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Degradation of organophosphorus compounds by X-ray irradiation

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Abstract

The degradation of organophosphorus pesticide diazinon in aqueous media with a white X-ray beam from a conventional X-ray source was studied. The concentration of the pesticide in the solution (40 mg dm^{-3}) decreases exponentially with the exposure time, i.e. with the absorbed dose: 50% degradation is obtained at the dose of about 160 Gy. The compounds detected in the irradiation samples suggest that diazinon is converted mainly into 2-isopropyl-4-methyl-6-hydroxypyrimidine, which is also its main hydrolysis product.

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1. Introduction

Organophosphorus compounds used in agriculture as pesticides represent an attempt to maximise insecticide activity and minimise environmental persistence. They have replaced organochlorine compounds which persist and accumulate in the environment. Different pathways of organophosphates decomposition such as hydrolysis, photolytic oxidation, microbial transformations and other biological processes have been reported recently (Racke, 1992; Pehkonen and Zhang, 2002). Hydrolysis is the most common degradation pathway and it can occur at several reactive centres in a given organophosphorus pesticide molecule. The important factor affecting hydrolysis is the pH. Diazinon, for example, is rapidly hydrolysed at low or high pH values due to base- and also acid-catalysed processes (Fig. 1) (Freed et al., 1979; Racke, 1992; Dannenberg and Pehkonen, 1998; Pehkonen and Zhang, 2002).

Photolytic degradation of different organophosphorus compounds has been intensively studied (Mengyue et al., 1995). Chemical oxidation of selected

compounds can be obtained using photo-assisted Fenton reaction ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ light) (Pignatello and Sun, 1995). Chemical oxidation of diazinon through chlorination (Zhang and Pehkonen, 1999) and ozonization has also been studied (Meijers et al., 1995). In aqueous phase the oxidation product, diazoxon, may also hydrolyse to diethylphosphate and 2-isopropyl-4-methyl-6-hydroxypyrimidine. The final products of ozonization are acetic and formic acids.

To improve photodegradation aqueous suspensions of semiconductors in combination with UV irradiation have been used. Among the applied semiconductors titanium dioxide (TiO_2) has proven to be the most efficient one due to its capability to form electron-hole pairs under illumination with UV light. The combinations of $\text{UV-H}_2\text{O}_2$, UV-TiO_2 and $\text{UV-H}_2\text{O}_2\text{-TiO}_2$ have also been used for photo-degradation of some organophosphorus compounds, including diazinon (Doong and Chang, 1997).

Efficient photodegradation of different pesticides was obtained using high energy lasers working at different wavelengths (Canle et al., 2001; Trebše and Franko, 2002). The reactions do not involve the use of reagents which are hazardous from the ecological point of view.

Pesticides result mainly in polluted waste water from agricultural industrial sources, which may contain high

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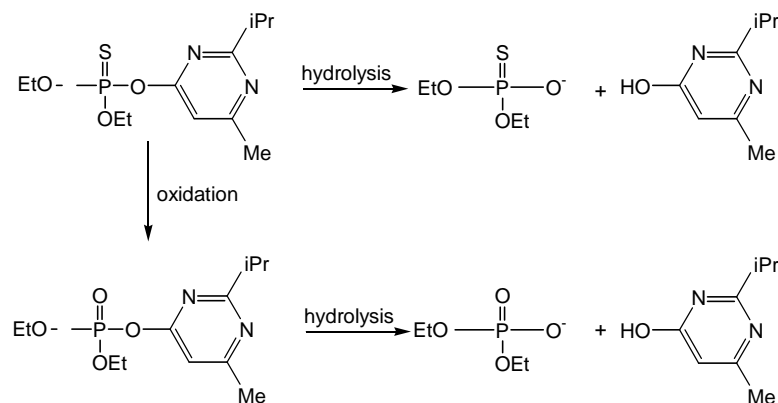


Fig. 1. Two most common degradation pathways of diazinon.

amounts of pesticides (up to several hundred mg dm^{-3}). The main characteristics of such waste water are extreme toxicity, low volume and well-defined location. An alternative for the treatment of the waste water is electron-beam irradiation in combination with other conventional treatment stages. This combination has been reported to remove organic dyes, heavy metals, phenols, etc. (Han et al., 2002). In the electron-beam process the organic materials react with the radicals generated by water radiolysis and the degradation products can be easily removed by conventional biological or chemical treatment (Pikaev et al., 1997).

