



# Photodegradation of clopyralid in TiO<sub>2</sub> suspensions: Identification of intermediates and reaction pathways

Daniela V. Šojić, Vesna B. Anderluh, Dejan Z. Orčić, Biljana F. Abramović\*

Faculty of Sciences, Department of Chemistry, Trg D. Obradovića 3, 21000 Novi Sad, Serbia

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## ABSTRACT

The work is concerned with the kinetics, identification of intermediates and reaction pathways of the photocatalytic degradation of the herbicide clopyralid (3,6-dichloropyridine-2-carboxylic acid) in UV illuminated aqueous suspensions of TiO<sub>2</sub> (Degussa P25). In the investigated concentration range (0.5–3.0 mM) the photocatalytic degradation kinetics of clopyralid in the first stage of the reaction follows approximately a pseudo-first kinetic order. The highest reaction rate was observed at 4 mg mL<sup>-1</sup> of catalyst concentration, the apparent activation energy of the reaction being 7.74 kJ mol<sup>-1</sup>. The effect of the presence of hydrogen peroxide, potassium bromate, and ammonium persulfate, acting as electron acceptors along with molecular oxygen, were also studied. By studying the effect of ethanol as a hydroxyl radical scavenger it was shown that the heterogeneous catalysis takes place mainly via hydroxyl radicals. The reaction intermediates (3,6-dichloropyridin-2-ol, 3,6-dichloro hydroxypyridine-2-carboxylic acid, and 3,3',6,6'-tetrachloro-2,4'-bipyridine-2'-carboxylic acid) were identified and the kinetics of their appearance/disappearance was followed by LC–MS/MS (ESI+). Tentative photodegradation pathways were proposed and discussed.

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## 1. Introduction

Many pyridine derivatives have found widespread use as pesticides [1]. Because of their frequent use, chemical stability and resistance to biodegradation, there is a strong need for finding efficient methods for their removal and transforming to the products that are not harmful to the environment. Since heterogeneous photocatalysis with titanium dioxide as semiconductor appeared as one of the most efficient methods for eliminating a number of pesticides from water [2–5], study of the efficiency of the photocatalytic degradation of pyridine derivatives has recently attracted significant attention of researchers [4,6–12].

Clopyralid (3,6-dichloropyridine-2-carboxylic acid, CAS No. 1702-17-6, C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>NO<sub>2</sub>, M<sub>r</sub> 192.00), is a systemic herbicide from the chemical class of pyridine compounds, i.e., pesticides of picolinic acid. Clopyralid has been used effectively for controlling annual and perennial broadleaf weeds in certain crops and turf. It also provides effective control of certain brush species on rangeland and pastures [13]. The acidic form of clopyralid and three clopyralid salts (triethylamine, triisopropylamine, and monoethanolamine) [14],

which are very soluble in water, are commonly used in commercial herbicide products. Because they do not adsorb to soil particles, and are not readily decomposed in some soils, they may leach into groundwater. Groundwater may be contaminated if clopyralid is applied onto the areas where soils are very permeable and the water table is shallow. There is a potential for clopyralid to contaminate groundwater if it is applied to soils containing sinkholes or severely fractured surfaces [15]. As reported in the literature [16], it is one of the pesticides that is often found in drinking water.

In our recent paper [17] we studied the stability of water solutions of clopyralid in the presence/absence of daylight at pH 1.0–9.0. It was found that the water solution of clopyralid was stable for at least 2 months. Because of that we have also carried preliminary investigations of the efficiency of photocatalytic degradation of clopyralid in the presence TiO<sub>2</sub>. As photocatalytic degradation appeared to be more efficient than direct photolysis, the aim of this work was to identify the intermediates and reaction pathways of the photocatalytic degradation of clopyralid in the UV-illuminated aqueous suspensions of TiO<sub>2</sub> (Degussa P25). To this end we studied the effects of the substrate and catalyst concentrations, pH, temperature, hydroxyl radical (OH<sup>•</sup>) scavenger, as well as the effect of several electron acceptors on the rate of this degradation reaction. Finally, some intermediates were identified and tentative photodegradation pathways were proposed.

\* Corresponding author. Tel.: +381 21 4852753; fax: +381 21 454065.

E-mail addresses: [daniela@ih.ns.ac.yu](mailto:daniela@ih.ns.ac.yu) (D.V. Šojić), [orcicedejan@gmail.com](mailto:orcicedejan@gmail.com) (D.Z. Orčić), [abramovic@ih.ns.ac.yu](mailto:abramovic@ih.ns.ac.yu) (B.F. Abramović).

## 2. Materials and methods

### 2.1. Chemicals and solutions

All chemicals were of reagent grade and were used without further purification. Clopyralid, 99.4%, pestanal quality, was purchased from Riedel-de Haën; 35% HCl and 85% H<sub>3</sub>PO<sub>4</sub> were purchased from Lachema, Neratovice; while NaOH and NaCl were purchased from ZorkaPharm, Šabac. The other chemicals used, such as 30% H<sub>2</sub>O<sub>2</sub> and 96% ethanol, were obtained from Centrohém, Stara Pazova; KBrO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 60% HClO<sub>4</sub>, and 98.0% formic acid were obtained from Merck, while 99.8% acetonitrile (ACN) was a product of J. T. Baker. The stock solutions containing 1000 ppm of ammonium/nitrate (ION 510 Oakton) were also used. All solutions were made using doubly distilled water. The TiO<sub>2</sub> Degussa P25 (75% anatase and 25% rutile form, 50 ± 15 m<sup>2</sup> g<sup>-1</sup>, about 20 nm, non-porous) was used as photocatalyst.

### 2.2. Photodegradation procedure

Photocatalytic degradation was carried out in a cell made of Pyrex glass (total volume of ca. 40 mL, liquid layer thickness 35 mm), with a plain window on which the light beam was focused, equipped with a magnetic stirring bar and a water circulating jacket. A 125 W medium-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm), together with an appropriate concave mirror, was used as the radiation source. The lamp output was calculated to be ca. 8.8 × 10<sup>-9</sup> Einstein cm<sup>-3</sup> min<sup>-1</sup> (potassium ferrioxalate actinometry).

The effects of clopyralid and catalyst concentrations, temperature, pH, hydroxyl radical scavenger, and electron acceptors were studied. Experiments were carried out using 20 mL of 1.0 mM of the clopyralid solution (unless otherwise stated) and 40 mg of TiO<sub>2</sub> Degussa P25 (except for the study of the effect of catalyst dosage). After that, the aqueous suspension of TiO<sub>2</sub> was sonicated (ultrasound frequency 50 Hz) in the dark for 15 min before illumination, to make the photocatalyst particles uniform and attain adsorption equilibrium. The suspension thus obtained was thermostated at 40 ± 0.5 °C (except for the case when the influence of temperature was investigated), and then irradiated at a constant stream of O<sub>2</sub> (3.0 mL min<sup>-1</sup>) to serve as electron acceptor in the reaction. During the irradiation, the mixture was stirred at a constant speed. All experiments were performed at the natural pH (ca. 3.2), except when studying the influence of the initial pH (1.0–10.5) on photocatalytic degradation of clopyralid. In that case the pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HClO<sub>4</sub> or NaOH. Where applicable, about 0.3 M ethanol, as a hydroxyl radical scavenger, was used. In the investigation of the influence of electron acceptors, apart from constant streaming of O<sub>2</sub>, a 3 mM solution of H<sub>2</sub>O<sub>2</sub>, KBrO<sub>3</sub>, or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added to the clopyralid solution and irradiation was carried out by standard procedure.

