

## GROUNDWATER REMEDIATION USING BIOLOGICAL AND PHOTOCATALYTIC METHODS

SÁNDOR GUBA,<sup>1\*</sup> VIOLA SOMOGYI,<sup>2</sup> AND ERZSÉBET SZABÓNÉ BÁRDOS<sup>3</sup>

<sup>1</sup> Institute of Physics and Mechatronics, University of Pannonia, Egyetem u. 10, Veszprém, 8200, HUNGARY

<sup>2</sup> Institute of Environmental Engineering, University of Pannonia, Egyetem u. 10, Veszprém, 8200, HUNGARY

<sup>3</sup> Department of General and Inorganic Chemistry, University of Pannonia, Egyetem u. 10, Veszprém, 8200, HUNGARY

The degradability of two commercially available pesticides was studied using heterogeneous photocatalytic and activated sludge treatment methods. The first pesticide contained 5% quizalofop-P-ethyl as an active ingredient and petroleum naphtha as a solvent, the latter causing difficulties both in photocatalytic and biological treatment methods. The active ingredient of the second compound was acetamiprid. The photocatalysis proved to be effective both under laboratory conditions (using UV light) and when exposed to sunlight, but the pesticides remained stable during the employed biological treatment. Preliminary information on its behaviour in soil was obtained from transport modelling.

**Keywords:** heterogeneous photocatalysis, groundwater remediation, quizalofop-P-ethyl, acetamiprid, biological treatment

### 1. Introduction

The drinking water supply of Hungary largely relies on underground water resources. The water quality has been endangered by both industry over the last century and the still significant pesticide-intensive agriculture. Excessive amounts of pesticides contaminating soil may be fully or partially degraded by natural chemical and biochemical reactions. The latter may lead to bioaccumulation. The transport into groundwater and/or surface water bodies is affected by several factors, such as precipitation, evapotranspiration, infiltration, and runoff besides the physicochemical characteristics of soil and the attributes of the substance.

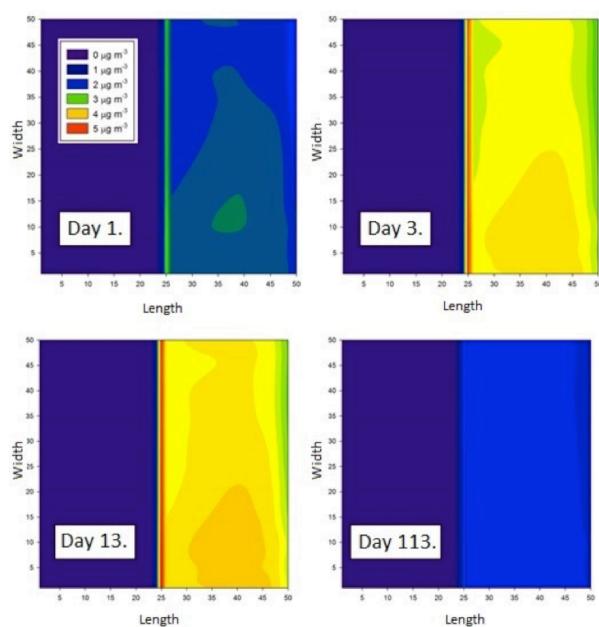
The application of pesticides is an inefficient procedure, since only a small amount is utilised for the desired purpose. Most of the compound is released unused into the soil and if it degrades partially or at a slower pace, the pesticide might accumulate and enter the food chain. In order to avoid the release of pesticides that are persistent and harmful to the environment and humans, it is necessary to have licencing procedures and strict controls on the use of such materials [1]. In Hungary, authorisation is regulated by the Decree 89/2004 of the Ministry of Agriculture and Rural Development in agreement with the Council Directive 91/414/EEC [2].

A common method to treat contaminated aquifers is groundwater pump-and-treat technology [3], where extraction wells are used to remove the contaminated water that is treated with adequate techniques after which it is re-injected into the aquifer or released into a surface water body. The treatment method is dependent on the degradability and toxicity of the pollutant.