The irradiation treatment seems promising also for the purification of waters polluted with the organophosphorus pesticides. In this paper, we present a study of the degradation process of organophosphate pesticide diazinon by X-ray irradiation. Diazinon, is one of the most widely used pesticides in Slovenia.

2. Experimental

Chemicals: Diazinon (*O,O*-diethyl-*O*-(diisopropyl-6-methyl-4-pyrimidyl)phosphorothioate), was provided by Pestanal. Ethylacetate (HPLC grade) has been purchased from Merck. Sample solutions have been prepared in deionised (nanopure) water.

Experimental set-up: Saturated aqueous solution of the pesticide (volume: 4 ml, concentration $C_0 = 40 \text{ mg dm}^{-3}$) was inserted in 1.5 cm long lucite cell with 1 mm thick lucite windows. The whole volume of the solution in the cell was exposed to the unfiltered X-ray beam from a conventional X-ray source. During irradiation the cell was placed 28 cm from the source (anode). Mo X-ray tube (Philips PW 1316/91) with a focal spot of $0.2 \text{ mm} \times 12 \text{ mm}$ at 6° take-off angle, operating at the high voltage of 55 kV and a current of 45 mA was used. The flux of the continuous X-ray beam was stabilised within 0.01%.

The dose rate on the sample was estimated using an approximate formula for the dose rate calculation in air in the collimated X-ray beam from the classical continuously operated X-ray tube (Edmonds, 1984):

$$\dot{D} [\text{mGy s}^{-1}] = K \left(\frac{U^{1.79} I}{d^2} \right) \left(\frac{1}{x} + 0.114 \right), \quad (1)$$

where U [kV] is the voltage, I [mA] the anode current, d [cm] is the distance from the anode, and x [mm] the thickness of the Al filter. We calibrated the formula with a set of direct measurements of the dose rate using the low level secondary standard ionisation chamber type TK-30 dosimeter. From the measured data with different Al filters in the thickness range from 0.25 to 2 mm we obtained a calibration constant of $K = 0.33$.

In case of sample irradiation no Al filter was used. Instead, the incident white beam from the X-ray tube is partially filtered by 1 mm thick lucite window. In this way we estimated that in our experimental set-up, operating at the anode current of 45 mA, the average absorbed dose rate in the sample was about 50 mGy s^{-1} (Turner, 1995).

Immediately after irradiation extraction was employed using ethylacetate. Gas chromatography in combination with flame ionisation detection was used for the identification and quantification of the compounds.

GC analyses: HP 6890 series (GC) with FID detector was used for GC analyses. GC conditions were as follows: Supelco SPB-1 ($30 \text{ m} \times 0.53 \text{ mm}$) column and helium as a carrier gas were used; the initial temperature was 80°C ; temperature increased initially by $15^\circ \text{ min}^{-1}$ up to 280°C ; injector port temperature was 250°C , detector temperature was 250°C . One microlitre of the sample was injected in the splitless mode. Retention time for diazinon was 13.9 min.

Toxicity measurements: Toxicity measurements of irradiated samples were performed by the standard described in the literature (Pogačnik and Franko, 1999).

