Jihočeská univerzita v Českých Budějovicích
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Photochemical Degradation of a Phenyl-urea Pesticide Chlorotoluron

Magisterská práce

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Zemanová, M., 2008: Photochemical degradation of a phenyl-urea pesticide chlorotoluron. Master Thesis, in English. – 27 pp., Faculty of Science, University of South Bohemia, České Budějovice, Czech Republic.

Annotation:
Chlorotoluron photochemical degradation in homogeneous phase (aqueous solutions) was studied. Photolysis by UV radiation, influence of metal (ferric, ferrous) ions, pH, and solvent composition on the reaction rate was investigated. Photosensitizing effect of humic samples was tested. Kinetic characteristics (rate constants, overall quantum yield), products of reactions and extent of mineralization was evaluated.

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28. dubna 2008

Martina Zemanová

Poděkování
Chtěla bych poděkovat svojí školitelce Šárce Klementové, díky níž tato práce vznikla, a která mě po celou dobu studia podporovala. Především bych jí však chtěla poděkovat za trpělivost, kterou se mnou měla.

Contents

Aims of the study

The aim of the study was to research photochemical degradation of phenyl-urea pesticide, chlorotoluron, by UV radiation; to find out if catalysis by ferric ions is possible. Next target was to determinate products of degradation and also to study kinetics of the reactions.

Introduction

The application of herbicides on agricultural soils is a well established effective practice to control weed growth. Another area of herbicide application is roads and railways where herbicides are used to maintain the quality of the track and a safe working environment for the railway personnel (Torstenson, 2001).

Among herbicides, phenyl-urea derivatives represent a prominent group of herbicides. Since their discovery in the early 1950s, the variety and amount of this herbicide group have increased markedly.

Slow biodegradation of these substances (Khadrani et al., 1999; Tomlin, 2003) together with washing and leaching processes lead to their passing to surface and ground waters.

The pollution of waters by herbicides and their by-products is a topic of considerable environmental interest owing to the increasing number of pesticide detection in monitoring studies in aquatic systems conducted in many areas of the world, especially US (Barbash et al., 2001; Godfrey, 1995) and Europe – Germany (Liska et al., 1992), Great Britain (Drage et al., 1998), Greece (Albanis et al., 1998) and Spain (Carabias-Martínez et al., 2000; Carabias-Martínez et al., 2003b).

In several studies, the highest values detected in water samples – up to 1.2 μg/l (Carabias-Martínez et al., 2000; Carabias-Martínez et al., 2002) – were found for chlorotoluron, one of the phenylurea family derivatives.

Chlorotoluron is a selective herbicide firstly reported in 1969 (Tomlin, 2003). The formula of chlorotoluron is shown in Fig. 1. Chlorotoluron is effective both as a residual soil-acting herbicide and a contact foliar spray against germinating grass and broad leaved weeds in many crops, mainly cereals.

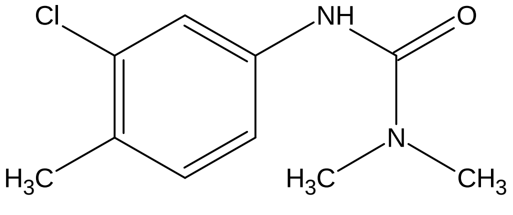


Fig. 1: Formula of chlorotoluron.

Chlorotoluron, as generally most of the phenylurea pesticides, exhibit a great persistence when applied on soil 30 – 40 days, and even greater when leached into water, more than 200 days (Tomlin, 2003).

Biotransformation of chlorotoluron by soil microorganisms (bacterial and fungi) was reported by several authors (Khadrani et al., 1999; Tixier et al., 2002; Bolte et al., 2004). It was shown, that the resistance to the attack of microorganisms is connected with the presence of chlorine atom on the aromatic ring; the major degradation pathway proceeds through hydroxylation of the methyl groups.

Biodegradation by some bacterial strains leads to the formation of very toxic substituted anilines, so the transformation yields compounds even more toxic than the parent herbicide molecule (Tixier et al., 2002; Bolte et al., 2004).

Chlorotoluron was shown to be degraded by light in the presence of iron (III) oxides (Bolte et al., 2004) or iron (III) aquacomplexes (Poulain et al., 2003), by reactive oxygen species such as hydroxyl radicals induced photochemically in the photo-Fenton processes (Benitez et al., 2007), or in the photocatalytic reactions on semiconductors (Lhomme et al., 2005; Haque et al., 2006).

Photochemical behavior of chlorotoluron was studied under various conditions. Tixier et al. (2000) studied chlorotoluron photolysis by wavelengths lower than 300 nm (254, 280 nm) in aqueous solutions and photodegradation of chlorotoluron dispersed on sand (by 290 – 310 nm light). Some products of degradation were identified (see Fig. 2 and Fig. 3).

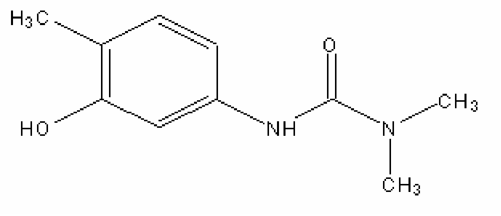
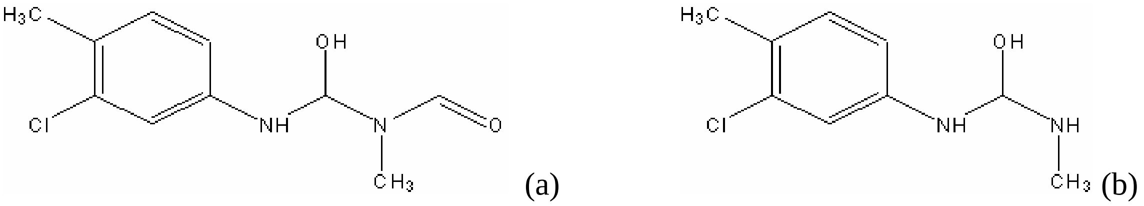


Fig. 2: Product of photodegradation of chlorotoluron identified in water by Tixier et al. (2000).



(a) (b)

Fig. 3: Products of photodegradation of chlorotoluron identified on sand by Tixier et al. (2000).

In water, the substitution of chloride atom by a hydroxyl group occurs (Fig. 2), while on sand the side chain is degraded (Fig. 3)

Lhomme et al. (2005) studied the degradation of chlorotoluron in photocatalytic process using TiO_2 semiconductor as catalyst and irradiation by UV light (365 nm). The influence of parameters such as adsorption capacity, initial concentration of chlorotoluron and TiO_2 forms (coated or in suspension) was investigated. The results showed the importance of operational conditions and reactor geometry on the degradation rate. The analysis of intermediates and products suggested that the reaction begins as a hydroxyl radical attack on the phenyl ring and methyl groups of the chlorotoluron before the opening of the aromatic ring.