### 2.3. Analytical procedure

For the LC–DAD kinetic studies of clopyralid photodegradation, aliquots of 0.50 mL of the reaction mixture were taken at the beginning of the experiment and at regular time intervals (volume variation ca. 10%), then 5.0 mL<sup>-1</sup> of 0.1 M HCl were added, and the solution diluted to 10.00 mL with doubly distilled water. The suspensions containing photocatalyst were filtered through Millipore (Millex-GV, 0.22 μm) membrane filter. After that, a 20-μL sample was injected and analyzed on an Agilent Technologies 1100 Series liquid chromatograph, equipped with a UV/VIS DAD set at 225 nm (maximum of absorption for clopyralid), as well as at

210, 260, 270 and 280 nm (for intermediates) and an Eclipse XDB-C18 (150 mm × 4.6 mm i.d., particle size 5 μm, 25 °C) column. The mobile phase (flow rate 1 mL min<sup>-1</sup>, pH 2.56) was a mixture of ACN and water (3:7, v/v), the water being acidified with 0.1% H<sub>3</sub>PO<sub>4</sub>.

For the spectrophotometric monitoring, samples were prepared in the same way as for LC measurements and UV spectra were recorded on a Secomam Anthelie Advanced 2 spectrophotometer. Kinetics of the pyridine moiety degradation was monitored at 225 nm.

The changes in chloride concentration were monitored using a chloride ion selective electrode (Mettler Toledo Me-51340400). Ammonium and nitrate were assayed using Cole-Palmer ammonia and nitrate ion electrodes on an ION 510 Oakton instrument. Changes in the pH during the degradation were monitored using a combined glass electrode (pH-Electrode SenTix 20, WTW) connected to the pH-meter (pH/Cond 340i, WTW). In all cases, correlation coefficients obtained for calibration curves were higher than 0.99.

For the LC–MS/MS (ESI+) evaluation of intermediates, more concentrated solutions (3 and 41 mM) of clopyralid were prepared. Aliquots were taken in the beginning of the experiment and at regular time intervals during irradiation and after filtration to separate the TiO<sub>2</sub> particles without subsequent dilution. Then, a 5-μL sample was injected and analyzed on an Agilent Technologies 1200 series LC with Agilent Technologies 6410 series electrospray ionization triple–quadrupole MS/MS and an Agilent Technologies Zorbax SB-C18 (30 mm × 2.1 mm i.d., particle size 3.5 μm, 25 °C) column. The mobile phase (flow rate 0.5 mL min<sup>-1</sup>) was a mixture of ACN and water (gradient: 0 min 10% ACN, 2 min 90% ACN and, 6 min 90% ACN, post-time 3 min), whereby water was acidified with 1% formic acid. Positive electrospray (capillary voltage of 4.0 kV) was used for ionization of analytes, with nitrogen (temperature 350 °C, flow 11 L min<sup>-1</sup>) as nebulizer gas. High-purity nitrogen was used as the collision gas. Full scan mode (*m/z* range 25–500, scan time 250 ms, cone voltage 80 V), was used to select precursor ion for clopyralid and each degradation product, as well as to examine isotopic peaks distribution (Table 1). Then, product ion scan MS/MS mode (cone voltage 60 V, scan time 250 ms, collision energy 0–60 V in increments of 10 V, precursor ions *m/z*: 164.0, 192.0, 208.0 and 337.0) was used for structure elucidation of each degradation product. Finally, the multiple reaction monitoring (MRM) mode (parameters are given in Table 1) was used for obtaining peak areas of the analytes, in order to track the reaction kinetics. For total organic carbon (TOC) analysis, samples were irradiated for different time intervals and analyzed on a Elementar Liqui TOC II.

## 3. Results and discussion

### 3.1. Effect of pH

The solution pH is an important factor in the heterogeneous photocatalytic reactions since it influences the photocatalyst's surface charge and the size of aggregates of its particles, and hence it has been subject of numerous studies [6,7,18–22]. Because of that we investigated the pH effect in the range between 1.0 and 10.5 (Fig. 1) on the photodegradation rate of clopyralid in the aqueous suspension of TiO<sub>2</sub>. It was found that an increase of the reaction pH from 1.0 to 3.2 caused a significant increase in the degradation rate in the first period of irradiation, to show a distinct decay at a further increase, to be followed by a significant increase at the pH above 9.0 (inset of Fig. 1).

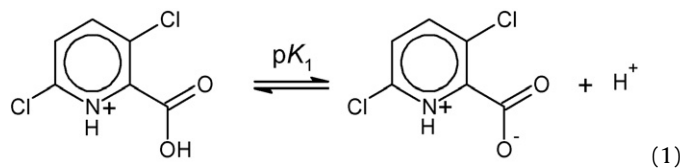
The interpretation of the pH effect on the photocatalytic process is a very difficult task because of the influence of a number of factors such as electrostatic interactions between the semicon-

**Table 1**  
MS/MS fragmentation data of intermediates obtained at five collision energies. The bold collision energies and product ions were selected for MRM MS/MS method.

