Vis spectra changes of methomyl (16.4 mg/l) in aqueous TiO<sub>2</sub> dispersion (concentration of TiO<sub>2</sub>: 1 g/l) irradiated with UV lamp (366 nm).

### The effect of the catalyst concentration

The effect of the catalyst concentration (TiO<sub>2</sub>) on the photodegradation efficiency was shown in Figure 3. The photodegradation efficiency increased with increased concentration of the photocatalyst, reached the highest value at 2.0 g/l and then decreased. The possible explanation for this phenomenon is the fact that when all insecticide molecules are adsorbed on TiO<sub>2</sub>, the addition of higher quantities of TiO<sub>2</sub> would have no effect on the photodegradation efficiency. Negligible degradation effect was observed if catalyst or irradiation were applied separately.

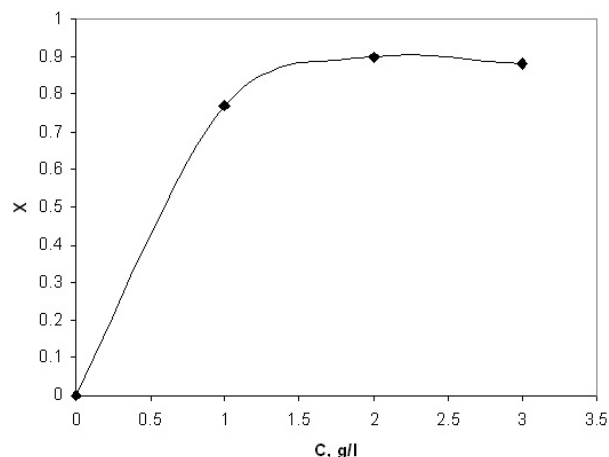


Figure 3. The effect of the concentration of TiO<sub>2</sub> on the photodegradation efficiency ( $X = (C_0 - C)/C_0$ ) of methomyl at irradiation time of 6.0 h (concentration of methomyl: 16.4 mg/l).

### The effect of pH

It is well known that pH value has an influence on the rate of degradation of some organic compounds in photocatalytic processes [10,11]. The photodegradation of methomyl was studied at three different pH values (3.5, 5.6 and 9.0). The pH was adjusted by the addition of HCl (3.5) or NaOH (9.0). The third value is the pH of the pure insecticide solution in deionised water. The obtained results (Figure 4) imply that the photodegradation rate is highest in the acidic solution and lowest in the alkaline solution.

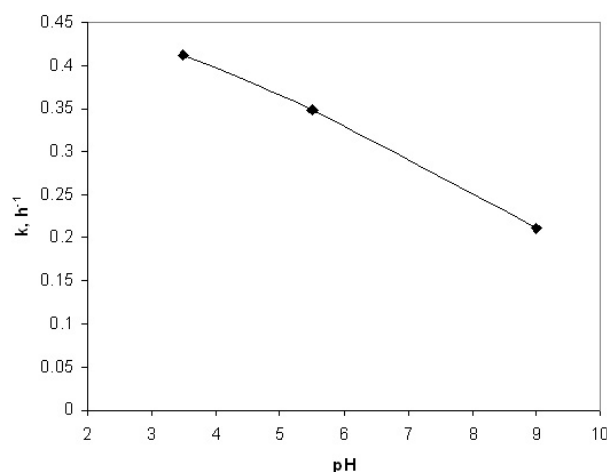


Figure 4. The effect of pH on the photodegradation rate of methomyl (insecticide concentration: 16.4 mg/l; catalyst concentration: 2.0 g/l of TiO<sub>2</sub>).

### The effect of NaCl

A common inorganic ion, chloride ion, was employed as sodium chloride to study the photodegradation rate of methomyl. The influence of different concentrations of sodium chloride (0-5 % w/v) on the pho-

todegradation rate of methomyl is presented in Figure 5. The decrease of the photodegradation of methomyl in the presence of chloride ions is due to the hole scavenging properties of chloride ions [12].

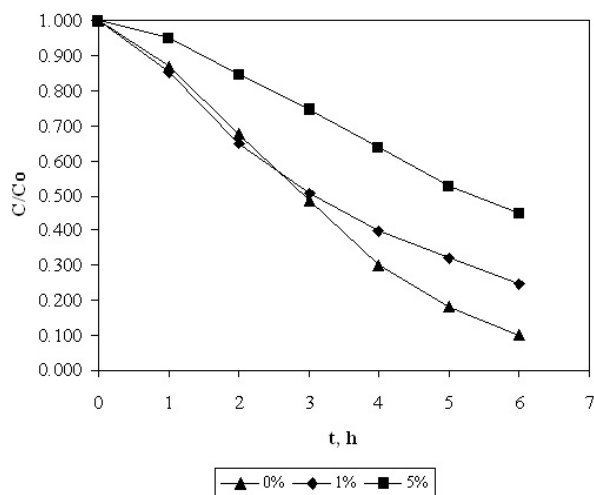


Figure 5. The effect of NaCl concentration on the photodegradation rate of methomyl (insecticide concentration: 16.4 mg/l, catalyst concentration: 2.0 g/l of TiO<sub>2</sub>).