Haque et al. (2006) studied the photocatalytic degradation of chlorotoluron in aqueous suspensions of titanium dioxide irradiated by light of 320 nm under variety of conditions such as type of TiO_2, catalyst concentration, substrate concentration, pH, temperature, and in presence of different electron acceptors such as hydrogen peroxide (H_2O_2), potassium persulfate ($K_2S_2O_8$), and potassium bromate ($KBrO_3$) beside molecular oxygen. They found out that using TiO_2 as a catalyst was pH dependent (reaction was slower in alkaline pH) and that electron acceptors enhanced reaction rate – the most efficacious was potassium bromate (enhanced reaction rate from 1.299 mol $l^{-1}min^{-1}$ x 10^{-5} up to 1.642 mol $l^{-1}min^{-1}$ x 10^{-5}). They described three possible degradation pathway of chlorotoluron - (1) substitution of chloride ion by hydroxy group on aromatic ring, (2) demethylation of N group on beside chain, (3) from chlorotoluron arise 3-chloro-4-methylalanine.

Amorisco et al. (2006) studied photocatalytic degradation of chlorotoluron by UV/TiO_2 (240 nm) and they discovered following degradation processes: (1) substitution of chloride ion by hydroxy group on aromatic ring, (2) substitution of methyl group by hydroxy group on aromatic ring, (3) demethylation of N group on beside chain.

Photoinitiated degradation of chlorotoluron in the presence of iron (III) aquacomplexes has been investigated under irradiation at 365 nm by Poulain et al. (2003) and at 254 nm by Benitez et al. (2007). Poulain et al. (2003) studied degradation of chlorotoluron in mixture with ferric ions at various oxygen concentrations and in the presence of 2-propanol. They used 2-propanol as a hydroxyl radicals scavenger and they found out that the higher concentration of oxygen in the reaction mixture the higher reaction rate. They also described degradation products presented in Fig. 4.

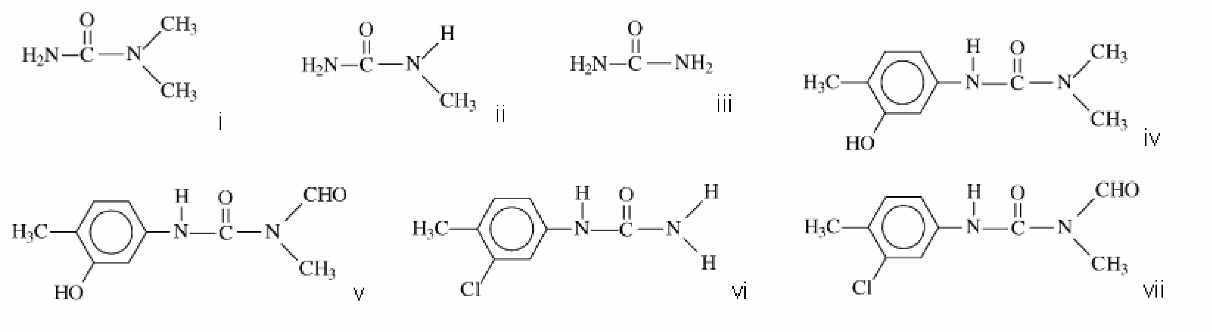


Fig. 4: Degradation products discovered by Poulain et al. (2003).

Benitez et al. (2007) studied degradation of chlorotoluron with the use of Fe(II) in mixture with H_2O_2 (so-called photo-Fenton system) in various concentrations. They achieved degradation rate 7.5 mol $l^{-1}s^{-1}$.

Benitez et al. (2006) studied photochemical degradation of phenyl-urea herbicides (linuron, chlorotoluron, diuron, isoproturon) by UV irradiation (254 nm) and UV combined with H_2O_2 in two various concentrations (1×10^{-3} M and 5×10^{-3} M) in different conditions as pH and temperature. They found out that reaction was slower in alkaline pH values and in lower temperatures. The reaction best proceeded using UV/ H_2O_2 (5×10^{-3} M). They also tested influence of solvent (ultra-pure water, mineral water, groundwater and lake water) on the reaction, and found out that the degradation was fastest in ultra-pure water. They used *tert*-butyl alcohol as a scavenger of hydroxyl radicals and the reaction was almost stopped.

Analyses of phenyl-urea pesticides are usually carried out by using chromatographic methods. High performance liquid chromatography (HPLC) is often used for phenyl-urea pesticides separation (Carabiaz-Martínez et al., 2002; Lin et al., 2003; Goger et al., 2001), UV or mass spectrometry is used for detection (Carabiaz-Martínez et al., 2004). Since European limits for pesticides concentration are 0.1 μg/l - for a mixture of pesticides 0.5 μg/l (Council Directive, 1998), pre-concentration of samples is often necessary (Gerecke et al., 2001; Carabiaz-Martínez et al., 2003a; Carabias-Martínez et al., 2003b; Carabiaz-Martínez et al., 2004; Lin et al., 2003).

In the presented thesis, I investigated photoinitiated degradation of chlorotoluron in homogenous aquatic media under UV irradiation. I studied direct photolysis, influence of metal (iron III) ions on the reaction and photosensitizing effect of several humic samples.

The aim of the study was to describe kinetic characteristics of the reactions, to identify some of the products and evaluate the importance of photochemical degradation as a natural degradation pathway in the aquatic environment.

Material and Methods

Chemicals

Chlorotoluron (3-(3-chloro-4-methylphenyl)-1-1-dimethylurea), purity 99.0 %, was obtained from Dr Ehrenstorfer (Germany). Three types of stock solutions of chlorotoluron were prepare: a) 5 mg of Chlorotoluron in 500 ml of water was stirred for 12 hours; b) 5 mg of chlorotoluron was diluted in 5ml of methanol (Fluka, HPLC grade) and diluted with water up to 100 ml; c) 5 mg of chlorotoluron was diluted in 100 ml of methanol. Deionized water was prepared by Filtr Premier CDP 6920 (USA). $FeCl_3 \cdot 6H_2O$ purchased from Lachema. Chemicals for actinometry (iron (III) sulphate hydrate, 1,10-phenantroline monohydrate, sodium acetate, potassium oxalate monohydrate, glycine), H_2SO_4 and H_2O_2 were purchased from Sigma.

Methods

UV/VIS absorption spectra were measured by UV/VIS spectrophotometer Shimadzu, UV 1601, with UV Probe software.

Irradiation was carried out in a photochemical reactor Rayonet RPR 100 equipped with RPR 3000 Å lamps (254 – 350 nm, maximum intensity 300 nm). Chlorotoluron was irradiated in either glass or quartz cuvettes (glass cuvettes were used when filtered radiation – $\lambda > 300$ nm was needed). Irradiation was performed for 90, resp. 180 minutes.

Actinometry measurement: Actinometry was carried out according to Murov et al. (1993) using an optically thick solution of potassium ferrioxalate.

Potassium ferrioxalate actinometry is based on the reaction:

$$2Fe^{3+} + C_2O_4^{2-} \xrightarrow{h\upsilon} 2\,Fe^{2+} + 2CO_2 \tag{1}$$

The amount of ferrous ions produced during irradiation was measured via spectrophotometric determination of its 1,10-phenantroline complex at 510 nm. (Ferric ions form only a week complex with 1,10-phenantroline which is transparent at 510 nm).