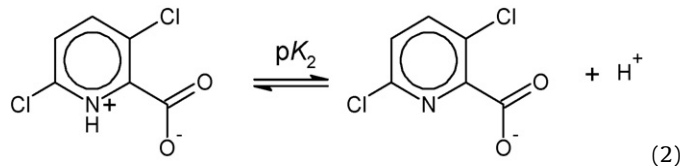
| Analyte                                                  | Retention time (min) | $M_w$ (g mol <sup>-1</sup> ) | Precursor ion ( $m/z$ ) | Collision energy (V) | Product ions ( $m/z$ , % rel. abundance)                                         |
|----------------------------------------------------------|----------------------|------------------------------|-------------------------|----------------------|----------------------------------------------------------------------------------|
| 3,6-Dichloro hydroxypyridine-2-carboxylic acid           | 0.521                | 208                          | 208                     | 0                    | 208(100), 190(30)                                                                |
|                                                          |                      |                              |                         | 20                   | 190(13), 162(100), 107(30)                                                       |
|                                                          |                      |                              |                         | 30                   | 162(28), 134(12), 107(100)                                                       |
|                                                          |                      |                              |                         | <b>40</b>            | <b>107(100)</b>                                                                  |
|                                                          |                      |                              |                         | 50                   | 107(100), 98(12), 83(14)                                                         |
| 3,6-Dichloro hydroxypyridine-2-carboxylic acid           | 0.919                | 208                          | 208                     | 0                    | 208(49), 190(100)                                                                |
|                                                          |                      |                              |                         | 20                   | 190(18), 162(100), 107(29)                                                       |
|                                                          |                      |                              |                         | 30                   | 162(41), 107(100), 98(12)                                                        |
|                                                          |                      |                              |                         | <b>40</b>            | <b>107(100)</b> , 98(12)                                                         |
|                                                          |                      |                              |                         | 50                   | 107(100), 98(12)                                                                 |
| Clopyralid                                               | 0.997                | 192                          | 192                     | 0                    | 192(100), 174(59)                                                                |
|                                                          |                      |                              |                         | 10                   | 174(100), 146(71)                                                                |
|                                                          |                      |                              |                         | <b>20</b>            | <b>146(100)</b>                                                                  |
|                                                          |                      |                              |                         | 30                   | 146(100), 110(81)                                                                |
|                                                          |                      |                              |                         | 40                   | 146(23), 110(100), 75(13)                                                        |
| 3,6-Dichloro-pyridin-2-ol                                | 1.310                | 164                          | 164                     | 0                    | 164(100)                                                                         |
|                                                          |                      |                              |                         | <b>20</b>            | 164(74), 146(66), <b>128(100)</b> , 110(17), 100(23), 73(57)                     |
|                                                          |                      |                              |                         | 30                   | 146(48), 128(18), 110(73), 100(10), 73(100)                                      |
|                                                          |                      |                              |                         | 40                   | 146(11), 110(85), 75(23), 73(100), 62(11)                                        |
|                                                          |                      |                              |                         | 50                   | 110(55), 84(13), 75(62), 73(100), 62(18)                                         |
| 3,3',6,6'-Tetrachloro-2,4'-bipyridine-2'-carboxylic acid | 3.108                | 338                          | 337                     | 0                    | 337(100), 319(52)                                                                |
|                                                          |                      |                              |                         | <b>20</b>            | 319(10), <b>291(100)</b>                                                         |
|                                                          |                      |                              |                         | 30                   | 291(100), 256(44), 255(14), 220(11)                                              |
|                                                          |                      |                              |                         | 40                   | 291(55), 256(100), 255(24), 221(62), 220(62)                                     |
|                                                          |                      |                              |                         | 50                   | 256(59), 229(13), 221(100), 220(96), 219(13), 195(12), 186(37), 185(20), 158(13) |

ductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The point of zero charge of TiO<sub>2</sub> (Degussa P25) is reported to be at pH ~ 6.25 [6]. Thus, the TiO<sub>2</sub> surface will remain positively charged (TiOH<sub>2</sub><sup>+</sup>) in acidic media (pH < 6.25) and negatively charged (TiO<sup>-</sup>) in alkaline media (pH > 6.25), hence influencing the clopyralid adsorption and the rate of its degradation. Taking into account that the pK values of clopyralid are 1.4 ± 0.1 and 4.4 ± 0.1 [23], the lower pK<sub>1</sub> value being

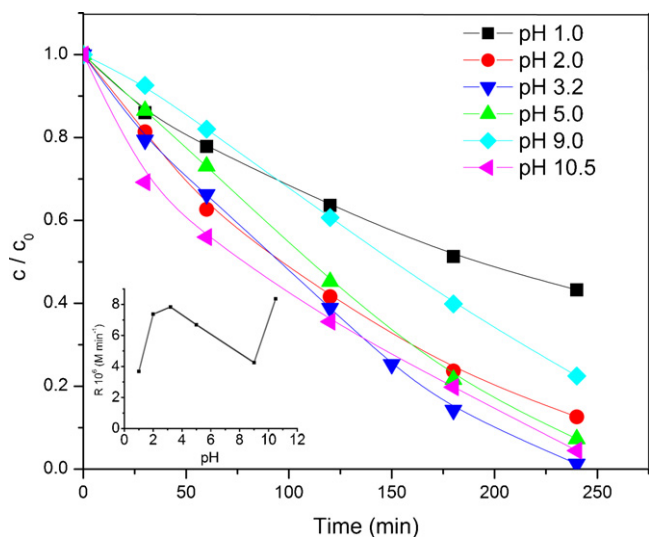
assigned to the dissociation of the carboxylic group (Eq. (1)):



and the higher pK<sub>2</sub> value to the protonation-dissociation of the heterocyclic nitrogen (Eq. (2)):



it can be supposed that the great increase in the photodegradation rate (by about 2 times, inset of Fig. 1) in the pH interval from 1.0 to 3.2 was a consequence of the dissociation of the carboxylic group and deprotonation of the pyridine nitrogen (to a significantly smaller extent). In this way, favorable electrical forces are generated that are manifested as the attraction between the positively charged surface of the catalyst and clopyralid anion. However, already at the pH 5.0, a distinct decrease of the photodegradation rate was observed, probably as a consequence of the decrease in the number of positive sites on the catalyst surface. A further increase in pH caused a small decrease in the photodegradation rate, which was probably a consequence of the influence of several factors. Namely, at pH > 6.25, the TiO<sub>2</sub> surface is negatively charged, causing the repulsion of the clopyralid anion. Besides, unfavorable



**Fig. 1.** Effect of initial pH on the kinetics of clopyralid (1.0 mM) photocatalytic degradation. The inset shows the effect of initial pH on clopyralid rate degradation determined for the first 120 min of irradiation.

electrical forces are generated, i.e., the repulsion between the negatively charged surface of the catalyst and  $\text{OH}^-$ . However, at higher  $\text{OH}^-$  concentrations (pH 10.5), a significant increase of the reaction rate in the first stage of the reaction was observed. This can be explained by the increased  $\text{OH}^\bullet$  production due to a higher concentration of  $\text{OH}^-$  ions in the solution [8,24].

Finally, it should be pointed out that in the case of the initial pH > 5.0 a pH decrease was observed during the photocatalytic degradation, so that after 240 min of irradiation the pH fell from 9.0 to about 5, and from pH 10.5 to about 6, which explains the relatively small difference in the overall amount of clopyralid degradation after 240 min at pH  $\geq 2.0$ . The drop of the pH was likely due to the generation of low molecular-weight organic acids and hydrochloric acid in the oxidation of clopyralid, which will be discussed later. The pH 3.2 was chosen as optimal for the photocatalytic degradation although the degradation rate at this pH in the initial period was a bit smaller than at pH 10.5. However, with the further irradiation, the degradation rate at pH 3.2 became comparatively slightly higher. Besides, as the clopyralid solution itself has a pH 3.2, no adjustment was needed.

All kinetic curves in the first period of the reaction could be fitted reasonably well by an exponential decay curve suggesting the pseudo-first kinetics order except for chloride generation (zero kinetics order). The resulting apparent first-order rate constant was used in all the subsequent plots to calculate the degradation rate for the decomposition of clopyralid using the following equation:

$$-\frac{dc}{dt} = k_a c_0 \quad (3)$$

where  $c$  is the clopyralid concentration,  $c_0$  the initial concentration of clopyralid and  $k_a$  apparent first-order rate constant [25] except for chloride generation.

### 3.2. Effect of clopyralid concentration

The photocatalytic degradation rate increased with increase in the clopyralid concentration from 0.5 to 1.5 mM (Table 2). A further increase in the substrate concentration led to a decrease in the degradation rate. Such behavior may be explained by the increased concentration of the clopyralid, so that increasingly more of its molecules could be adsorbed on the photocatalyst surface, needing thus a larger catalyst area for their degradation. However, as the intensity of light, irradiation time and amount of catalyst were constant, the relative amounts of  $\text{O}_2^-$  and  $\text{OH}^\bullet$  radicals on the catalyst surface did not increase. As a consequence, the relative degradation efficiency of the clopyralid decreased with increase in its concentration [6,7].

