

Photocatalytic decomposition of triclopyr over aqueous semiconductor suspensions

I. Poullos*, M. Kositzi, A. Kouras

Lab. Phys. Chem., Dept. of Chemistry, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

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Abstract

The photocatalytic degradation of 3,5,6-trichloro-2-pyridinyloxyacetic acid (Triclopyr), a pyridine analogue of the phenoxy herbicides, has been investigated in aqueous heterogeneous solutions containing TiO_2 or ZnO as photocatalyst. The disappearance of the organic molecule follows approximately a pseudo-first kinetic order according to the Langmuir–Hinselwood model. As mineralization products, CO_2 and Cl^- ions have been identified, whereas the nitrogen atom forms only NH_4^+ ions. Various commercial photocatalysts were compared with respect to their overall efficiency, as well as the production of CO_2 . The effect of pH and H_2O_2 on the reaction rate was ascertained. The photooxidation of Triclopyr has also been monitored with FTIR spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Triclopyr; Garlon; TiO_2 ; Photocatalysis; Photooxidation

1. Introduction

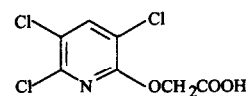
Increasing attention has been given recently, to photocatalytic reactions occurring on semiconductor particles suspended in aqueous solutions. The illumination of these particles with light energy greater than the bandgap energy ($h\nu > E_g$) produces excited high energy states of electron and hole pairs (e^-/h^+), which can migrate to the surface of the particle and initiate a wide range of chemical redox reactions leading to complete mineralization of the organic pollutants. It has been demonstrated, that semiconducting materials mediating photocatalytic oxidation of a variety of aliphatic and aromatic compounds, can be an alternative to conventional methods for the destruction of organic pollutants in water and air [1–4]. Experimental observations indicate almost complete oxidation of most of the organic compounds to CO_2 via photocatalytic processes. The quantitative formation of CO_2 is of great significance in water treatment, because it provides unequivocal evidence for the total destruction of organic pollutants present in water. The disappearance of these compounds could take place via formation of partially oxidized intermediates, that could be even more toxic than the original pollutants.

Additionally, an advantage of the photocatalytic process is its mild operation conditions and that it can be powered by

sunlight, reducing significantly the electric power required and therefore reducing the operating costs [5,6].

A variety of semiconductor powders (oxides, sulphides, etc.) acting as photocatalysts have been used. Most attention was given to TiO_2 because of its high photocatalytic activity, its resistance to photocorrosion, its biological immunity and low cost.

This paper presents results describing the photocatalytic decomposition of Triclopyr, a pyridine analogue of the phenoxy herbicides, over TiO_2 and ZnO powders. Its structure is presented below.



(3,5,6-trichloro-2-pyridinyloxyacetic acid, CAS 553335-06-3)

It is part of a study concerning the photodegradation of various substituted pyridines, which have been frequently used as pesticides, insecticides or surfactants [7–10].

Triclopyr is a frequently used herbicide for postemergence control of a wide range of annual and perennial broadleaf weeds and woody plant species. Its hydrolysis half-life ($t_{1/2}$) is greater than three months in darkened, sterile, buffered water. The aqueous photolysis of Triclopyr has been examined previously in laboratory experiments [11] and in

* Corresponding author.

field studies [12], but nothing, as far as we know, has been reported about its photocatalytic destruction.

According to Woodburn et al. [11], the pseudo first-order half-lives of photolysis in pH-buffered water and natural river water averaged 0.5 and 1.3 days respectively. Also, in sterile buffered water the major product of photodegradation was 5-chloro-3,6-dihydroxy-2-pyridinyloxyacetic acid, while in the river water oxamic acid was identified as the major photoproduct.

2. Experimental

Triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) of purum quality was generously donated by Dow Helanco and was used as received.

TiO₂ P-25 Degussa (anatase/rutile = 3.6/1, surface area 56 m² g⁻¹, nonporous) was used for all photocatalytic experiments, except otherwise mentioned in the text.

Experiments were performed in an open thermostated Pyrex cell of 250 ml capacity (9 cm diameter, 3.5 cm height). The reaction mixture in the cell was maintained as a suspension by magnetic stirring. The suspension was left for 30 min in the dark in order to achieve the maximum adsorption of the herbicide onto semiconductor surface. The irradiation was carried out using four parallel 15 W blacklight blue fluorescent tubes, mounted in standard 15 W fluorescent tube holders (Philips TLD 15 W/08, 45 cm length, 2.6 cm diameter). According to the producer each tube has a total radiative output of 2.2 W between 340–400 nm with maximum emission at 370 nm. The distance between the reaction vessel and the lamps was 5 cm.