The following solutions were prepared for actinometry:

A - 0.2 M $Fe_2(SO_4)_3$: 10 g $Fe_2(SO_4)_3 \cdot n\,H_2O$ + 5.5 ml conc. H_2SO_4 was dissolved and diluted with double deionized water to the final volume of 100 ml. 0.3 g of glycine was added;

B - 1.2 M $(COOK)_2$: 22 g $(COOK)_2$ was dissolved in deionized water and diluted to the final volume of 100 ml;

C - buffer solution: 8.2 g of sodium acetate + 1 ml conc. H_2SO_4 dissolved and diluted with deionized water to the final volume of 100 ml;
D – phenantroline: 0.2 % solution of 1,10-phenantroline monohydrate in deionized water.

When actinometer solution was needed, 5 ml of the $Fe_2(SO_4)_3$ solution and 5 mL of the $(COOK)_2$ solution was mixed in a 100 ml volumetric flask and was diluted to the mark with water. The stock solutions have a shelf life of about one month.

Intensity measurement:

a) a volume of the $K_3Fe(C_2O_4)_3$ solution equal to that of the sample to be irradiated was put into reaction vessels (all steps described in the procedure of intensity measurements had to be carried out in the dark or under the dim red light);
b) the ferrioxalate solution was irradiated in appropriate cuvette for an appropriate period of time – it had to be determined experimentally, to give, after working-up the sample, an absorbance between 0.2 - 1.8; for the reaction vessel used in this work the suitable time interval was 5 – 30 seconds and 10 – 40 seconds for quartz and glass cuvette, respectively;
c) an aliquot (1 ml) of irradiated solution was transferred into a flask with 2 ml of 1,10-phenantroline solution (solution D) and 0.5 ml of buffer solution (solution C);10 ml of water was added and the solution was gently mixed;
d) a blank sample was prepared by using o non-irradiated volume of actinometer equal to the aliquot of irradiated solution withdrawn;
e) absorbance of the solutions (irradiated and non-irradiated) was measured at 510 nm and the difference was taken; absorbance of the blank should be checked to test the quality of the actinometer solution – if an absorbance value greater than A = 0.06 is obtained for the blank, a new solution should be prepared).

Calculation of light intensity (I):

From the values given by Murov (1993), the appropriate quantum yield for ferrous production was chosen (for our calculation the value of $\Phi = 1.24 \times 10^{-5}$ ein min^{-1}).

Using the absorbance (A) obtained, the intensity I (in einstein/min) was calculated by the following equation:

$$I = (AV_2V_3)/(\varepsilon d\Phi_\lambda tV_1) \qquad (2)$$

where

A – Absorbance (at 510 nm) of irradiated actinometer solution corrected for absorption of blank

d – Path lenght (in cm) of absortion cell used in measurement of A

ε – Extinction coefficient of ferrous 1,10-phenanthroline complex at 510 nm (~1.11 x 10^4 $Lmol^{-1}cm^{-1}$)

Φ_λ – quantum yield of ferrous production at wavelength of light used

V_1 – Volume (in mililiters) of irradiated actinometer solution withdraw

V_2 – Volume (in liters) of actinometer irradiated

V_3 – Volume (in mililiters) of volumetric flask used for dilution of irradiated aliquot (10 mL)

t – irradiated time in minutes.

The obtained values of light intensity are 1.22 x 10^{-5} einstein/min and 7.1x 10^{-6} enstein/min for quartz and glass cuvette, resp., under the experimental condition used in the study.

HPLC was performed by the use of high pressure pump ConstaMetric 3200 (Thermo Separation Products), UV detector Delta Chrom UVD 200 (Watrex) and the C18 column Reprosil 100, 250 x 4 mm, filled with 5µm particles. The detector was set at 245 nm. The mobile phase was methanol-water (60:40, v/v). The flow rate was 1mL/min. The volume injected was 20 µl by the injector Rheodyne 7725i. The mobile phase was degassed by ultrasound Kraintex 941 44 HUL (Slovakia). The chromatographic station equipped with program CSW 1.7 was used to evaluation of the obtained data.

HPLC/MS conditions

Analyses were performed on LCQ quadrupole linear ion trap mass spectrometer (Thermo Electron Corp., U.S.A.) in ESI ionization mode. For chromatographic separation, reversed phase column Synergy Hydro RP80A 150x1mm, 4um particle size was used. Column temperature was set at 30°C. Mobile phase: 55% methanol in water (with 10mM ammonium acetate buffer) and flow rate 50u l/min.

Ion chromatography

Ion chromatography was performed by (DIONEX IC 25) with 10 mM KOH as an eluent (eluent generator EG 40), column Ion Pack AS 17.2 mm diameter, injection volume 8 and 10 µl. Data were evaluated by chromatographic software Chromeleon 6.20.

Total organic carbon measurement

Total organic carbon (TOC) was measured by TOC analyzer Shimadzu model TOC 5000 A, in which organic compounds are chemically oxidized (mixture of sulfuric acid and hydrogen peroxide), combusted by heat (Pt catalyst, 600 °C); the resulted CO_2 was detected by IR detector.

Reaction kinetics

For kinetic analysis, first-order reaction rate model and model for consecutive reactions were adopted from Chang (2005). Reaction rate constants were obtained by using the first-order decay equation

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{3}$$

where [A] represents the concentration of chlorotoluron at the time t, $[A]_0$ is the initial concentration of chlorotoluron, k is the first-order reaction rate constant. When ln [A] os plotted against irradiation time t, slope of the straight line gives the value –k.

In the intermediates and product analysis, I used the consecutive reaction model for evaluation of the main intermediate degradation rate constant. In consecutive reaction described by the scheme

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{4}$$

where A is a reactant, B is an intermediate and C is a product, and k_1 and k_2 are the rate constants of respective reactions, the time course of concentration B depends on the ratio k_1 : k_2.

If the rate of intermediate formation is equal to its decay, that is if $k_1 = k_2$, the time courses of the reactant and the intermediate are represented by the curves as in Fig. 5.

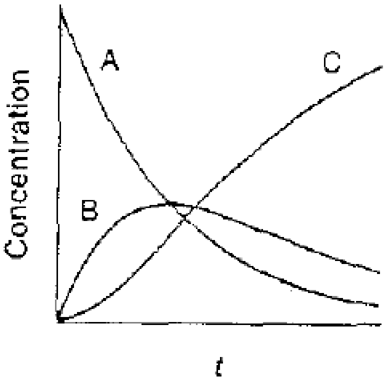


Fig. 5: Time course of intermediate concentration for $k_1 = k_2$ in a consecutive reaction.

Results

Chlorotoluron absorbs electromagnetic radiation of wavelengths shorter than 305 nm (see Fig. 6).