### 3.3. Effect of catalyst concentration

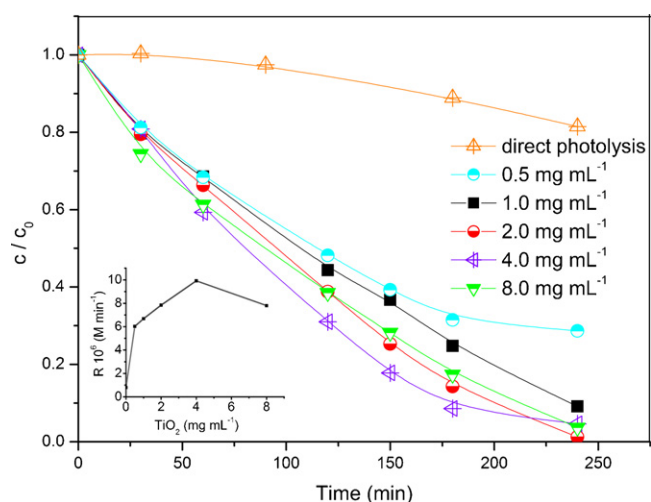
The addition of the photocatalyst has markedly improved the degradation rate of clopyralid in comparison to direct photolysis, i.e., in the absence of  $\text{TiO}_2$  (Fig. 2). With the increase in  $\text{TiO}_2$  content to  $4 \text{ mg mL}^{-1}$  the degradation rate showed an increase, but a further increase caused a rate decrease (Fig. 2, inset). Theoretically, the increase in the catalyst content above an optimum value

**Table 2**

Effect of initial clopyralid concentration ( $c_0$ ) on its photocatalytic degradation rate ( $R$ ).

| $c_0$ (mM) | $R \times 10^6$ ( $\text{M min}^{-1}$ ) <sup>a</sup> |
|------------|------------------------------------------------------|
| 0.5        | 4.51                                                 |
| 1.0        | 6.86                                                 |
| 1.5        | 8.72                                                 |
| 3.0        | 7.74                                                 |

<sup>a</sup> Degradation rate determined for the first 60 min of irradiation.

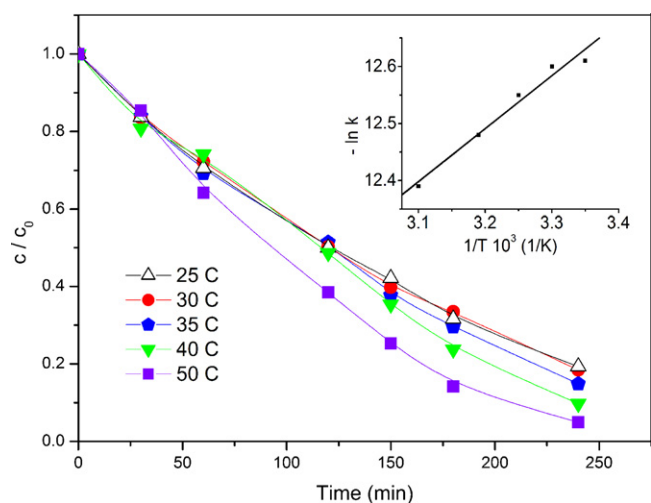


**Fig. 2.** Kinetics of clopyralid (1.0 mM) photocatalytic degradation in the presence of the different  $\text{TiO}_2$  contents. The inset represents the effect of  $\text{TiO}_2$  content on clopyralid rate degradation determined for the first 120 min of irradiation.

had no effect on the photodegradation rate since all the light available was already utilized. However, higher  $\text{TiO}_2$  contents led to the aggregation of its particles and thus to a decrease in the contact surface between the reactant and photocatalyst, which caused a decrease in the number of active sites, resulting in a lower rate of photodegradation. Besides, the increase in the solution turbidity and light dispersion on the particles could also be the cause of a lower degradation rate [26]. Also, when  $\text{TiO}_2$  was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embedded the positive effect coming from the dosage increment and therefore the overall performance reduced [27].

### 3.4. Effect of temperature

The degradation rate increased with increase in temperature (Fig. 3), which was probably a consequence of an increased frequency of molecular collisions in the solution, although this effect was not very pronounced. The inset in Fig. 3 represents the corresponding Arrhenius plot on the basis of which we determined the overall apparent activation energy to be  $7.74 \text{ kJ mol}^{-1}$ . This value is in good agreement with results reported in the litera-



**Fig. 3.** Effect of temperature on the kinetics of clopyralid (1.0 mM) photocatalytic degradation. The inset represents the Arrhenius plot of,  $-\ln k$  against  $1/T$ .

ture [3,24,28], quoting the values of the overall apparent activation energy of photocatalytic oxidation of different substrates in the range from 5.5 to 28.4 kJ mol<sup>-1</sup>. The small effect of temperature on the rate of photocatalytic degradation can be explained by a low value of the activation energy in comparison with common heat reactions.

### 3.5. Effect of electron acceptors

One of the more serious problems in using TiO<sub>2</sub> as a photocatalyst is the occurrence of the electron–hole pair recombination, which is very pronounced in the absence of the appropriate electron acceptor, yielding potentially a lowered efficiency of the photocatalytic process [6]. The most commonly used electron acceptor is the O<sub>2</sub>. As can be seen from Fig. 4, the presence of O<sub>2</sub> accelerated the degradation rate by more than two times. In order to enhance the formation of OH• and also inhibit electron–hole recombination, H<sub>2</sub>O<sub>2</sub>, KBrO<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> are most frequently used electron acceptors [6,7,18,19]. The respective one-electron reduction potentials (measured against SHE) of different species are  $E(\text{O}_2/\text{O}_2^{\bullet-}) = -155$  mV,  $E(\text{H}_2\text{O}_2/\text{OH}^{\bullet}) = 800$  mV and  $E(\text{BrO}_3^-/\text{BrO}_2^{\bullet}) = 1150$  mV,  $E(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\bullet-}) = 1100$  mV [29]. From a thermodynamic point of view, all the mentioned substances should therefore be more efficient electron acceptors than O<sub>2</sub>. The addition of the mentioned electron acceptors showed significant but the different effects on the kinetic of photocatalytic degradation of clopyralid (Fig. 4). Namely, in the beginning of the reaction, all the electron acceptors accelerated the degradation process. The influence of these electron acceptors diminished in the order: (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > H<sub>2</sub>O<sub>2</sub> > KBrO<sub>3</sub>. Similar results have been found by Qourzal et al. [30]. However, in the course of the further degradation process in the presence of the acceptors, a decrease in the degradation rate could be observed. One possible explanation might be the change in the reaction mechanism of the photocatalytic degradation of clopyralid. This phenomenon was most pronounced in the case of KBrO<sub>3</sub>. Inhibition of the degradation by KBrO<sub>3</sub> may be due to the scavenging of OH• and holes by BrO<sub>3</sub><sup>-</sup> and UV screening of TiO<sub>2</sub> particles due to the presence of BrO<sub>3</sub><sup>-</sup> [31]. Also, when H<sub>2</sub>O<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were used as an electron acceptor, a decrease of the reaction rate was observed only after a longer reaction time ( $t > 120$  min and 170 min, respectively). In some cases, H<sub>2</sub>O<sub>2</sub> may act as a hole or OH• scavenger or react with TiO<sub>2</sub> and form peroxy compounds which are detrimental to the photocatalytic action [32].