In all cases, during the experiments, 200 ml of the Triclopyr solution containing the appropriate quantity of the semiconductor powder, was magnetically stirred before and during the illumination. At specific time intervals, samples of 5 ml were withdrawn. To remove the TiO₂ particles, the solution was filtered through a 0.45 μm filter (Schleicher and Schuell). Changes in the concentration of Triclopyr were observed from its characteristic absorption at 295 nm, using a UV-visible spectrophotometer (Shimadzu UV-160 A).

In order to determine the CO₂ release, a second apparatus was used. It consisted of a borosilicate glass vessel of 6 cm diameter and of 13.5 cm height hermetically sealed with a silicone rubber. The reaction vessel was fitted with a central 11 W lamp (Osram Dulux S 11 W/78) and had inlet and outlet ports for bubbling the desired gas, under which the reaction was taking place. CO₂ formed during the photooxidation in the reaction vessel, was followed by measuring the conductivity increase of an ultra pure water, with a conductivity meter according to Matthews et al. [13].

The pH value of the solutions was monitored with a Metrohm pH-meter and the reaction temperature was kept constant at 25 ± 0.1°C.

The ions NH₄⁺, NO₃⁻ and Cl⁻ were analyzed using a DIONEX 4500i Ion Analyzer equipped with cation and anion

micromembrane suppressors and a DIONEX electrical conductivity detector.

3. Results and discussion

3.1. Photodecomposition kinetics of triclopyr

At first, experiments concerning the photocatalytic decomposition of 10 mg l⁻¹ Triclopyr (3.9 · 10⁻⁵ M) were performed, in the presence of a variety of semiconductor catalysts as TiO₂ P-25, ZnO from Merck, TiO₂ UV-100 Hombikat from Schachtleben Chemie and TiO₂ modified with WO₃ or MoO₃. Among them ZnO and TiO₂ P-25 were those with the best results.

Results of the photolysis of a 10 mg l⁻¹ Triclopyr solution containing 2 g l⁻¹ TiO₂ P-25 or 2 g l⁻¹ ZnO are shown in Fig. 1a and b respectively. The amount of the Triclopyr present in the supernatant is plotted as a function of irradiation time. From Fig. 1 it is clear, that the photolysis of an air equilibrated Triclopyr solution in the presence of ZnO or TiO₂ leads to the disappearance of the compound. Under these experimental conditions in the presence of 2 g l⁻¹ TiO₂, ~95% of the initial concentration of the herbicide was removed after 15 min of light exposure, while in the same time and in the presence of ZnO the degradation was almost complete. Due to the photocorrosion presented by ZnO, especially in low pH on the one and due to photostability and constant crystalline composition of anatase-based TiO₂ P-25 powders on the other hand, this catalyst was used throughout the work.

The effect of the quantity of the photocatalyst on the reaction rate, shows an increase until 2 g l⁻¹ TiO₂ are used, and then it becomes constant.

On the contrary, a very small decrease in the concentration of Triclopyr was observed by illumination in the absence of

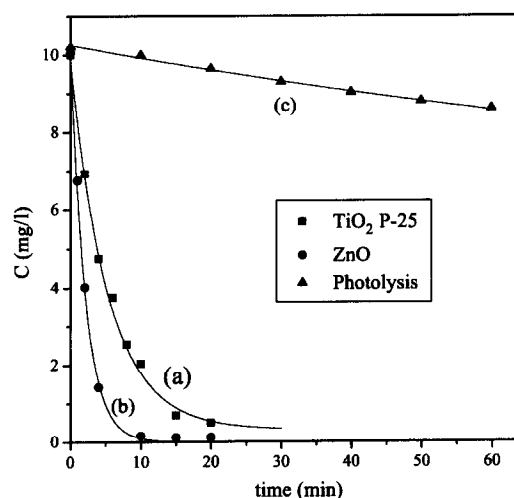


Fig. 1. Photodegradation of 10 mg l⁻¹ Triclopyr as a function of irradiation time in the presence of (a) 2 g l⁻¹ TiO₂ P-25 and (b) 2 g l⁻¹ ZnO; (c) irradiation without catalyst.

TiO₂ (Fig. 1c). After 60 min of irradiation, direct photolysis contributed less than 14% to the degradation of Triclopyr.