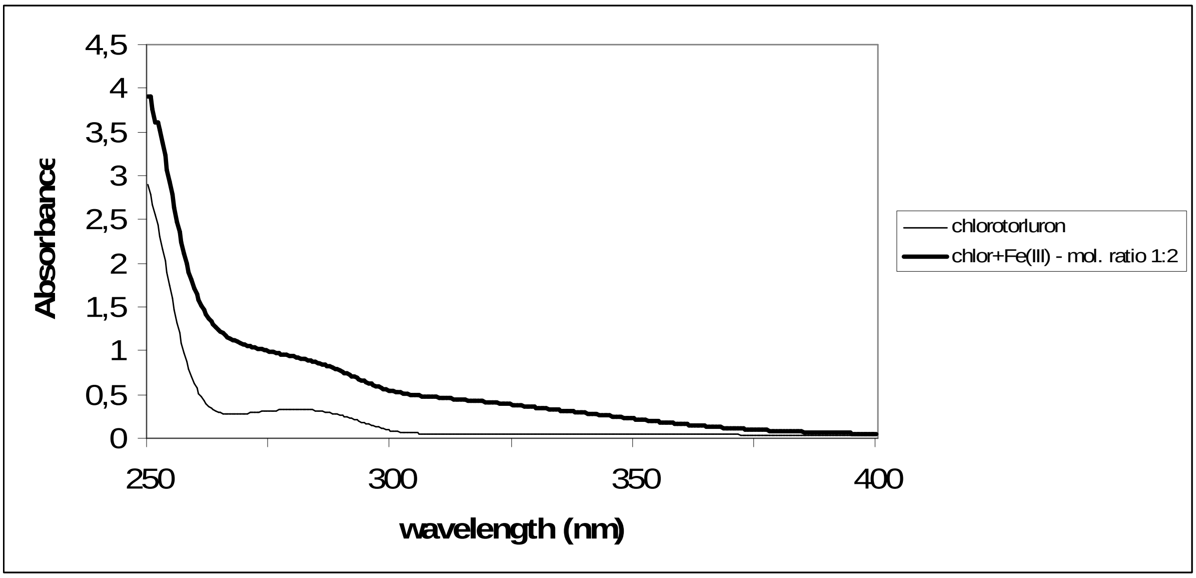


Fig. 6: Absorbance of chlorotoluron concentration with and without addition of Fe (III).

Addition of ferric ions to the chlorotoluron solution causes an increase of absorption and broadening of the absorbed wavelengths range (Fig. 6). The absorption spectrum of the Fe(III) – chlorotoluron complex shows absorption up to 375 nm, and the absorption maximum is 5 times higher than with chlorotoluron alone.

Irradiation of chlorotoluron (without any metal ions added) by the radiation of wavelengths shorter than 300 nm leads to chlorotoluron degradation (Fig. 7).

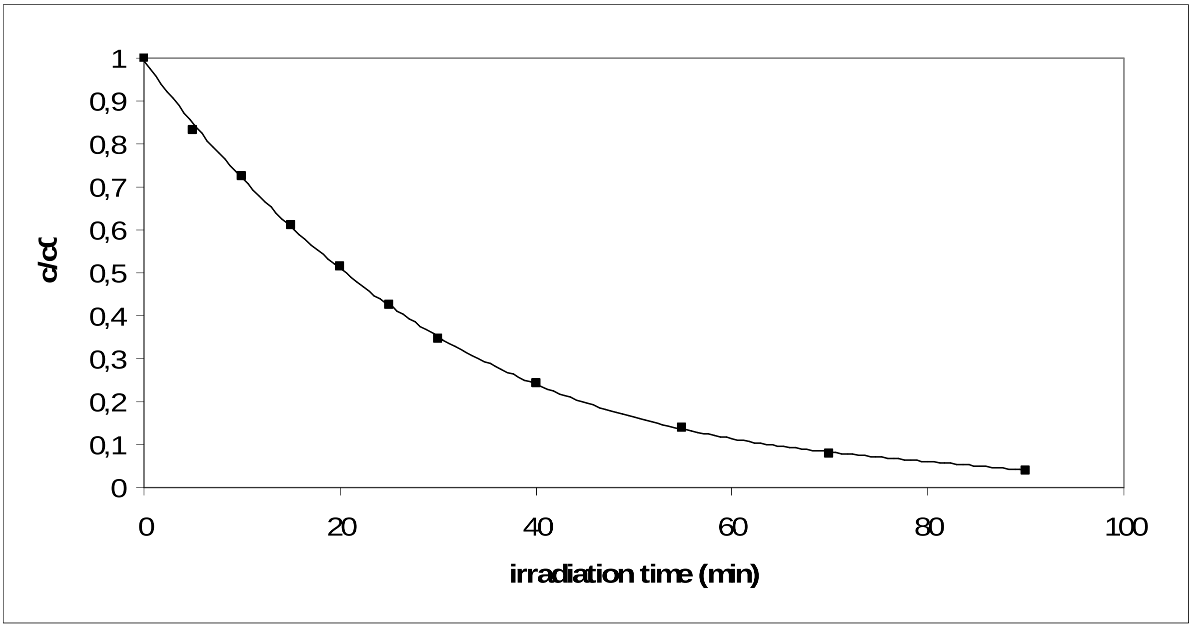


Fig. 7: UV degradation of chlorotoluron (without glass filter).

Almost all the substrate is degraded in 90 minutes of irradiation. The first-order reaction rate constant for the reaction is 0.036 min^{-1}.

If glass filter is used to cut off the environmentally irrelevant short-wavelength radiation (under 290 nm), almost no reaction is observed (first-order reaction rate constant is 0.001 min^{-1}), since the incident light is not absorbed by the chlorotoluron molecules.

As shown in Fig. 6, chlorotoluron form a complex with ferric ions which absorbs high-energy solar radiation. I studied therefore whether the ferric ions could affect the reaction. Results are summarized in Table 1.

addition of Fe (III)	**molar ratio (clt:Fe)**	**k (min^{-1})**
without		**0.001**
8.9 x 10^{-5} mol/l	2:1	**0.001**
4.45 x 10^{-4} mol/l	1:2	**0.003**
8.9 x 10^{-4} mol/l	1:4.5	**0.003**

Table 1: Influence of quantity of additional Fe (III) to the rate of the reaction (used glass filter).

It is obvious that irradiation of the substrate by longer wavelength (glass filter was used in the experiments) leads only to insignificant increase of the reaction rate, even if ferric ions : chlorotoluron molar ration was 4.5 : 1.

Since ferrous ions (not ferric ones) are usually the catalytically active form, I tested in the next step whether the ferric ions were reduced to ferrous ones during irradiation; the result of the experiment showed that all ferric ions were reduced within five minutes from the start of irradiation.

When absorption spectrum of chlorotoluron plus ferrous ions was measured, I found out that it is identical to the absorption spectrum of chlorotoluron at the same concentration. It suggests that the reaction mixture of chlorotoluron with added ferric ions, where ferric ions are quickly reduced under irradiation, cannot absorb the incident radiation and thus the reaction cannot proceed.

Fig. 8 shows degradation of chlorotoluron by the unfiltered light with and without addition of ferric ions (glass filter was not used in this case).