Bioremediation cannot be used in cases when the compound is not biodegradable or even toxic to microorganisms. Oxidative methods, such as heterogeneous photocatalysis may be adequate in such cases [4]. In this process, the radicals formed due to the photogenerated charge-carriers on the surface of the semiconductor. They react with the pollutant molecule initiating its degradation. The catalyst is often reusable and recycled. The semiconductor catalyst has to be chemically and biologically inert, but photocatalytically active. It should be easily produced and economical. Since TiO<sub>2</sub> fits these requirements, it is the best among the semiconductors for extensive use [5]. Research over the past years has proved that on a laboratory scale different organic compounds (aliphatic and aromatic hydrocarbons [6], alcohols and organic acids [7], phenols [8] and chlorinated compounds [9]) could be effectively degraded to inorganic end products using heterogeneous photocatalysis [10].

The aim of this paper is to report on the degradability of organic contaminants in the soil and groundwater with biological and photocatalytic methods using model compounds. Their behaviour in the soil

\*Correspondence: [gubas@almos.uni-pannon.hu](mailto:gubas@almos.uni-pannon.hu)



**Figure 1.** The concentration of quizalofop-P-ethyl in the second layer in the case of normal use (a unit equals 2 m).

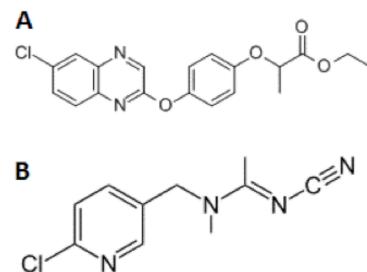
was determined by hydraulic and transport models. The model compounds were a herbicide (Leopard 5 EC) and an insecticide (Mospilan 20 SG). Both fall into category III meaning that they are available without a special licence. Their metabolites remain stable in soil for a long period.

## 2. Methods and Materials

The substance with the brand name Leopard 5 EC contains 5% quizalofop-P-ethyl (Scheme 1A) as an active ingredient, 77-83% petroleum naphtha as a solvent and other emulsifying excipients. The active substance is especially dangerous to mammals, aquatic organisms, and birds and moderately toxic to bees. It is insoluble in water; it emulsifies due to the additives. Its metabolites are more soluble in water, but do not hydrolyse. Their half-lives are between 35 and 39 days.

The active ingredient of the insecticide called Mospilan 20 SG is 20% acetamiprid (Scheme 1B), which is highly toxic to mammals and birds and moderately toxic to aquatic organisms. The substance is very soluble in water, hence its high mobility upon infiltration. Its metabolite is not easily degraded under natural conditions in soil and water (its half-life is 133 days), and it is moderately toxic to aquatic life.

Heterogeneous photocatalytic irradiation experiments were performed in a photoreactor with an effective volume of  $2.5 \text{ dm}^3$ . Internal recirculation was provided in the tube reactor.  $\text{TiO}_2$  was used as a catalyst with a concentration of  $1 \text{ g dm}^{-3}$ , while the air flow was  $40 \text{ dm}^3 \text{ h}^{-1}$ . The radiation source placed in the axis of the reactor was a 40 W fluorescent lamp specially manufactured for such purposes. The vast majority of light emitted is of a longer wavelength than 300 nm.



**Scheme 1.** Schematic structures of pesticides studied in this work (A: quizalofop-p-ethyl, Ref: DPX 79376, <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/583.htm> (11.05.2015); B: acetamiprid, Ref: NI 35, <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/11.htm> (11.05.2015)).

Biological treatment was carried out in an activated sludge, aerated sequenced batch reactor. An operating cycle lasted for a day. The effective volume of the reactor was  $5 \text{ dm}^3$  and the sludge concentration was kept at  $4 \text{ g dm}^{-3}$ . The rate of aeration was kept constant throughout the process. A non-adapted municipal sludge was used for the experiments.