The influence of the initial concentration of the solute on the photocatalytic degradation rate of most of the organic compounds is described by a pseudo-first kinetic order, which is rationalized in terms of the Langmuir–Hinselwood model, modified to accommodate reactions occurring at a solid–liquid interface [14,15],

$$r_0 = -\frac{dC}{dt} = \frac{k_r K C_0}{1 + K C_0} \quad (1)$$

where r_0 is the initial rate of disappearance of the organic substrate and C_0 is its initial concentration. K represents the equilibrium constant for adsorption of the organic substrate onto TiO₂ and k_r reflects the limiting rate of reaction at maximum coverage for the experimental conditions. A standard means of using this equation is to demonstrate linearity of the data when plotted as the inverse initial rate vs. inverse initial concentration:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K} \frac{1}{C_0} \quad (2)$$

Fig. 2 presents plots from experiments carried out using various initial concentrations of Triclopyr (2.5, 5, 7.5, 10 and 15 mg l⁻¹) versus irradiation time. The lines drawn through the data points represent good approximations over a wide range of solute concentrations.

In Table 1 the initial reaction rates (r_0) from the photodecomposition of the above compound vs. irradiation time, under various experimental conditions are presented. The r_0 values were independently obtained both by a polynomial fit of the $C-t$ data of Fig. 2 and also by multilinear regression to the following integrated form of Eq. (1):

$$t = \frac{1}{k_r K} \ln \frac{C_0}{C} + \frac{1}{k_r} (C_0 - C) \quad (3)$$

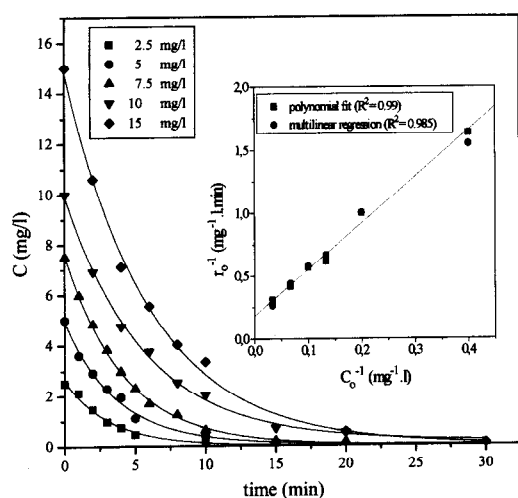


Fig. 2. Plot of the photodegradation of Triclopyr vs. irradiation time, at various initial concentrations for constant concentration of TiO₂ P-25 at 2 g l⁻¹; the inset shows the linear transform of r_0^{-1} vs. C_0^{-1} ; data from Table 1.

Table 1

Initial reaction rate values from the photodecomposition of 10 mg l⁻¹ Triclopyr under various experimental conditions

Experimental conditions	r_0 (mg l ⁻¹ min ⁻¹)
Triclopyr (mg l ⁻¹) ^a 2.5	0.61 ± 0.085
5	1.00 ± 0.089
7.5	1.52 ± 0.028
10	1.76 ± 0.112
15	2.39 ± 0.286
30	3.23 ± 0.153
TiO ₂ P-25 (2 g l ⁻¹)	1.76 ± 0.112
ZnO (2 g l ⁻¹)	3.94 ± 0.30
TiO ₂ UV-100 (2 g l ⁻¹)	0.690 ± 0.122
Humic acid (mg l ⁻¹) ^b 1	1.340 ± 0.153
5	1.016 ± 0.151
10	0.870 ± 0.92
Solar exposure ^b 9.7 mW cm ⁻²	0.680 ± 0.061
2.7 mW cm ⁻²	0.141 ± 0.021

^aIn the presence of 2 g l⁻¹ TiO₂ P-25.

^bIn the presence of 10 mg l⁻¹ Triclopyr and 2 g l⁻¹ TiO₂ P-25.

where t is the time in minutes required for the initial concentration of solute C_0 to decrease to C [16].

The dependence of r_0^{-1} values on the respective inverse initial concentrations of Triclopyr for constant concentration of TiO₂ P-25 at 2 g l⁻¹ is shown in inset of Fig. 2, where it is seen that the results of both these methods are in reasonable agreement. The k_r and K values calculated according to Eq. (2) from the slope of the straight line and from the intercept with the C_0^{-1} -axis were 5.14 mg l⁻¹ min⁻¹ ($2 \cdot 10^{-5}$ M min⁻¹) and 0.053 mg⁻¹ l ($1.36 \cdot 10^4$ M⁻¹) for the polynomial fit and 4.72 mg l⁻¹ min⁻¹ ($1.84 \cdot 10^{-5}$ M min⁻¹) and 0.061 mg⁻¹ l ($1.56 \cdot 10^4$ M⁻¹) for the multilinear regression.

