UV-INDUCED PHOTOOXIDATION OF PHENYL UREA PESTICIDES TOXICOLOGY ASPECTS

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ABSTRACT

Phenylurea herbicides, like diuron, monuron, linuron, are photosynthesis inhibitors killing the entire plant by this effect. These pesticides and their intermediates formed due to their UV induced transformation could be toxic and carcinogenic to animals and humans. Thus, the investigation of the UV induced transformation of these phenyl urea pesticides from toxicology aspects is suitable. In this work, the ecotoxicology effect of the multicomponent solutions formed during the UV photolysis (254 nm) was investigated by Daphtoxkit F^{TM} Magna and Algaltoxkit F^{TM}. The genotoxicology effect of the multicomponent solutions was investigated using the Ames tests.

INTRODUCTION

Pesticide pollution of environmental is a pervasive problem with widespread ecological consequences. In response, the European Community has implemented programmes for the development of technologies which are useful for reducing pesticide input into water runoff. Wastewaters from agricultural industries and pesticide manufacturing plants may have pesticide contamination levels as high as 500 mg/l [1]. European regulations (European Union Drinking Water Directive 98/83/EC) on drinking water quality set a maximum concentration of 0.1 μg/L for individual pesticides and some of their degradation products, and 0.5 μg/L for total pesticides present. Nevertheless, the concentrations of some pesticides frequently exceed these levels. Diuron and monuron are widely used chlorine containing phenylurea herbicides, which are employed to control a wide variety of annual and perennial broadleaf and grassy weeds. Nowadays, diuron, which is considered a Priority Hazardous Substance by the European Commission, can be detected not only in the agricultural and natural waters but also in drinking waters [2-4]. The commercially available low-pressure mercury vapour lamp (having main output at 254 nm) is a widely applied light source in water disinfection technologies. At the same time, 254 nm light is effective for the photodecomposition of several aromatic pollutants by direct photolysis. However, the efficiency of the UV photolysis in the elimination of the target substances is strongly limited by their molar absorptivity and the quantum yield of the phototransformation.

MATERIALS AND METHODS

The low-pressure mercury vapor lamp (GCL307T5VH/CELL, LightTech, Hungary, 227 mm arc length) was applied as light source. This lamp has a high purity silica sleeve (307 mm long and 20.5 mm external diameter of the sleeve,) which transmits both 254 and 185 nm

light. The electric input of the lamp is 15 W and the effective power-output is 4.0 W in the UV range. The emitted photon flow of the light sources was measured by potassium ferrioxalate actinometry. The photon flow of the 254 nm component was found to be $3.45(\pm 0.09)\times 10^{-5}$ einstein s^{-1}.

The low-pressure mercury vapour lamp with envelope (320 mm long and 28 mm internal diameter) was centered in the water-cooled, tubular glass reactor (length 340 mm, inner diameter 46 mm). Air (375 cm^3 min^{-1}) was driven through the solution during the time of irradiation. The thermostated (25 ± 0.5 °C) solution (500 cm^3) was circulated (375 cm^3 min^{-1}) continuously and stirred with a magnetic stirrer bar in the reservoir. The kinetic measurements were commenced by switching on the light source.

The concentration of diuron, monuron and fenuron was measured with an HPLC system consisting of a Merck-Hitachi L-7100 low-pressure gradient pump equipped with a Merck-Hitachi L-4250 UV-Vis detector (λ = 210 nm) applying a Lichrospher RP 18 column and acetonitrile/water (50/50) mixture as eluent.

In our work toxicology measurements were carried out by different ways. These tests were done to determine the toxicity of the samples after the 0, 12.5, 25, 50, 75 and 100% decomposition of parent compound. Two standard toxicity assays were applied for aquatic toxicity assessment: *Dapnia magna* (ISO 6341, 1996) and *Pseudokirchneriella subcapitata* (ISO 8692, 2004). The *Dapnia magna 24-48 acute immobilisation tests were* conducted according to internationaly accepted Standard Methods (OECD Guideline 201 and ISO 6341; Daphtoxkit F^{TM} magna). The tests are performed using neonates which are hatched in about three days from eggs at 20-22 °C, under continuous illumination of 6000 lux. Immobility at 24 h and 48 h is the bioassay endpoint, assumed to be equivalent with the mortality. The microalgae growth inhibitory tests with *Pseudokirchneriella subcapitata* were conducted according to internationally accepted Standard Methods (OECD Guideline 201 and ISO 8692; Algaltoxkit F^{TM}). In this test the optical density at 670 nm is used to measure the algal growth inhibition. The Ames genotoxicity test employs several histidine auxotrophic strains of *Salmonella typhimurium*, which have been selected on the bases of their sensitivity to distinct types of mutagens. These reverse mutation tests are performed by mixing the test substance solution and the tester strain together in a rich liquid medium, which contains only small amounts of histidine. Histidine permits the inoculated test organism to undergo a limited number of divisions, but it is insufficient to permit normal growth. However, if the strain undergoes a reverse mutation, (spontaneous, or induced by the test substance or a positive control material) the organism no longer requires histidine to grow and can produce visible revertant colonies after spreading the treated cell suspension on the surface of minimal medium.