3. Results and discussion

Pesticide decomposition: Irradiation times between 30 and 120 min at a constant dose rate were chosen to study the dependence of the pesticide decomposition on the absorbed dose. The concentration of the pesticide (C) in the solution decreases exponentially with the exposure time, i.e. with the absorbed dose D :

$$C = C_0 e^{-t/\tau} = C_0 e^{-D/D_\tau}, \quad (2)$$

where C_0 is the initial concentration, while τ and D_τ are the characteristic time and dose constants: $D_\tau = \tau \cdot \dot{D}$.

At irradiation conditions described above (dose rate of 50 mGy s^{-1}), the characteristic time τ of the exponential decrease obtained by a best-fit procedure from the measured data (Fig. 2) was $74 \pm 9 \text{ min}$, and a corresponding dose constant D_τ was estimated to be 220 Gy . Therefore, a 50% degradation of the pesticide in the sample was achieved in $\tau_{1/2} = 51 \pm 6 \text{ min}$, corresponding to the absorbed dose of about 160 Gy .

The major reactions in the water radiolysis involve the formation of e_{aq}^- , OH and H, and in the presence of oxygen also O_2^- , reactive intermediates. As it is known from the literature these intermediates react with high rates with similar organic molecules as diazinon. From the high decomposition yields it is probable that all of the intermediates take part in the destruction of the pesticide. The exponential-like decrease of the pesticide concentration with the irradiation time is probably due to the secondary reactions of the reacted molecules with the reactive intermediates produced in water radiolysis. So there is a chain of consecutive reactions.

During the irradiation with a constant flux of the X-ray beam (i.e. at a constant dose rate), the concentration of the radicals and ions generated by water radiolysis in the solution is maintained at a constant high level,

proportional to the absorbed dose rate. The degradation rate of the pesticide molecules in the water solution at a given moment during the irradiation process is proportional to the concentration of the pesticide in the solution C , and to the concentration of the radicals, which trigger the degradation (and therewith to the dose rate):

$$\frac{dC}{dt} = kC, \quad (3)$$

where k is a reaction constant proportional to the dose rate. Integration of the Eq. (3) gives the exponential time dependence for the pesticide degradation (2) as obtained experimentally. The characteristic time for the pesticide decomposition τ is therefore inversely proportional to the applied dose rate:

$$\tau = \frac{1}{k} \propto \frac{1}{\dot{D}}. \quad (4)$$

The result is confirmed by irradiation of the pesticide at a lower dose rate (18 mGy s^{-1}) i.e. at anode current of 20 mA instead of 45 mA . The characteristic time τ increased for a corresponding factor of ~ 2.3 .

The compounds detected in the irradiation samples suggest that diazinon is mainly converted into 2-isopropyl-4-methyl-6-hydroxypyrimidine just like during hydrolysis shown in Fig. 1. There is no proof for the eventual oxidation of sulphur and formation of more toxic diazoxon, although the toxicity tests of the irradiated samples have shown slightly increased inhibition of enzyme acetylcholinesterase measured by a biosensor. Further investigations on degradation processes of diazinon and its metabolite by X-ray irradiation in combination with toxicity monitoring are in progress.

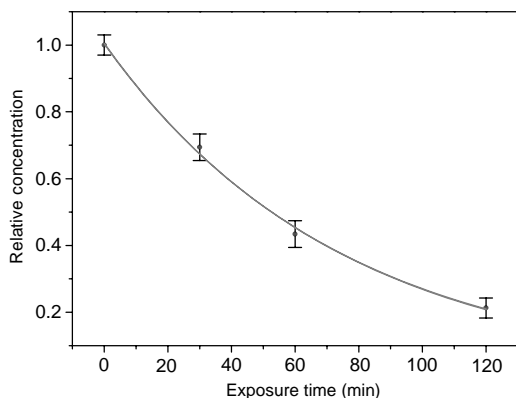


Fig. 2. Decrease in pesticide concentration with time, when exposed to white X-ray beam at a constant dose rate of about 50 mGy s^{-1} : experimental values (dots with vertical error bars), and best-fit exponential function (solid line).

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