As mentioned above K represents the equilibrium constant for the adsorption of Triclopyr onto TiO₂ and k_r reflects the limiting rate of reaction at maximum coverage for the given experimental conditions and accordingly has no absolute meaning.

3.2. Effect of oxidants

The addition of other powerful oxidizing species such as H₂O₂, K₂S₂O₈ and KBrO₃ to TiO₂ suspensions, is a well known procedure and in many cases leads to an increase of the rate of photooxidation [17,18].

In our case the photocatalytic degradation of 10 mg l⁻¹ Triclopyr has been studied at different H₂O₂, as well as K₂S₂O₈ concentrations. The reaction kinetics was not different from those obtained in the absence of oxidants.

H₂O₂ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (Eq. (4)). It also forms OH· radicals according to Eq. (5).



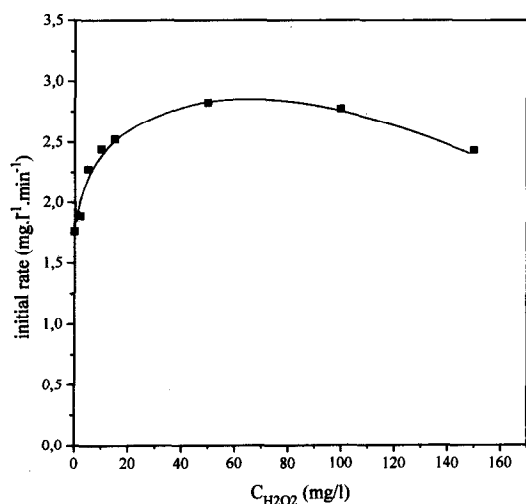
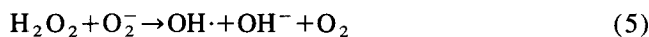


Fig. 3. Effect of H_2O_2 concentration on the initial rate of photodegradation of 10 mg l^{-1} Triclopyr in the presence of 2 g l^{-1} TiO_2 P-25.



In the presence of excess H_2O_2 , it may act as a hole or $OH \cdot$ scavenger or react with TiO_2 and form peroxy compounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H_2O_2 for the maximum effect.

The effect of the concentration of H_2O_2 on the initial reaction rate (r_0) of Triclopyr degradation is shown in Fig. 3. The photocatalytic efficiency increases as the concentration of H_2O_2 is increased and it reaches the optimum in the area of 50–100 mg l^{-1} . Consequently it decreases as the concentration of the H_2O_2 increases beyond the optimum value. Under these conditions the addition of H_2O_2 accelerates the degradation only by a factor of 2. This positive effect is too small compared to the one observed during photooxidation in other cases [19–21].

The small effect of H_2O_2 is also obvious in the complete oxidation of Triclopyr. From Fig. 5, where are given the values of CO_2 produced in the presence and absence of H_2O_2 , it is apparent that, practically, H_2O_2 does not affect the photomineralization of Triclopyr. Similar results have also been taken in the case of the photocatalytic degradation of dichloropyridine isomers [10]. Also, when $K_2S_2O_8$ was used as an oxidant, no effect on the reaction rate has been observed.

3.3. Effect of pH

pH can be one of the most important parameters for the photocatalytic process and so it was of interest to study its influence on the photooxidation of Triclopyr. Since the photooxidation is accompanied by the release of protons, its efficiency may then change, because of the reversible protonation of the TiO_2 surface [4].

For the alteration of pH in the acid and alkaline area, there was used 5 M $HClO_4$ and 5 M $NaOH$ solutions respectively. Complete removal of CO_2 from the less acidic reaction

mixtures, during the mineralization experiments, was ensured by addition of conc. $HClO_4$ after photolysis.

The initial reaction rate of the photooxidation of Triclopyr, the percentage of photomineralization after 20 min reaction time, as well as the amount of Triclopyr adsorbed in the dark (%) onto TiO_2 , in the pH-range from 2 to 13 units are given in Fig. 4.