RESULTS AND DISCUSSION

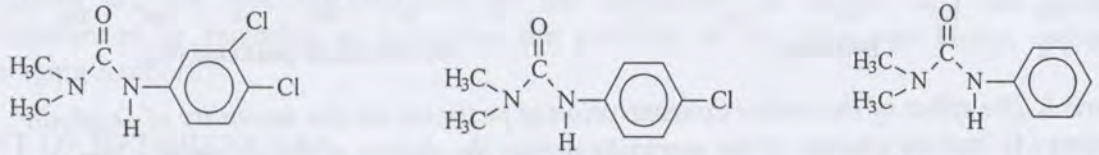

Figure 1.*The structure of the investigated compounds*

The structure of the investigated compounds is shown in Figure 1. The first step of this work was the determination of the molar absorptivity of the target substances at 254 nm. Because of the high molar absorptivity of diuron and monuron at 254 nm (15 000 mol^{-1} dm^3 cm^{-1} and 12 500 mol^{-1} dm^3 cm^{-1}), the UV photolysis is a quite efficient method for their degradation. On

the other hand, the rate of transformation of monuron is about two times higher than that of diuron, opposite that the molar absorptivity of diuron is higher. Both, molar absorptivity (4 500 mol^{-1} dm^3 cm^{-1}) and the rate of transformation of fenuron is much smaller than that of the chlorinated phenyl urea pesticides (Fig. 2). The kinetic measurements were achieved both in unbuffered and buffered solutions. Phosphate buffer has no effect on the rate of transformation and the formation of intermediates. (Fig. 2)

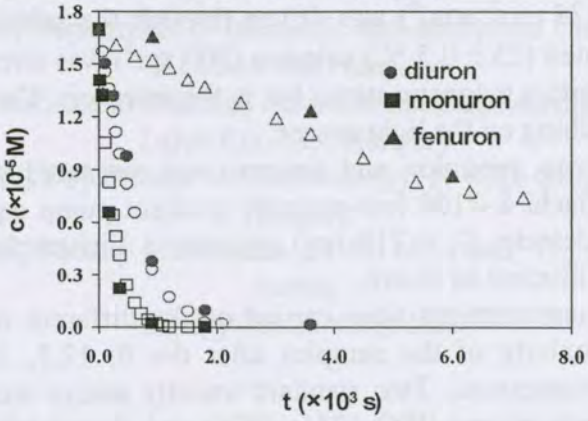

Figure 2. *Kinetic curves determined in buffered (phosphate buffer, pH = 7.2, empty symbols) and unbuffered solutions (full symbols)*

Using Daphtoxkit F™ Magna ecotoxicology test, the mortality rate of Daphnia Magna was 100% at the initial concentration ($1{,}7\times10^{-4}$ M) of diuron and monuron and decreased with decrease of the concentration (Fig. 3A). Fenuron has no effect on the Daphnia Magna even at the highest concentration ($1{,}7\times10^{-4}$ M). In the case of the diuron and monuron, the toxicity decreased during the UV treatment. At the same time, in the case of the fenuron, the toxicity of the solution strongly increased likely because of the formation of highly toxic intermediates (Fig. 3B). The time dependence of the mortality rate suggest that the(se) highly toxic intermediate(s) can not be decomposed due to the 254 nm UV light irradiation.