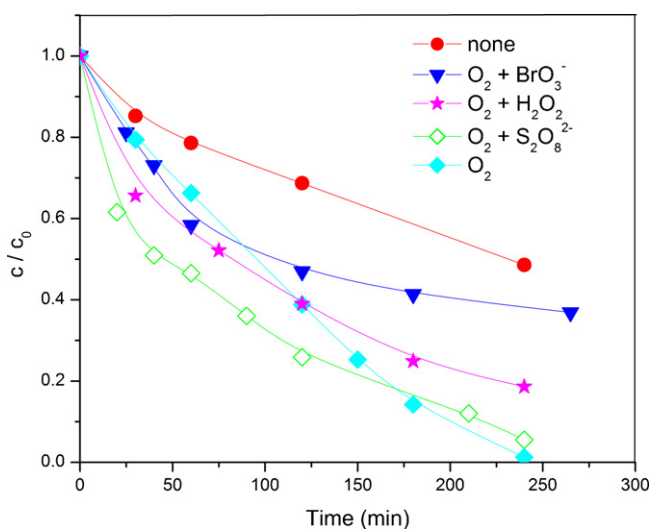


Fig. 4. Kinetics of clopyralid (1.0 mM) photocatalytic degradation in the presence/absence of different electron acceptors.

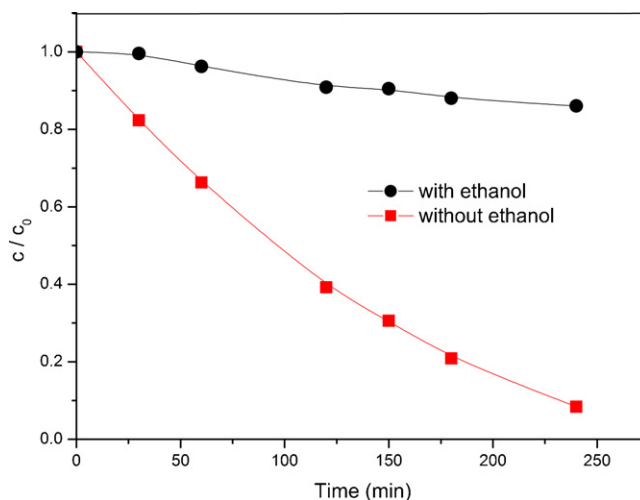


Fig. 5. Effect of ethanol on the kinetics of clopyralid (1.0 mM) photocatalytic degradation.

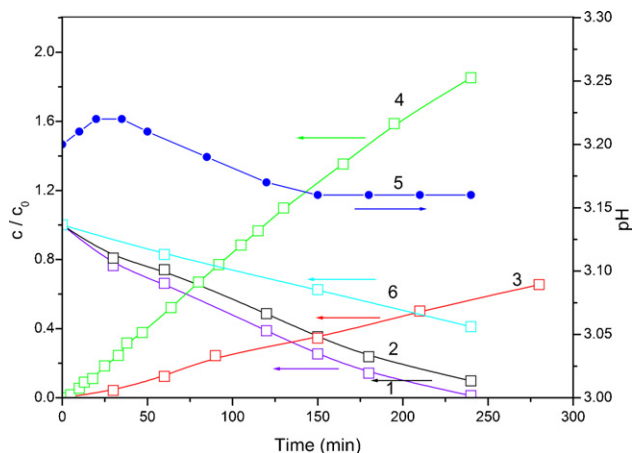
The potential effect of all the mentioned electron acceptors on the degradation of clopyralid in the presence of TiO<sub>2</sub> was also investigated in the absence of light. Analysis of the samples showed no observable loss of the clopyralid in any of these cases. Blank experiments were also carried out by irradiating the aqueous solution of the herbicide containing all the mentioned electron acceptors in the absence of TiO<sub>2</sub>. It appeared that the rate of degradation of clopyralid was similar to the rate of direct photolysis with UV irradiation, i.e., the effect of additives was observed only in the presence of TiO<sub>2</sub>.

### 3.6. Effect of hydroxyl radical scavenger

In order to investigate whether the heterogeneous photocatalysis takes place via OH•, 400 μL of ethanol were added to the reaction mixture containing clopyralid and TiO<sub>2</sub> at 25 °C. Namely, it is known that alcohols (e.g. ethanol and methanol) act as OH• scavengers [33,34]. The results obtained indicate that the degradation rate was about ten times slower ( $R = 0.64 \times 10^{-6}$  M min<sup>-1</sup>) compared to that in the absence of ethanol ( $R = 6.86 \times 10^{-6}$  M min<sup>-1</sup>) (Fig. 5), which proved that the reaction of photocatalytic degradation proceeded mainly via OH• [33].

### 3.7. Kinetics and mechanism of photodegradation

Since clopyralid contains covalently bonded chlorine, which is converted to chloride during the photocatalytic degradation, the kinetics of chloride generation was monitored by potentiometric measurements (Fig. 6, curve 4). It was found that the rate of chloride release was  $8.45 \times 10^{-6}$  M min<sup>-1</sup> (zero kinetics order). As this rate was approximately twice the value of the rate of pyridine moiety degradation ( $R = 4.31 \times 10^{-6}$  M min<sup>-1</sup>, applying zero kinetics order for comparison) (Fig. 6, curve 2) it can be concluded that the degradation of pyridine ring took place simultaneously with chloride release, i.e., no stable chlorinated intermediates of acyclic structure were formed. Also, the slope of the spectrophotometrically obtained kinetic curve (Fig. 6, curve 2) was somewhat smaller compared to that obtained by LC (Fig. 6, curve 1), which is understandable if we bear in mind that spectrophotometry monitored the kinetics of degradation of the pyridine moiety (clopyralid and its degradation products with pyridine moiety), whereas LC (at the retention time of 3.2 min), measured only the change of clopyralid concentration.



**Fig. 6.** Photocatalytic degradation of clopyralid (1.0 mM): (1) disappearance of clopyralid; (2) disappearance of pyridine moiety; (3)  $\text{NH}_4^+$  formation; (4)  $\text{Cl}^-$  formation; (5) pH; (6) TOC.