As can be seen from Fig. 4, when the initial pH of the suspension varied from 2 to 13, the dark adsorption as well as the photocatalytic activity reached a maximum at $pH \sim 3.5\text{--}4$ and go to zero at $pH = 13$. The effect of pH on the photocatalytic reaction can be mainly explained by the surface charge of TiO_2 and its relation to the acid dissociation constant of Triclopyr ($pK = 2.93$). The dark adsorption of Triclopyr onto TiO_2 surface, as can be seen in Fig. 4, is probably the first step and determines the efficiency of the photooxidation.

Below $pH = 4$ the predominant species are the undissociated Triclopyr molecules, rather than the corresponding anions. As result a decrease of the dark adsorption takes place, which leads also to a decrease of the photocatalytic activity. On the contrary above $pH = 4$ a decrease of the r_0 , the dark adsorption and the photomineralization of Tripyr has been observed, reflecting the difficulty of the pyridinyloxyacetic anions to approach the negatively charged TiO_2 surface, when increasing the solution pH (point of zero charge, pzc, of $TiO_2 \sim 6$).

The increase of the mineralization observed between 6–8 pH units may be attributed to cationic species produced during the decomposition of Triclopyr, which due to their positive charge, can more easily approach the negatively charged TiO_2 surface.

On the other hand, in high pH values, a drastic decrease of the photooxidation is being observed. In the case that the photocatalytic process was determined only by the $OH \cdot$ radicals, there should have been a significant increase of the

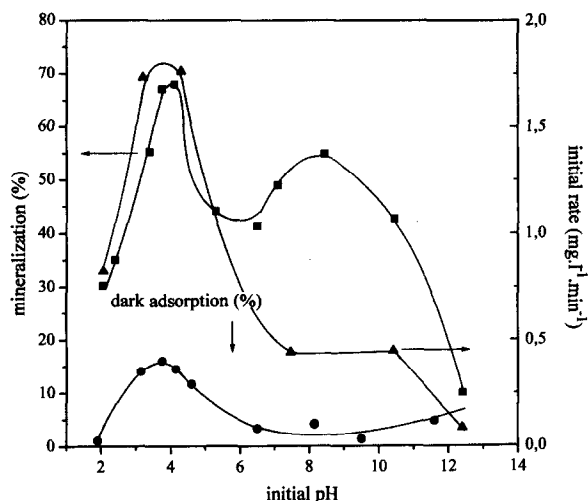


Fig. 4. Effect of pH on the photocatalytic degradation of 10 mg l^{-1} Triclopyr: (●) dark adsorption, (■) percentage of mineralization, at 20 min irradiation time, (▲) initial reaction rate; catalyst 2 g l^{-1} TiO_2 P-25.

reaction's rate, as known from other cases [22–24], due to the high concentration of the photogenerated $\text{OH}\cdot$ radicals in this pH region.

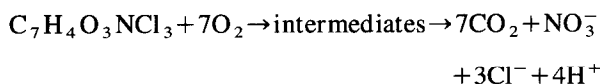
The drastic decrease of photooxidation at high pH values, as well as the small effect of H_2O_2 on the oxidation, reveals that except of the $\text{OH}\cdot$ radicals also the photogenerated holes may be responsible for the oxidation of Triclopyr.

Our results are better rationalized by a dual hole-radical mechanism, in which direct h^+ oxidation of carboxylic group of Triclopyr occurs, in competition with h^+ oxidation of surface hydroxyl ions, which mainly attack the heterocyclic ring (see Section 3.4).

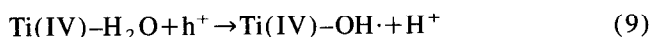
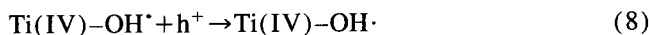
3.4. Photodegradation products

As mentioned above, the complete decomposition to CO_2 via photocatalytic reactions is of great significance in water treatment, because it is the unequivocal evidence for the total destruction of organic compounds in water. For this reason, the complete oxidation of Triclopyr was studied in a separate apparatus described in Section 2.

The overall equation, valid after long irradiation time in the presence of excess oxygen, which describes the photocatalytic mineralization of Triclopyr is presented below:



It is well established, that by the irradiation of an aqueous TiO_2 suspension, with light energy greater than its band gap energy ($E_g > 3.2$ eV), conduction band electrons (e^-) and valence band holes (h^+) are generated. After this primary event, part of the photogenerated carriers recombine in the bulk of the semiconductor with heat emission, while the rest reach the surface, where the holes as well as the electrons act as powerful oxidants and reductants respectively. The photogenerated electrons react with the adsorbed molecular O_2 on the Ti(III)-sites, reducing it to superoxide radical anion O_2^- , while the photogenerated holes can oxidize either the organic molecules directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to $\text{OH}\cdot$ radicals, and together with other highly oxidant species (peroxide radicals) are reported to be responsible for the primary oxidizing step in photocatalysis [4,25,26]. According to this, the relevant steps of the photodegradation process at the semiconductor surface can be expressed as follows:



The $\text{OH}\cdot$ radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with an oxidation

potential of 2.8 V. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading finally to their complete mineralization.