Modelling was carried out using Processing MODFLOW for Windows (PMWIN) 5.3. This version is freely available, while later versions can be obtained commercially. The test area was chosen to be the size of 1 acre divided vertically into three homogenous layers with average Hungarian properties. Simulations were run for 1–3–13–113 day intervals. The environmental factors taken into consideration were the following: groundwater flow and porosity, infiltration due to precipitation ( $1.9 \text{ mm day}^{-1}$ ), and evapotranspiration ( $1.2 \text{ m day}^{-1}$ ) [11]. The hydraulic conductivity was  $129.6 \text{ mm day}^{-1}$  for all three layers [12].

## 3. Results and Analysis

### 3.1. Leopard 5 EC

The degradability of the substance with heterogeneous photocatalysis was examined under laboratory (UV-light) and natural (sunlight) conditions. The initial concentration of the active ingredient was  $3.26 \text{ g dm}^{-3}$ . The solution was heavily foaming whilst the reactor was being filled. During irradiation, the majority of the catalyst deposited onto the bottom or adhered to the walls of the reactor and buffer tank after an hour despite being stirred. The organic carbon content of the mixture did not change, which indicates that no degradation took place.

In the biological treatment, the components of the solution entering the cycle were:  $100 \text{ cm}^3$  of herbicide with a concentration of  $3.26 \text{ g dm}^{-3}$ ,  $100 \text{ cm}^3$  of acetic acid ( $0.93 \text{ g dm}^{-3}$ ),  $10 \text{ cm}^3$  of ammonium chloride solution ( $30 \text{ mg N dm}^{-3}$ ), and  $10 \text{ cm}^3$  of sodium phosphate ( $30 \text{ mg P dm}^{-3}$ ). After turning the stirrer and aeration on the liquid started to foam heavily and smelled strongly of oil. At the end of the cycle in the settling phase the effluent was turbid. Colloids and a part of the activated sludge deposited on the wall of the

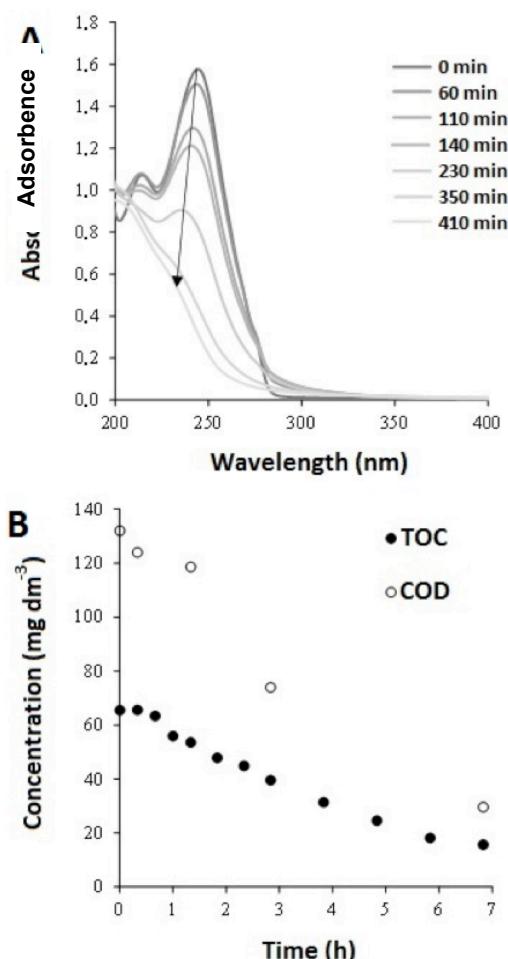


Figure 2. Spectra of Mospilan suspension treated with catalyst (optical path length: 0.5 cm) (A); chemical oxygen demand and total organic carbon concentrations as function of time (B).

sequenced batch reactor and surface of the sensors and dried there. The following cycle ended with the same results. The treatment using activated sludge turned out to be ineffective due to the experienced foaming and cumulated active ingredient. Inspections revealed that the degradation of the solvent did not start either.

The transport models created with the software (*Fig.1*) showed that pesticide under normal conditions of use did not threaten drinking water resources and due to hydrolysis the concentration decreased by half in the second stratum over 113 days. In the case of accidental spillages (the same amount of compound was hypothetically released over a 2 m<sup>2</sup> area) the effect was significant, the concentration was a thousand times greater compared to normal use scenarios.