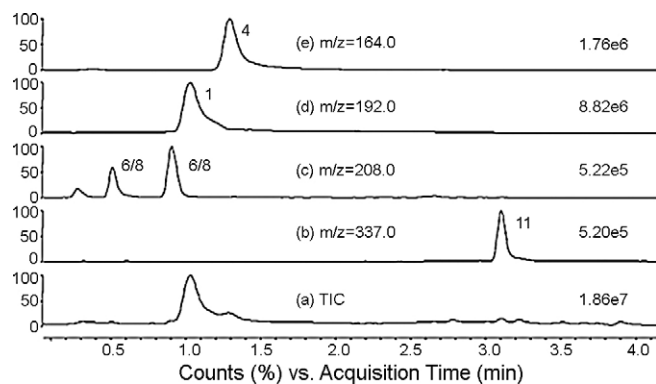
As is known [12], in the course of photodegradation, the organic nitrogen is transformed mainly to ammonium ion and/or nitrite/nitrate, and sometimes to nitrogen. The ratio of ammonium to nitrate depends on the chemical structure of the substrate and reaction conditions [35]. In the potentiometric monitoring of ammonium and nitrate evolution with the corresponding indicator electrodes, it was found that in the first 4 h only ammonium ions were formed (Fig. 6, curve 3). In this case too, the reaction rate was  $2.06 \times 10^{-6} \text{ M min}^{-1}$ , which was somewhat lower than the rate of chloride release, that is the pyridine moiety degradation, which suggests that nitrogen-containing intermediates in the acyclic structure were formed. This is in agreement with the previous results obtained in the study of the degradation mechanism of 2-amino-5-chloropyridine [11] and 3-amino-2-chloropyridine [12].

Monitoring of the kinetics of photocatalytic degradation via the change in the pH has mainly been investigated for simple molecules, where practically no intermediates are formed, and therefore the formation of hydronium ions directly corresponds to the kinetics of degradation of the initial compound [20]. This is generally not the case with more complex molecules, where the change in pH cannot be used for kinetic analysis, but even so, its monitoring during a photocatalytic process gives a valuable insight into the changes in the investigated system. Thus, the loss of carboxylic group in the initial phase of photodegradation led to the formation of less acidic intermediates, which caused a smaller increase in the pH (Fig. 6, curve 5). However, after 30 min of irradiation the decrease in pH was less pronounced, which suggests simultaneous formation of chloride and ammonium ions, the chloride release reaction being somewhat faster than that of ammonium ions.

As is known [36,37], photocatalytic degradation of pesticides is accompanied by the formation of intermediates which can potentially be harmful to the environment. To study the intermediates formed by clopyralid photodegradation we chose the LC-MS/MS (ESI+), as the GC-MS spectrum of clopyralid does not have an  $\text{M}^+$  ion; hence the derivatization of the compound would be necessary to form its methyl ester [38]. Fig. 7 shows the LC-MS chromatograms after 360 min of photocatalytic degradation of clopyralid.

The LC-MS and LC-MS/MS (ESI+) analyses of the irradiated solution of clopyralid indicated the formation of several intermediates, whose kinetic curves are shown in Fig. 8.

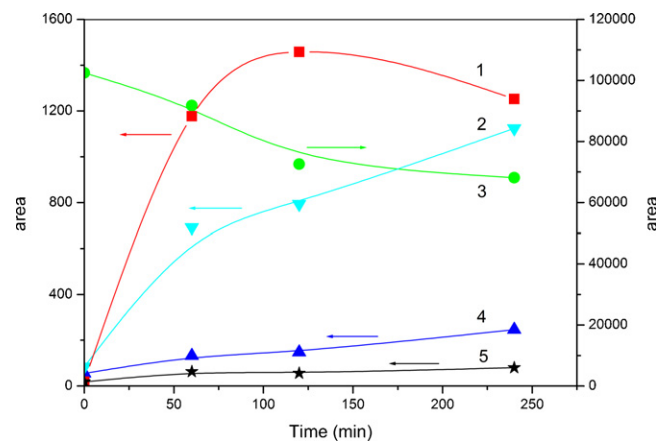
On the basis of the identified intermediates and kinetic data, we proposed a tentative scheme of clopyralid photocatalytic degradation. In the first stage, the clopyralid 1, upon the transfer of one electron can form the radical anion 2, which may undergo



**Fig. 7.** LC-MS total ion chromatogram (a) and extracted ions chromatograms (b–e) of clopyralid and their intermediates, obtained after 360 min of photocatalytic degradation of clopyralid (41 mM). The numbers (1), (4), (6), (8) and (11) correspond to compounds in Fig. 9.

the loss of the carboxyl group to give radical 3 (Fig. 9). Attack of the  $\text{OH}^\bullet$  on the radical species 3 yields an identified intermediate 3,6-dichloropyridin-2-ol 4. Similarly, clopyralid, upon addition of an  $\text{OH}^\bullet$  at the para position (5) and the loss of a proton, yields the formation of the identified intermediate 3,6-dichloro-4-hydroxypyridine-2-carboxylic acid 6. In the same way, the  $\text{OH}^\bullet$  binds also in the meta position of 7, which, after the loss of a proton, yields the identified intermediate 3,6-dichloro-5-hydroxypyridine-2-carboxylic acid 8. Furthermore, the simultaneous opening of the pyridine ring and release of chloride may be an explanation why no intermediates are formed in which chlorine would be replaced by e.g. hydroxyl group, which could be expected according to the reports of some authors [4,7–9,11,12,18,39]. These intermediates finally degraded to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ , and  $\text{NH}_4^+$ .  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were postulated on the basis TOC measurement (Fig. 6, curve 6), whereby the complete mineralization was attained after about 12 h of irradiation. Chloride and  $\text{NH}_4^+$  were measured potentiometrically with the corresponding electrodes.

In view of the high clopyralid concentration used in the LC-MS/MS (ESI+) determination, the dimer 11 was also identified as one of the photodegradation products. Namely, clopyralid loses an electron to give a radical cation species 9. The radical cation species 9 loses an  $\text{H}^+$  to give a radical species 10, which reacts with the radical species 3, giving the identified product 3,3',6,6'-tetrachloro-2,4'-bipyridine-2'-carboxylic acid 11. Similar results were also obtained by some other authors in their stud-



**Fig. 8.** Kinetics of the photocatalytic degradation of clopyralid (3.0 mM) and of the resulting appearance/disappearance of their intermediates by LC-MS/MS (ESI+): (1) 3,6-dichloropyridin-2-ol; (2, 4) 3,6-dichloro-4-hydroxypyridine-2-carboxylic acid; (3) clopyralid; (5) 3,3',6,6'-tetrachloro-2,4'-bipyridine-2'-carboxylic acid.