The main final products from the photodecomposition of Triclopyr under the given experimental conditions, were CO_2 , NH_4^+ and Cl^- .

Fig. 5 shows the formation of CO_2 vs. illumination time of a solution containing 10 mg l^{-1} Triclopyr in the presence of 2 g l^{-1} TiO_2 P-25, 2 g l^{-1} ZnO and 2 g l^{-1} TiO_2 UV-100, as well as in the presence of 2 g l^{-1} TiO_2 P-25 and 50 mg l^{-1} H_2O_2 . The concentration of 50 mg l^{-1} H_2O_2 according to Fig. 3, is the one with the greater influence on the acceleration of the photodegradation of Triclopyr.

In the presence of TiO_2 P-25, only 50% of Triclopyr was converted to CO_2 in the first 15 min, while 95% (Fig. 1) was decomposed in the same time, showing the presence of intermediates. Full oxidation requires more than 60 min. The addition of 50 mg l^{-1} H_2O_2 in a suspension of TiO_2 /Triclopyr, as shown in Fig. 5, does not alter significantly the photomineralization process of Triclopyr, and this agrees also with the results of the degradation experiments in the presence of various concentrations of H_2O_2 (Fig. 3).

In the presence of ZnO, as can also be seen in Fig. 5, only 27.5% of Triclopyr was mineralized within the first 10 min and then it remained stable. Taking into account that the percentage of carbon of the oxyacetic part is the 28% of the total organic carbon in the Triclopyr molecule, one can presume that in the presence of ZnO, the bond between the pyridine molecule and the oxyacetic part is breaking and only the oxyacetic part is converted into CO_2 , while the rest of the molecule turns into an hydroxychloropyridine. According to the above, when only ZnO is present, the degradation of pyridine ring is not possible. The addition of H_2O_2 after the establishment of the balance, had as a result the extra degradation of Triclopyr, however without reaching the levels of TiO_2 P-25.

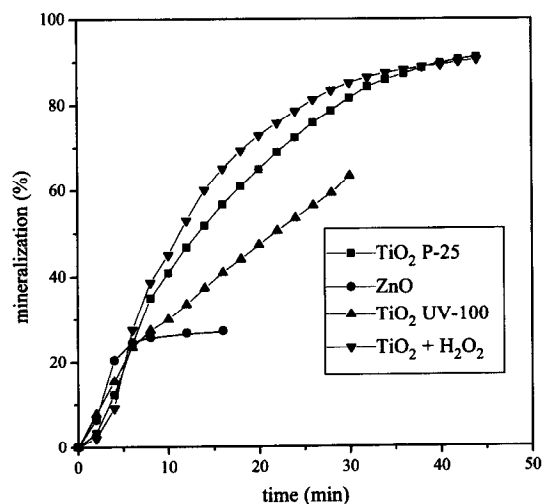


Fig. 5. CO_2 formation as a function of irradiation time during the photocatalytic degradation of Triclopyr in the presence of 2 g l^{-1} TiO_2 -P25, 2 g l^{-1} TiO_2 P-25 + 50 mg l^{-1} H_2O_2 , 2 g l^{-1} ZnO and 2 g l^{-1} TiO_2 UV-100.

In the case of TiO₂ UV-100, a similar behaviour as in ZnO has been observed during the first 5 min. After this period, destruction of the pyridine molecule takes place, but with lower efficiency compared to that when TiO₂-P25 has been used. This is specifically valid for the degradation of Triclopyr, while earlier studies have clearly shown that TiO₂ UV-100 was a much better photocatalyst for the degradation of aliphatic compounds, such as tetrachloromethane or dichloroacetic acid [27].

The superiority of TiO₂ P-25 may be attributed to the morphology of crystallites, which was proposed to be one of the most critical properties for the photocatalytic efficiency of P-25 among various grades of TiO₂. Crystallographic study shows that it consists of multiphases of amorphous, anatase and rutile forms. The close proximity of these phases and in some cases the overlapping of forms, makes it difficult to differentiate and has been cited to be the reason for long lasting excitation of electrons from the valence band to the conductive bands, allowing for efficient and effective degradation of organic compounds [28,29].