### 3.2. Mospilan 20 SG

In the experiments the concentration of Mospilan used was 170 mg dm<sup>-3</sup> in agreement with the suggested concentration of application. A 20% active ingredient content was achieved by an acetamiprid solution with a concentration of 34 mg dm<sup>-3</sup>. Photodegradation was monitored by recording the UV-VIS spectra of the mixture and measuring the organic carbon content (TOC).

The solution was first irradiated with UV-light without a catalyst under atmospheric pressure for three hours. During this time neither the TOC concentration nor the pH of the mixture changed; the variation of the results stayed within the measurement error, which suggested that the insecticide was not degradable by UV-light in itself.

The second experiment was carried out with TiO<sub>2</sub> as a catalyst and the process was not stopped for seven hours. During this time the rate of light absorption between 200 and 300 nm gradually decreased and the maximum of the band shifted from 245 nm to 230 nm (*Fig.2*). These spectral changes indicate clearly that the compound degraded in the heterogeneous photocatalytic experiments.

The suspension was circulated in the reactor for 20 minutes before irradiation. From changes in TOC concentration, it can be concluded that during this period a proportion of the organic material had adsorbed onto the catalyst particles. The rate of adsorption in terms of TOC was 10%. By the end of the process, the TOC concentration of the suspension reduced by 76% while the COD amount became 78% less. According to the data, the initial rate of decay was calculated to be 13.59 mg dm<sup>-3</sup> h<sup>-1</sup> based on the curve fitted to the TOC.

A major advantage of the heterogeneous photocatalyst is that the reaction may be carried out with solar radiation; thus, costs and also environmentally harmful emissions can be reduced. Photons are on the one hand ‘pure’ reagents and on the other hand ‘pure’ energy. The changes in the spectrum, such as the decrease in absorbance and the shift in location of band peaks were the same under laboratory conditions, while the reaction rate was lower. The initial rate of decay due to solar radiation was 6.07 mg dm<sup>-3</sup> h<sup>-1</sup>. During measurements the UV-B radiation was “strong” (UV index 6.5, Hungarian Meteorological Service).

The results show that the heterogeneous photocatalytic degradation of the insecticide may be efficiently achieved by using sunlight. This can be utilised when disposing of different chemical residues. The organic contaminants may be mineralised using solar radiation on site in a carefully designed “reactor”.

The biodegradability of the pesticide was studied with a prepared solution based on an average concentration of application. In the first case, an additional substrate (acetic acid) was added to the sequenced batch reactor while in the second case only the insecticide was supposed to serve as a substrate. Based on the results (*Fig.3*), it can be stated that the biodegradation of Mospilan cannot be achieved with municipal activated sludge under the employed conditions.

The results of the transport model (*Fig.4*) show that acetamiprid acts in a similar way to quizalofop-P-ethyl. Since it does not hydrolyse the active ingredient, it would remain for longer in soil and accumulation might appear therefore the compound may more easily enter the food chain. In the case of accidental spillages of the substance over a small area, the effect would be more significant just as was the case with quizalofop-P-ethyl.