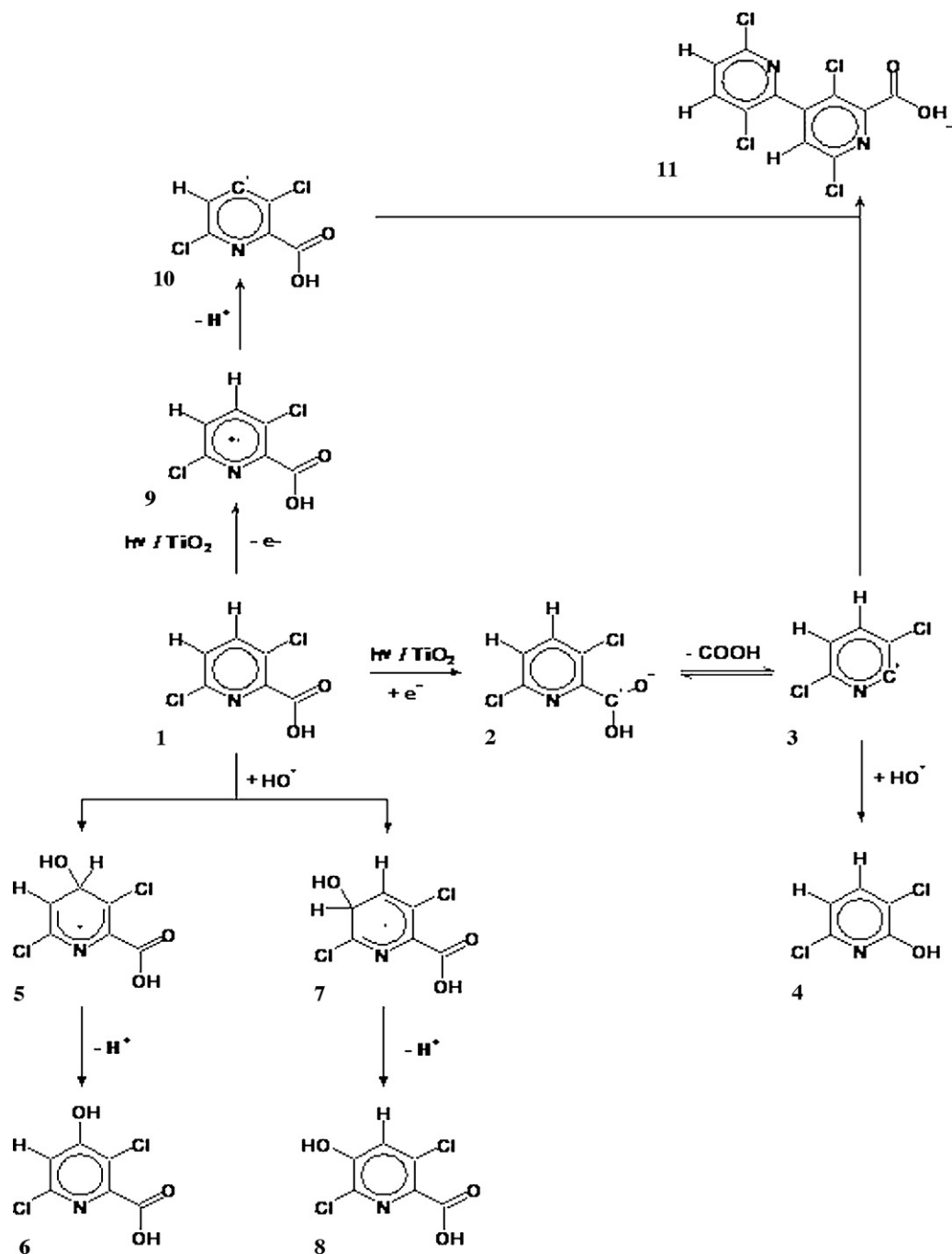


Fig. 9. Tentative pathways for photocatalytic degradation of clopyralid.

ies of the photodegradation of 4-bromoaniline [39] and pyridine [40].

#### 4. Conclusions

The results of this study clearly indicate that TiO<sub>2</sub> can efficiently catalyze the photodecomposition of clopyralid in the presence of UV light and oxygen. The results also indicate that the degradation rate is influenced by the different parameters such as pH, substrate and catalyst concentrations, temperature, presence/absence of various electron acceptors in addition to molecular oxygen. Namely, it was observed that the photodegradation of clopyralid was fastest at pH 3.2 because of the influence of various factors at the differ-

ent pHs of the system. The photocatalytic degradation of clopyralid in aqueous TiO<sub>2</sub> suspensions in the first period of degradation followed a pseudo-first-order kinetics. The experimentally determined optimum content of the photocatalyst was about 4 mg mL<sup>-1</sup>. Besides, the dependence of the photodegradation rate on temperature appeared to be small, the apparent activation energy being 7.74 kJ mol<sup>-1</sup>. The absence of molecular oxygen resulted in a significant decrease in the rate of clopyralid photodegradation, indicating the significance of the presence of oxygen as an electron acceptor. The influence of investigated electron acceptors in the first period of reaction decreased in the sequence: (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> > H<sub>2</sub>O<sub>2</sub> > KBrO<sub>3</sub>. However, in the course of further degradation of the substrate a decrease in the degradation rate was observed, especially in the case of KBrO<sub>3</sub>. It was found that the presence of ethanol as a

scavenger of hydroxyl radicals inhibited the clopyralid photodecomposition, suggesting that the reaction mechanism involved free hydroxyl radicals. The results of these investigations clearly demonstrated the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The spectrophotometric, LC–DAD, and LC–MS/MS (ESI+) monitoring of the process showed that several pyridine-containing intermediates were formed (3,6-dichloropyridin-2-ol, 3,6-dichloro hydroxypyridine-2-carboxylic acid, and 3,3',6,6'-tetrachloro-2,4'-bipyridine-2'-carboxylic acid). These intermediates underwent ring opening and finally degraded to CO<sub>2</sub>, H<sub>2</sub>O, HCl, and NH<sub>4</sub><sup>+</sup>. The analysis of the intermediate product formed during the photocatalytic degradation could be a useful source of information about the degradation pathways.