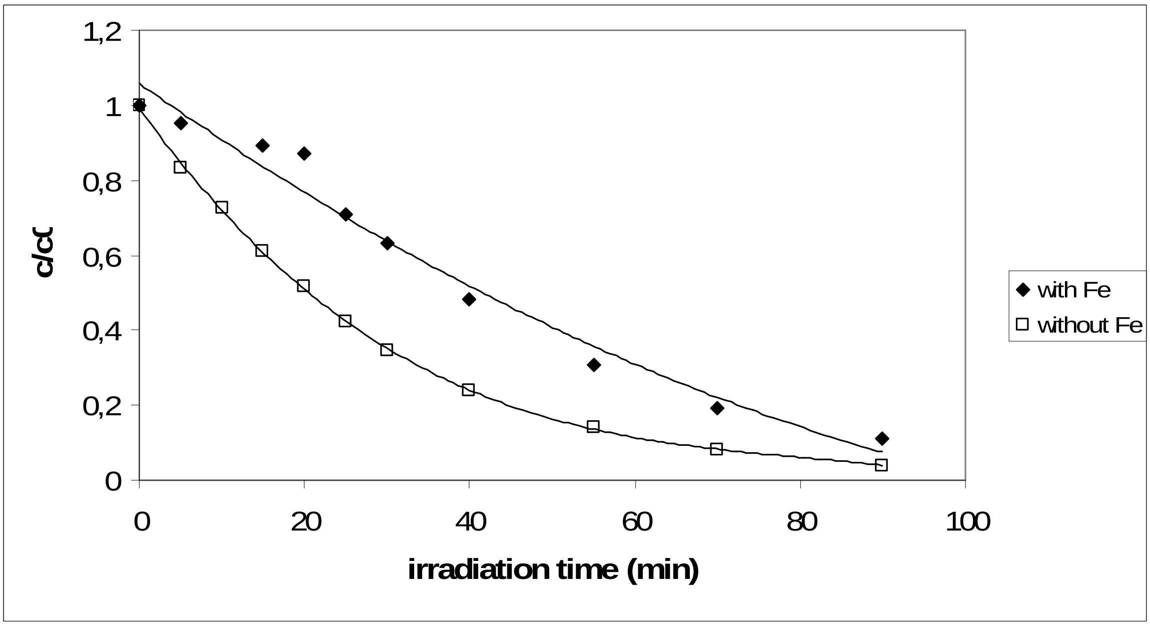


Fig. 8: UV degradation of chlorotoluron without using filter and with or without addition of Fe (III).

Reaction rate with the addition of ferric ions slightly decreases (k = 0.025 min^{-1}) in comparison with the reaction mixture without ferric ions added (k = 0.036 min^{-1}).

The influence of pH on the reaction (with unfiltered light) was tested in a broad range of pH values. Fig. 9 shows the chlorotoluron degradation under the highest and lowest pH values used in the experiment, i.e. pH = 2.0 and pH = 11.0, resp.

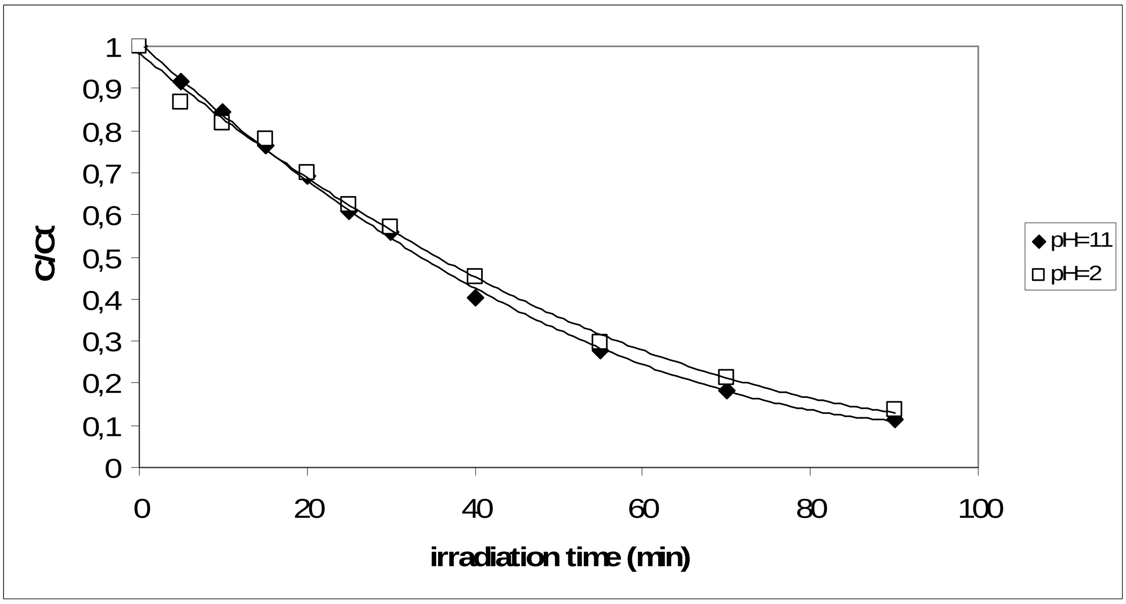


Fig. 9: Influence of pH to degradation of chlorotoluron (without glass filter).

As can be seen, the reaction proceeds at the same rate in the strongly alkaline and strongly acidic solutions.

Chlorotoluron, as a compound of low polarity, is usually dissolved in small amount of methanol before dilution with water to the final concentration. Since methanol may affect photochemical reactions, I wanted to find out whether the methanol could have an effect on the chlorotoluron degradation. I carried out an experiment with three chlorotoluron solutions: a) chlorotoluron dissolved in methanol; b) chlorotoluron dissolved in a mixture methanol-water (methanol : water = 5 : 95, v/v); c) chlorotoluron dissolved in Milli-Q water. The first-order reaction rate constant for the three reactions are given in Table 2.

solvent	**k (min^{-1})**
water	**0.065**
methanol/water	**0.036**
methanol	**0.012**

Table 2: First-order rate constants for chlorotoluron degradation in solvents with different content of methanol.

The reaction proceeds most readily in the Milli-Q water; reaction is slowed down if 5% methanol is used as a solvent. In 100 % methanol as a solvent, the reaction rate has the lowest value (3-times lower in comparison with water-methanol, and 6-times lower in comparison with water as a solvent).

In surface natural waters, humic substances may be present and may affect photoinitiated reactions. Therefore I tested the influence of humic substances on chlorotoluron photodegradation. Two humic samples were used for the experiments – peat bog water and a solution of humic acid isolated from upper soil forest horizon. The results are shown in Fig. 10.