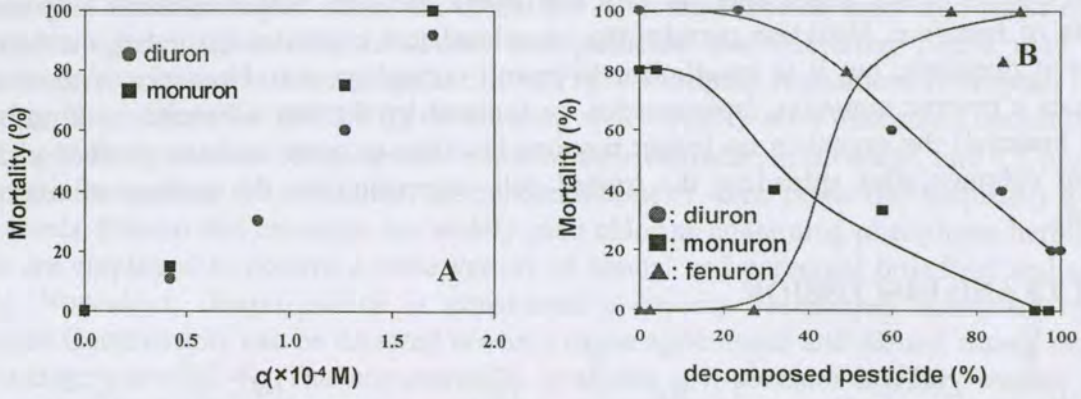

Figure 3. *The effect of the initial concentration of pesticide on the mortality of Daphnia Magna (A) and the change of the mortality versus the degree of the decomposition of pesticides at $1{,}7\times10^{-4}$ M initial concentration (B)*

The results of the Algaltoxkit F™ test showed that the *Pseudokirchneriella Subcapitata* is much more sensitive on the presence of these pesticides, than Daphnia Magna. The lowest investigated concentration ($1{,}1\times10^{-5}$ M) of each investigated pesticide inhibited completely the growing of algal. In the cases of the UV treated samples, the ecotoxicology effect decreased slightly until that time, the target substances decomposed completely (Fig. 4).

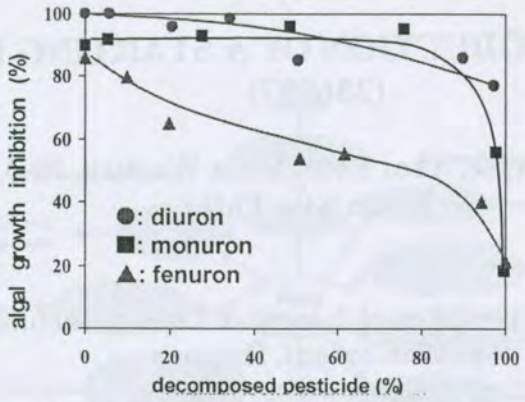

Figure 4. *The algal growth inhibition versus the degree of the decomposition of pesticides at $1,7\times10^{-4}$ M initial concentration*

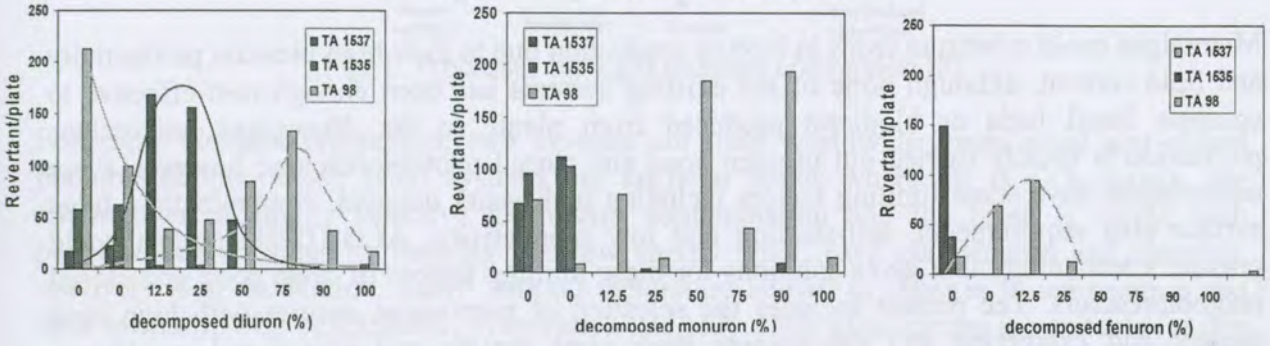

Figure 5. *Results of the Ames tests in the case of the decomposition of diuron (A), monuron (B) and fenuron (C)*

The results of the Ames tests (Fig 5) suggests that, during the UV initiated transformation the genotoxicology effect of the formed multicomponent solutions showed maximum type curves. The treated solution has no further genotoxicology effect after the total decomposition of the target substance.

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