Fig. 6 shows the concentration of Cl⁻ and NH₄⁺ produced during the photocatalytic decomposition of Triclopyr.

In all three cases the dechlorination of Triclopyr is faster than the mineralization process and in the presence of H₂O₂ (Fig. 6c) the expected value of Cl⁻ is observed in the first 30 min.

On the contrary, when only TiO₂ is present, the complete dechlorination of Triclopyr takes more than one hour, while in the presence of ZnO, only 75% of Cl is released.

The main degradation product originating from nitrogen, in the case of Triclopyr, is the ammonium ion. This is not in agreement with other experimental results in which the photocatalytic destruction of the N-containing molecules produced both NH₄⁺ and NO₃⁻ [30–32]. The reason that NO₃⁻ was absent in our case, might be the lower irradiation intensity, the low oxidation state of the nitrogen in Triclopyr, as well as the short illumination time. According to G. Low et al. [30] the NH₄⁺/NO₃⁻ ratio, decreases with the increase of the irradiation time and the solution pH. The formation rate of NO₃⁻ is low when N is at low oxidation state as in our case, since the conversion of NH₄⁺ to NO₃⁻ is very slow, as it could be predicted from the difference by 8 units in the oxidation state.

Fig. 6d and e show the formation of NH₄⁺ ion during the photocatalytic oxidation of Triclopyr in the presence of TiO₂ and TiO₂ + H₂O₂ respectively. The ammonium ion production increases regularly and after 1 h illumination, it reaches a value corresponding to 59% in the case of TiO₂ and 73% in the presence of H₂O₂ of the amount expected from complete mineralization. The positive effect of H₂O₂ is clear in this case and also in the case of the release of chloride ions. However, after one hour of illumination the nitrogen mass balance is lower than the stoichiometric, thus indicating that other nitrogen containing organic compounds should also be present in the solution. From the HPLC measurements there were observed small but detectable quantities of unidentified

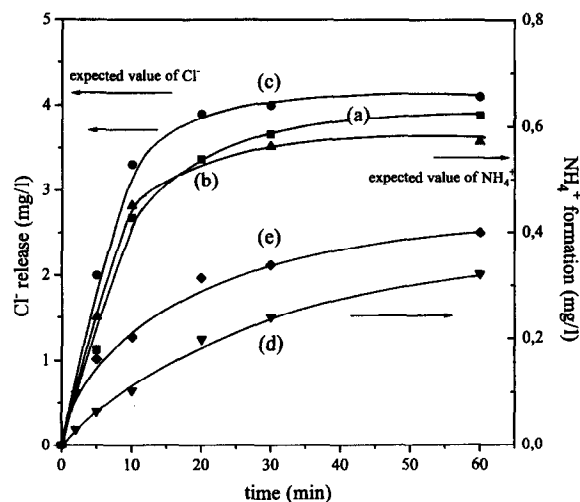


Fig. 6. Cl⁻ release and NH₄⁺ formation as a function of irradiation time during the photocatalytic degradation of 10 mg l⁻¹ Triclopyr. Cl⁻ release: 2 g l⁻¹ TiO₂ P-25 (a), 2 g l⁻¹ ZnO (b), 2 g l⁻¹ TiO₂ P-25 + 50 mg l⁻¹ H₂O₂ (c); NH₄⁺ formation: 2 g l⁻¹ TiO₂ P-25 (d), 2 g l⁻¹ TiO₂ + 50 mg l⁻¹ H₂O₂ (e).

cationic species, which led us to assume the existence of various amines. The determination of these compounds is a difficult procedure and lies outside the objective of this study.

Formic acid has been also detected as an intermediate product, which is completely oxidized after 60 min.

The reaction rate values of Cl⁻ release and NH₄⁺ formation calculated according to the results of Fig. 6 are presented in Table 2.

FTIR spectroscopy was also used in order to monitor the photomineralization course on the catalyst surface. Infrared spectra (4000–1000 cm⁻¹) were recorded on a Perkin-Elmer 1600 FTIR spectrometer in KBr pellets (concentration 3%). Spectra of the organic molecule and of the TiO₂-Triclopyr system were obtained as the result of collection of 16 transients at a resolution level 2 cm⁻¹.