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### References

- [1] C. Tomlin (Ed.), *The Pesticide Manual*, 10th ed., Crop Protection Publications, 1995, pp. 224–226.
- [2] N.M. Soboleva, A.A. Nosovich, V.V. Goncharuk, The heterogenic photocatalysis in water treatment processes, *J. Wat. Chem. Tech.* 29 (2007) 72–89.
- [3] J.-M. Herrmann, Heterogeneous photocatalysis: state of the art and present applications, *Top. Catal.* 34 (2005) 49–65.
- [4] I.K. Konstantinou, T.A. Albanis, Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Appl. Catal. B: Environ.* 42 (2003) 319–335.
- [5] H.D. Burrows, L.M. Canle, J.A. Santaballa, S. Steenken, Reaction pathways and mechanisms of photodegradation of pesticides, *J. Photochem. Photobiol. B: Biol.* 67 (2002) 71–108.
- [6] M. Qamar, M. Muneer, D. Bahnemann, Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueous suspensions of titanium dioxide, *J. Environ. Manage.* 80 (2006) 99–106.
- [7] M. Atiqur Rahman, M. Muneer, Heterogeneous photocatalytic degradation of picloram, dicamba, and floumeturon in aqueous suspensions of titanium dioxide, *J. Environ. Sci. Health* 40 (2005) 247–267.
- [8] M.A. Aramendía, A. Marinas, J.M. Marinas, J.M. Moreno, F.J. Urbano, Photocatalytic degradation of herbicide fluroxypyr in aqueous suspension of TiO<sub>2</sub>, *Catal. Today* 101 (2005) 187–193.
- [9] D.R. Stapleton, D. Mantzavinos, M. Papadaki, Photolytic (UVC) and photocatalytic (UVC/TiO<sub>2</sub>) decomposition of pyridines, *J. Hazard. Mater.* 146 (2007) 640–645.
- [10] D.R. Stapleton, R.J. Emery, D. Mantzavinos, M. Papadaki, Photolytic destruction of halogenated pyridines in wastewaters, *Process Saf. Environ.* 84 (2006) 313–316.
- [11] B.F. Abramović, V.B. Anderluh, A.S. Topalov, F.F. Gaál, Direct photolysis and photocatalytic degradation of 2-amino-5-chloropyridine, *J. Serb. Chem. Soc.* 68 (2003) 961–970.
- [12] B.F. Abramović, V.B. Anderluh, A.S. Topalov, F.F. Gaál, Titanium dioxide mediated photocatalytic degradation of 3-amino-2-chloropyridine, *Appl. Catal. B: Environ.* 48 (2004) 213–221 (and references therein).
- [13] *Dow AgroSciences*, Clopyralid a North American technical profile, July 1998, <http://wric.ucdavis.edu/jst/manage/ClopTechProfile.pdf> (November 8, 2008).
- [14] C. Cox, *Journal of Pesticide Reform*, 18 (Winter 1998) No 4 <http://www.mindfully.org/Pesticide/Clopyralid.htm> (November 8, 2008).
- [15] Pesticide Fact Sheet, Prepared for the U.S. Department of Agriculture, Forest Service by Information Ventures, Inc. [www.epa.gov/fedgrstr/EPA-PEST/1997/May/Day-16/p12913.htm](http://www.epa.gov/fedgrstr/EPA-PEST/1997/May/Day-16/p12913.htm) (November 31, 2008).
- [16] D.B. Donald, A.J. Cessna, E. Sverko, N.E. Glozier, Pesticides in surface drinking-water supplies of the northern Great Plains, *Environ. Health Perspect.* 115 (2007) 1183–1191.
- [17] B. Abramović, V. Anderluh, D. Šojić, F. Gaál, Photocatalytic removal of herbicide clopyralid from water, *J. Serb. Chem. Soc.* 72 (2007) 1477–1486.
- [18] M. Muneer, D. Bahnemann, Semiconductor-mediated photocatalyzed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromimidazole, in aqueous suspension, *Appl. Catal. B: Environ.* 36 (2002) 95–111.
- [19] M. Muneer, J. Theurich, D. Bahnemann, Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate, *J. Photochem. Photobiol. A: Chem.* 143 (2001) 213–219.
- [20] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: a kinetic and mechanistic study, *Langmuir* 12 (1996) 6368–6376.
- [21] H.K. Singh, M. Saquib, M.M. Haque, M. Muneer, D.W. Bahnemann, Titanium dioxide mediated photocatalysed degradation of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid, in aqueous suspensions, *J. Mol. Catal. A: Chem.* 264 (2007) 66–72.
- [22] W. Chu, W.K. Choy, T.Y. So, The effect of solution pH and peroxide in the TiO<sub>2</sub>-induced photocatalysis of chlorinated aniline, *J. Hazard. Mater.* 141 (2007) 86–91.
- [23] M.C. Corredor, J.M. Rodríguez Mellado, M. Ruiz Montoya, EC(EE) process in the reduction of the herbicide clopyralid on mercury electrodes, *Electrochim. Acta* 51 (2006) 4302–4308.
- [24] A. Lair, C. Ferronato, J.-M. Chovelon, J.-M. Herrmann, Naphthalene degradation in water by heterogeneous photocatalysis: an investigation of the influence of inorganic anions, *J. Photochem. Photobiol. A: Chem.* 193 (2008) 193–203.
- [25] H. Al-Ekabi, N. Serpone, Kinetic studies in heterogeneous photocatalysis. 1. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO<sub>2</sub> supported on a glass matrix, *J. Phys. Chem.* 92 (1988) 5726–5731.
- [26] D. Vione, C. Minero, V. Maurino, M.E. Carlotti, T. Picatonotto, E. Pelizzetti, Degradation of phenol and benzoic acid in the presence of a TiO<sub>2</sub>-based heterogeneous photocatalyst, *Appl. Catal. B: Environ.* 58 (2005) 79–88.
- [27] C.C. Wong, W. Chu, The direct photolysis and photocatalytic degradation of alachlor at different TiO<sub>2</sub> and UV sources, *Chemosphere* 50 (2003) 981–987.
- [28] D. Chen, A.K. Ray, Photodegradation kinetics of 4-nitrophenol in TiO<sub>2</sub> suspension, *Wat. Res.* 32 (1998) 3223–3234.
- [29] P. Wardman, Reduction potential of one-electron couples involving aqueous solution, *J. Phys. Chem. Ref. Data* 18 (1989) 1637–1755.
- [30] S. Qourzal, N. Barka, M. Tamimi, A. Assabbane, Y. Ait-Ichou, Photodegradation of 2-naphthol in water by artificial light illumination using TiO<sub>2</sub> photocatalyst: identification of intermediates and the reaction pathway, *Appl. Catal. A: Gen.* 334 (2008) 386–393.
- [31] R.A. Burns, C.J. Crittenden, D.W. Hand, V.H. Selzer, L.L. Sutter, S.R. Salman, Effect of inorganic ions in heterogeneous photocatalysis of TCE, *J. Environ. Eng.* 125 (1999) 77–85.
- [32] I. Poullos, M. Kositzki, A. Kouras, Photocatalytic decomposition of triclopyr over aqueous semiconductor suspensions, *J. Photochem. Photobiol. A: Chem.* 115 (1998) 175–183.
- [33] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>, *J. Photochem. Photobiol. A: Chem.* 162 (2004) 317–322.
- [34] I. Ilisz, A. Dombi, Investigation of the photodecomposition of phenol in near-UV-irradiated aqueous TiO<sub>2</sub> suspensions. II. Effect of charge-trapping species on product distribution, *Appl. Catal. A: Gen.* 180 (1999) 35–45.
- [35] R.M. Alberici, M.C. Canela, M.N. Eberlin, W.F. Jardim, Catalyst deactivation in the gas phase destruction of nitrogen-containing organic compounds using TiO<sub>2</sub>/UV–VIS, *Appl. Catal. B: Environ.* 30 (2001) 389–397.
- [36] X. Cai, J. Ye, G. Sheng, W. Liu, Time-dependent degradation and toxicity of diclofop-methyl in algal suspensions—emerging contaminants, *Environ. Sci. Pollut. Res.*, in press, doi:10.1007/s11356-008-0077-1.
- [37] S. Chiron, L. Comoretto, E. Rinaldi, V. Maurino, C. Minero, D. Vione, Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative, *Chemosphere* 74 (2009) 599–604.
- [38] W.L. Budde, Analytical mass spectrometry of herbicides, *Mass Spectrom. Rev.* 23 (2004) 1–24.
- [39] M. Abu Tariq, M. Faisal, M. Muneer, D. Bahnemann, Photochemical reactions of a few selected pesticide derivatives and other priority organic pollutants in aqueous suspensions of titanium dioxide, *J. Mol. Catal. A: Chem.* 265 (2007) 231–236.
- [40] C. Maillard-Dupuy, C. Guillard, H. Courbon, P. Pichat, Kinetics and products of the TiO<sub>2</sub> photocatalytic degradation of pyridine in water, *Environ. Sci. Technol.* 28 (1994) 2176–2183.