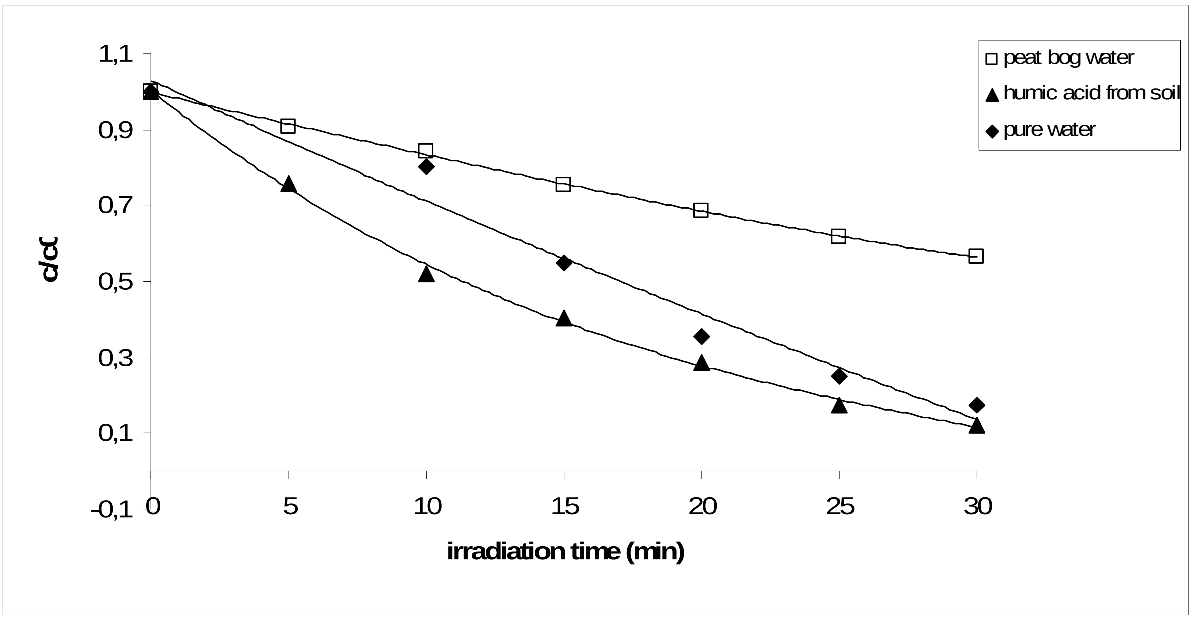


Fig. 10: Degradation of chlorotoluron in the presence of humic acids (unfiltered radiation).

The first-order reaction rate constants are summarized in Table 3. We can see that soil humic acid has a slight influence on chlorotoluron degradation rate – the reaction rate slightly increases (the first-order reaction rate constant has the value 0.070 min^{-1}).

Presence of	**k (min^{-1})**
Peat bog water	**0.019**
Humic acid from soil	**0.070**
Pure water	**0.065**

Table 3: Rate constants of chlorotoluron degradation in the presence of humic acids

In the presence of the peat bog water, the chlorotoluron degradation proceeds significantly more slowly in comparison with the reaction rate in deionized water.

I focused also on the products of chlorotoluron photochemical degradation.

Fig. 11 shows chlorotoluron degradation during 90 minutes irradiation, its main intermediate (curve – “main intermediate”) produced by the reaction (curve - “chlorotoluron”) and release of chloride ions (curve – “chloride ions”).

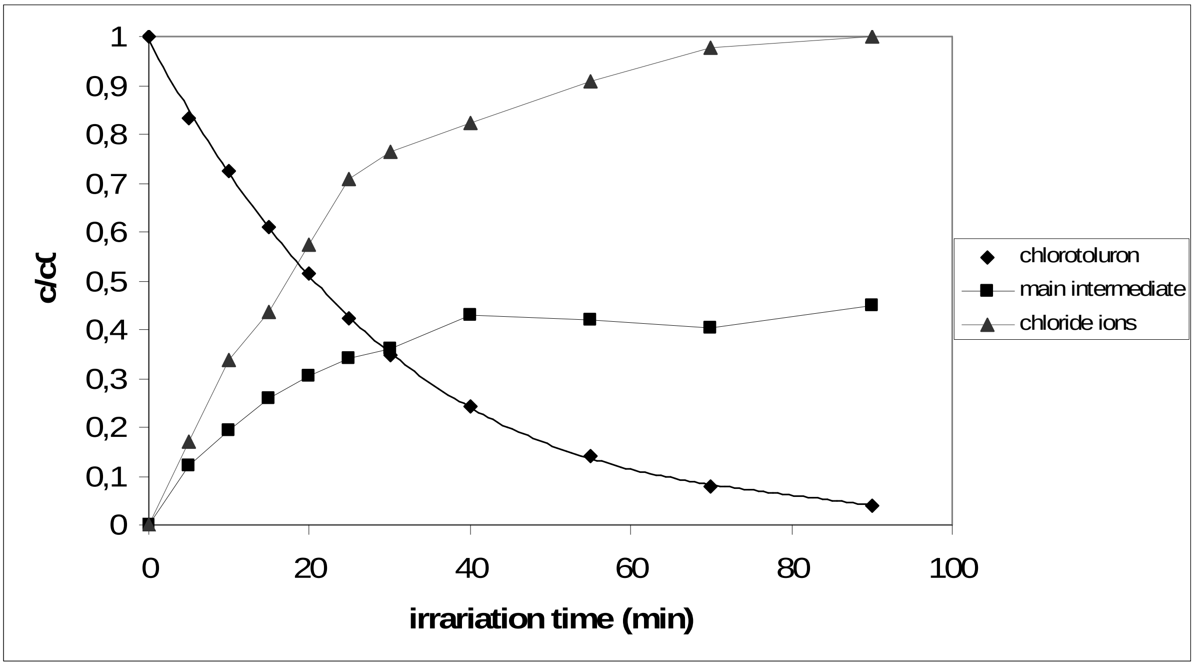


Fig. 11: UV degradation of chlorotoluron, its main product and chlorides release (without glass filter).

I assumed that the major product shown in HPLC chromatogram was formed in the process of substitution of chloride atom in the chlorotoluron molecule by hydroxyl group. Therefore I tested the reaction mixture for the chloride ions presence. The result is presented in Fig. 11 – curve “chloride ions”; the chloride ions concentration increased in the reaction mixture with 1 : 1 stoichiometry with respect to chlorotoluron degradation. This shows that one of the first steps in the degradation is releasing the chloride ion from aromatic cycle.

Fig. 12 shows a rise of minor intermediates and products of the chlorotoluron degradation. One main and approximately six minor products are generated in the reaction.