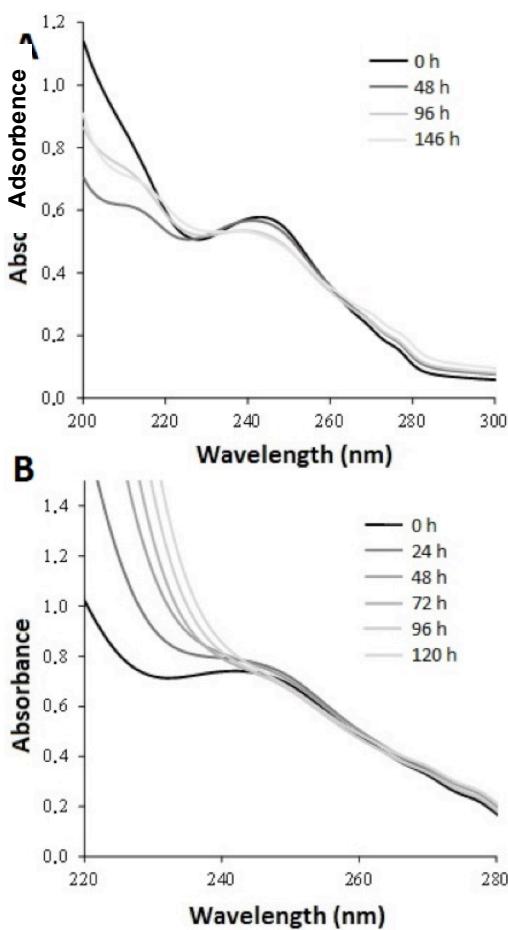


Figure 3. Changes in absorbance spectra during biological treatment with (A) and without additional substrate (B) (optical length: 0.5 cm).

The concentration in soil would be a thousand fold greater. Besides it would not decrease significantly over time, since the compound is stable in aqueous media.

#### 4. Conclusion

The studied Leopard 5 EC and Mospilan 20 SG pesticides are available to purchase without any permit, although they are toxic to different extents to mammals, birds and aquatic organisms. Their improper application might cause serious environmental damage. The degradability of the two substances was studied by means of heterogeneous photocatalysis and biological treatment.

In the case of Leopard 5 EC neither of the methods was successful. The petroleum naphta solvent and/or the emulsifiers poisoned the  $TiO_2$  catalyst. The dollops formed settled and the surface of the catalyst particles was reduced greatly due to the adhesion effect of the organic material. The photocatalytic degradation reaction could not take place. A similar process was observed in the biological reactor. The mixture together with the biomass adhered to the surface of the sequenced batch reactor and sensors. In both cases the conditions made the treatment processes impossible. In order to be able to study the degradation of the

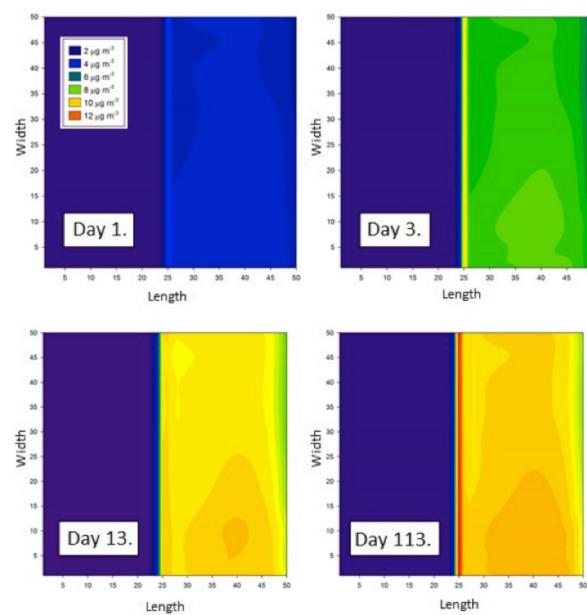


Figure 4. The concentration of acetamiprid in the second layer in the case of normal use (a unit equals 2 m).

compound, pre-treatment, possibly the destabilisation of the emulsion is needed.

Mospilan 20 SG could be treated using heterogeneous photocatalysis both under laboratory conditions (with a UV lamp) and utilising solar radiation. However, it can be stated that the insecticide cannot be treated with municipal activated sludge under the applied conditions based on the results of sequenced batch reactor experiments.

According to the simulation results, neither of the pesticides poses a threat to drinking water resources in the case of normal use in compliance with the specifications provided by the manufacturer. Nonetheless, Mospilan 20 SG is likely to accumulate if used multiple times or for extended periods. Should there be an emergency the impact on the environment might multiply.

The results of the present study show that unlicensed use does not necessarily mean easily degradable substances. The biological method was unsuccessful in both cases, photocatalysis is not applicable for water-immiscible chemicals but in the case of hydrophilic organic materials, the treatment may be efficient.

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