#### The effect of the catalyst type

ZnO is also frequently used in AOP. The biggest advantage of ZnO in comparison to TiO<sub>2</sub> is that it absorbs over a larger fraction of UV spectrum. On the other hand, ZnO exhibits a tendency to dissolve and photodecompose [13]. The obtained results (Figure 6) showed that the photodegradation was much faster when ZnO was used in comparison to the reaction with TiO<sub>2</sub>.

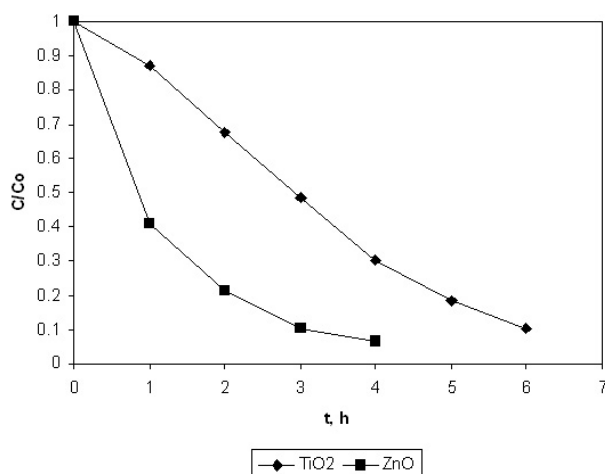


Figure 6. The effect of the catalyst type on the photodegradation rate of methomyl (insecticide concentration: 16.4 mg/l, catalyst concentration: 2.0 g/l).

## CONCLUSION

The obtained results of the photodegradation of methomyl by UV light (366 nm) indicated that the photodegradation was affected by the initial catalyst concentration, pH value and the type of catalyst. The presence of NaCl led to the inhibition of the photodegradation process.

## Acknowledgment

The authors are grateful to the Ministry of Science and Technological Development of Serbia for financial support through the Project TR20041.

## REFERENCES

- [1] C. D. S. Tomlin, *The Pesticide Manual*, Thirteenth Edition, BCPC Publications, Alton, 2003, p. 650
- [2] T. J. Strathmann, A. T. Stone: *Environ. Sci. Technol.* **35** (2001) 2461-2469
- [3] S. Devipriya, S. Yesodharan, *Sol. Energy Mater. Sol. Cells* **86** (2005) 309-348
- [4] I. Poullos, M. Kositzi, K. Pitarakis, S. Beltsios, I. Oikonomou, *International J. Environm. Poll.* **28** (2006) 33-44
- [5] M. Tamimi, M. Belmouden, S. Qourzal, A. Assabbane, Y. Ait-Ichou, *Fresenius Environ. Bull.* **15** (2006) 1226-1231
- [6] I. Oller, W. Gernjak, M. I. Maldonado, L. A. Perez-Estrada, J. A. Sanchez-Perez, S. Malato, *J. Hazard. Mat.* **138** (2006) 507-517
- [7] M. Tamimi, S. Qourzal, A. Assabbane, J.-M. Chovelon, C. Ferronato, Y. Ait-Ichou, *Photochem. Photobiol. Sci.* **5** (2006) 477-482
- [8] M.-P. Z. R. Zhang, Z.-F. Xia, G. Low, *Gaodeng Xuexiao Huaxue Xuebao* **19** (1998) 1475-1478
- [9] A. Tomašević, G. Bošković, D. Mijin, E. E. Kiss, *React. Kinet. Catal. Lett.* **91** (2007) 53-59
- [10] H. Gupta, S. Tanaka, *Water Sci. Technol.* **31** (1995) 47-54
- [11] G. Wu, X. Liu, D. Wei, J. Fan, L. Wang, *Water Res.* **35** (2001) 3927-3933
- [12] B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere* **46** (2002) 1173-1181
- [13] N. Daneshvar, S. Aber, M. S. Seyed Dorraji, A. R. Khatay, M. H. Rasoulifard, *Int. J. Chem. Biomol. Eng.* **1** (2008) 24-29.