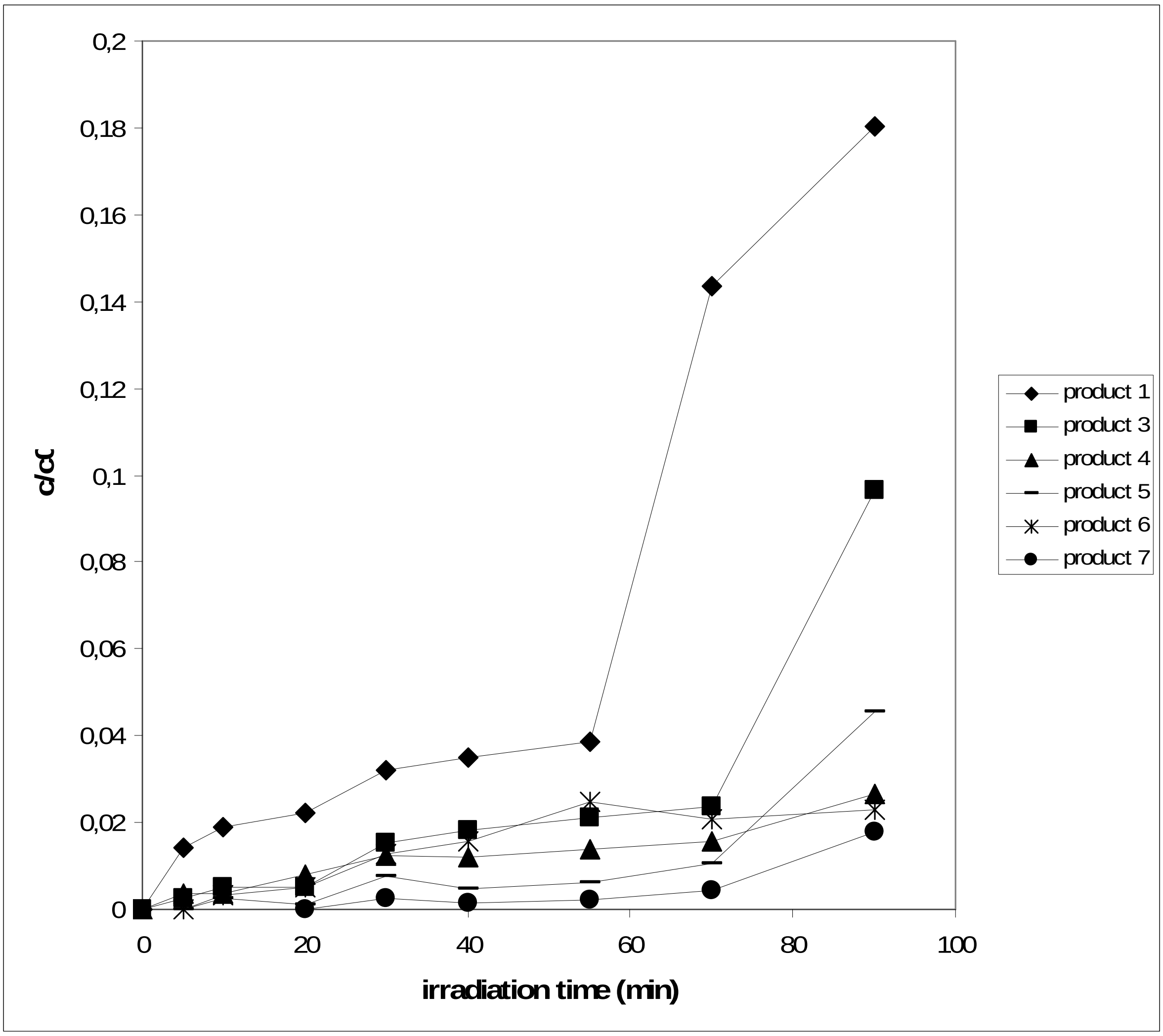


Fig. 12: Minor intermediates and products of chlorotoluron degradation detected by HPLC.

The HPLC analyses show one major intermediate and a series of minor intermediates and products formed mostly from the first major intermediate in consecutive reactions (see Fig. 11 and Fig. 12) – time delay in formation of products 3 – 7.

The overall quantum yield of the reaction calculated according to the equation 5.

$$\Phi = \frac{\text{number of degraded chlorotoluron molecules}}{\text{number of incident light quanta}} \qquad (5)$$

Number of incident light quanta was recieved from actinometry (1.2 x 10^{-5} ein min^{-1}) and number of degraded molecule (1.02 x 10^{-7}) is calculated from HPLC data. The quantum yield gained from the initial states of the reaction is 1.7 x 10^{-3}.

Fig. 13 shows mass spectra of chlorotoluron after 90 minute irradiation. Peak 213 is the peak of chlorotoluron molecule. Peak 195 is the peak of the main product where was substitute chloride ion by OH ion in the parent molecule.

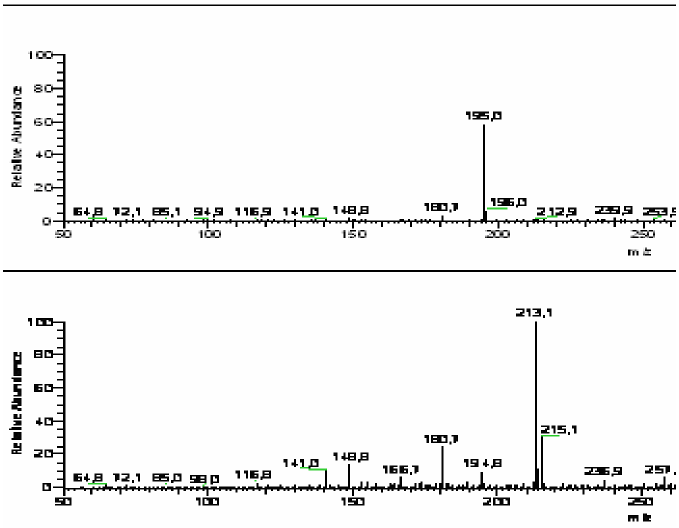


Fig. 13: Mass spectra after 90 minute irradiation

Mass spectroscopy provides a supportive evidence that the major intermediate in chlorotoluron degradation pathway is its hydroxy-derivative with hydroxyl group at the place of original chloride atom (Fig. 13).

Analysis of total organic carbon (TOC) contents in the reaction mixture under irradiation revealed that degradation proceeds to CO_2 as a final product; after 90 minutes of irradiation, 19.3 % of chlorotoluron carbon atoms were found to be oxidized to carbon dioxide.

Discussion:

Chlorotoluron cannot be photochemically degraded by light with wavelengths longer than 305 nm, i.e. by light naturally occuring at the earth´s surface.

Studies, where chlorotoluron degradation was achieved by radiation of wavelength longer than radiation absorbed by the substrate needed catylytic production of the oxidizing species – e.g. Fenton agent with ferrous ions and hydrogen peroxide (Benitez et al., 2007; Poulain et al., 2003), even in this system, long irradiation were needed for a pronounced effect (7 hours – Poulain et al., 2003).

Ferrous ions themselves have not shown any catalytic effect, and because they do not form an absorbing complex, direct excitation with longer wavelength is not possible.

Chlorotoluron forms a complex with ferric ions and this complex has a molar absorption coefficient approx. 1.3 times higher at the wavelength of chlorotoluron absorption maximum; moreover it absorbs radiation in broader range of wavelength, up to 350 nm. Thus I expected that addition of ferric ions might have a positive effect on the reaction rate. However, no significant effect was achieved, because ferric ions are quickly and quantitatively reduced in the reaction mixture and the non-absorbing Fe(II) – chlorotoluron complex arises. The same result was obtained by Benitez et al. (2007).

With other pesticides, photocatalytic effect of ferric ions (i.e. photochemical production of a catalytically active form a catalyst) was observed, e.g. in case of triazine herbicide atrazine (Klementová et al., 2000).

Under our conditions the pH has no effect on the reaction rate. It is in agreement with the assumption that degradation in our reaction mixture proceeds via direct photolysis after chlorotoluron excitation (the assumption is supported by the first-order reaction kinetics of the reaction). The same independence on pH was reported by Benitez et al. (2006) who made experiments under similar conditions as I did; he obtained almost the same degradation rates. For chlorotoluron in ultrapure water obtained first-order rate constant 0.070 min^{-1} for the degradation (my result under similar conditions is the first-order rate constant of the value 0.065 min^{-1}.).

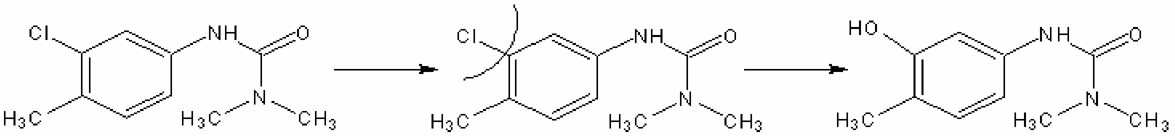
Haque et al. (2006) observed slightly higher degradation rates under acidic pH in degradation of chlorotoluron on TiO_2 (heterogeneous catalysis using semiconducters for producing hydroxyl radicals) using light of 365 nm; the rates slowly decreased with increase in pH (second-order reaction rates lay in the range from 1.653 mol l^{-1}min^{-1} x 10^{-5} for pH = 1.2 to 1.159 mol l^{-1}min^{-1} x 10^{-5} for pH = 11.2). The effect of pH in heterogeneous catalyst has a completely different mechanism from our reaction mixture, the protons participate in production of reactive oxygen species from H_2O an O_2 on TiO_2.

More researchers were trying to achieve chlorotoluron degradation by heterogeneous catalysis on semiconductors, especially TiO_2, but even with this effective method long irradiation times are needed – 8 hours (Parra et al., 2002), 12 hours (Lhomme et al., 2005).

Humic acids may act as sensitizers in photochemical processes and they can also produce hydroxyl radicals. Thus humic acids are considered to be a significant mediator of photochemical degradation of pollutants in natural waters, especially if the pollutants do not absorb the sun radiation reaching the earth´s surface. As shown in the results, I tested the chlorotoluron degradation in the presence of two kinds of humic acids – a peat bog water of high absorbance and a soil humic acid extract. Soil humic acid causes a slight increase of reaction rate. I know that both soil humic acid, as well as peat bog water, (Helekalová, thesis in prep.) produce hydoxyl radicals (peat bog water produces approximately two times more hydroxyl radicals than soil humic acid). These two humic samples differ significantly in absorption intensities (for wavelength 250 nm were measured absorption intensities for peat bog water $A_{250} = 2.5$ and for solution of humic acid $A_{250} = 0.5$) (Helekalová, thesis in prep.). We can assume that the increase of reaction rate in the presence of soil humic acids is the consequence of the contributions of both direct photolysis and hydroxyl radical oxidation of chlorotoluron degradation. The reaction is slower in the sample with peat bog water. It may be caused by inner filtration, because the sample contains highly coloured humic acids. If I compared influence of humic acids on the photodegradation of atrazine, also a negative effect on the reaction rate was observed, the reaction was slower in the presence of humic acids (Klementová et al., 2003), although different humic acids were used in the atrazine study.

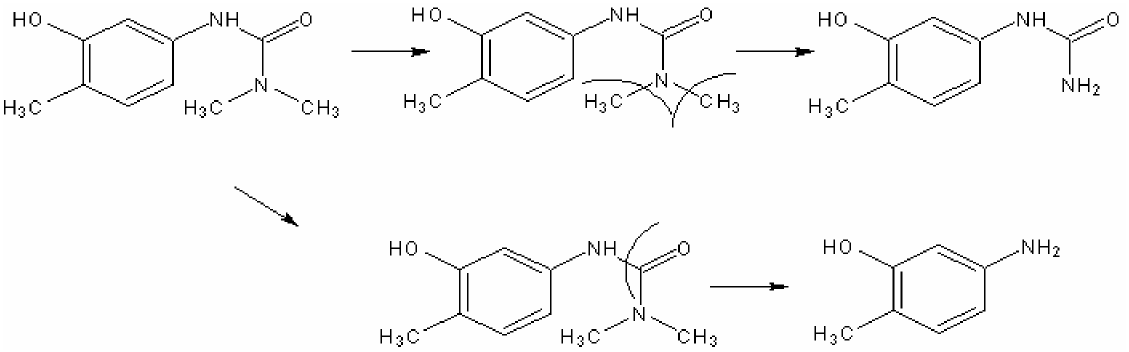
Reaction rate of chlorotoluron photodegradation depends on the type of solvent. If methanol was part of the solvent, the reaction proceeded more slowly. Since methanol was shown to be able acting as scavenger of hydroxyl radicals (Häggblom et al. 1993), this might be the reason for slowing down the reaction. Studies of chlorotoluron degradation in the presence of other alcohols, 2-propanol (Poulain et al., 2003) and *tert*-butyl alcohol (Benitez et al., 2006), support such an assumption.

According to the literature, two major degradation pathways can be distinguished in chlorotoluron degradation. In the first one, the chloride ion on the aromatic ring is substituted by a hydroxy group in the first step (Poulain et al., 2003; Haque et al., 2006; Lhomme et al. 2005) as shown in scheme 1.



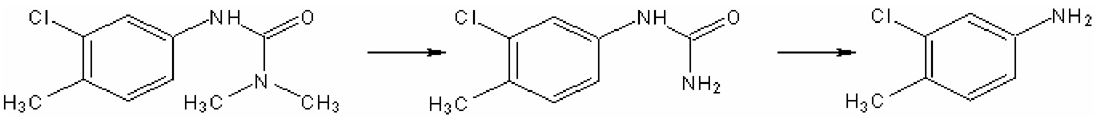
Scheme 1: First step of the chlorotoluron photodegradation.

On the basis of the information from the literature, I suggest possible degradation steps, such as demethylation of hydroxyderivative (main product of the degradation). Other possible degradation step is the degradation of hydroxyderivative up to 3-hydroxo-4-methylaniline. It means that the degradation proceeds as the gradual degradation of the side chain, as shows the reaction scheme 2.



Scheme 2: Gradual degradation of chlorotoluron´s side chain.

In the second possible pathway, the chlorotoluron is firstly demethylated on the N atom of the side chain, secondly the side chain is gradually degraded, as shown in scheme 3.



Scheme 3: Second possible degradation pathway of chlorotoluron.

Scheme 1 agrees with data reported by Tixier et al. (2000), Haque et al. (2006), Amorisco et al. (2006), Poulain et al. (2003); it also agrees with my results. Poulain et al. (2003) determined and identified intermediate of scheme 3. Haque et al. (2006) reported intermediate and product of scheme 3.

Poulain et al. (2003) achieved total mineralization after 25 hours irradiation (they irradiated chlrotoluron in mixture with Fe(III) by the light with the wavelength 365 nm) .

To summarize the results, it does not appear that photochemical degradation might be expected to play a significant role in chlorotoluron degradation in the aquatic environment. The degradation needs either high-energy UV radiation for photolysis or semiconductor catalyst for heterogeneous catalytic reaction or an addition of catalyst plus oxidative species (Fe + H_2O_2) for oxidation. High-energy UV radiation is not available in the environment at the earth surface – i.e. near water body levels; for the heterogeneous as well as for the homogeneous catalysis, special catalysts plus oxidative species are needed.

Thus – with chlorotoluron – photochemical degradation will remain only a possibility for waste water treatment.

Conclusions

Chlorotoluron is photochemically degradable in homogeneous aqueous solutions if irradiated by light capable of photolytic splitting of the molecule. Homogeneous photocatalysis by ferric ions does not occur in the reaction system. Humic substances have not a pronounced photosensitizing effect in the reaction.

Photolysis proceeds via numerous intermediates, the first step is a substitution of chloride ion by hydroxy group; final products of the photolysis reaction are carbon dioxide and water.

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