Fig. 7(1) shows the FTIR spectrum of Triclopyr before adsorption and illumination, while in Fig. 7(2) the photocatalytic oxidation followed, by comparing the FTIR spectra at 2 min (Fig. 7(2)b), 10 min (Fig. 7(2)c) and 2 h (Fig. 7(2)d) illumination. Fig. 7(2)a shows the FTIR spectrum of the system Triclopyr/TiO₂ in the dark.

The results imply that there is a considerable change of Triclopyr adsorbed on the catalyst with respect to the free molecule. Furthermore the degree of adsorption is verified to

Table 2
r₀ values of Cl⁻ release and NH₄⁺ formation during the photocatalytic mineralization of 10 mg l⁻¹ Triclopyr

Catalyst (2 g l ⁻¹)	r _{Cl⁻} (mg l ⁻¹ min ⁻¹)	r _{NH₄⁺} (μg l ⁻¹ min ⁻¹)
TiO ₂ P-25	0.339 ± 0.086	0.0153 ± 0.0007
ZnO	0.388 ± 0.038	—
TiO ₂ + 50 mg l ⁻¹ H ₂ O ₂	0.490 ± 0.015	0.0445 ± 0.009

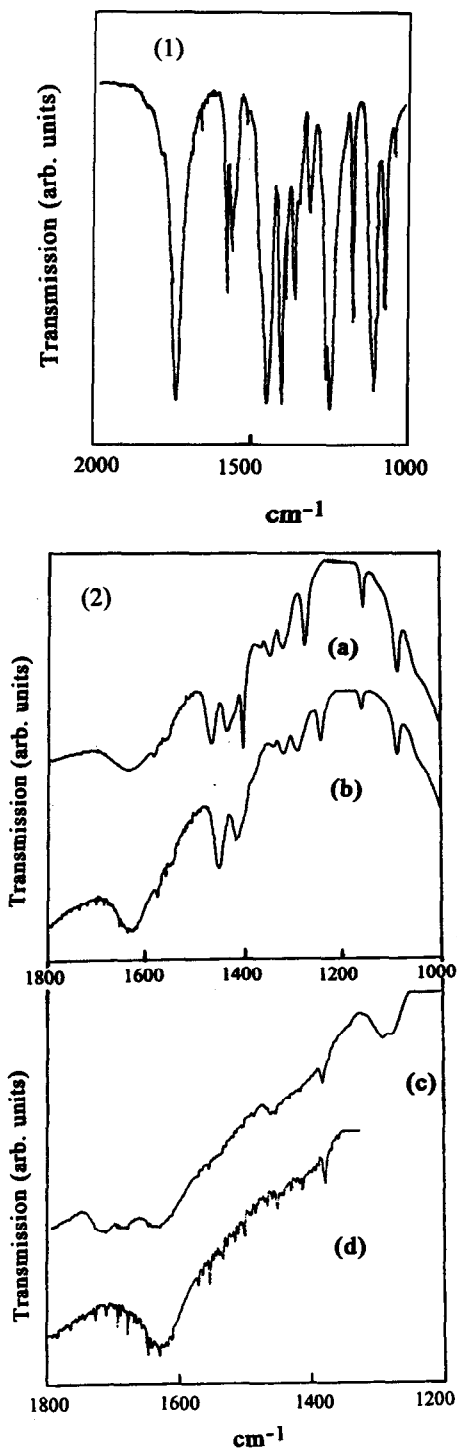


Fig. 7. 1. FTIR spectrum of Triclopyr before adsorption and photocatalytic oxidation, obtained in KBr pellets (conc. 3%) by Perkin–Elmer 1600 FTIR spectrometer. 2. FTIR spectra of Triclopyr/TiO₂ system: (a) in the dark, (b) 2 min irradiation, (c) 10 min irradiation and (d) after 2 h irradiation; for spectra (a), (b) and (c) the concentration of the appropriate filtrated and air-dried catalyst in KBr was 3%, while for spectrum (d) the conc. was 10%.

be very small. The organic substrate appears to form coordination complexes of both bidentate and bridging character as the characteristic carboxylate bands at 1572, 1452 and

1419 cm⁻¹ [33]. Furthermore, the ratio of these bands to others present in the fingerprint region relative to the corresponding bands in the free molecule suggest that after the initial breaking of the etheric bond, the carboxylate fragment remains more strongly coordinated to TiO₂. The carboxylate bands diminish drastically after 10 min irradiation and only minor carboxylate components remain attached to the TiO₂ surface after 2 h irradiation (Fig. 7(2) a, b, c, d).

The photocatalytic degradation of Triclopyr is a complicated process, with a mechanism, involving several chemical and photocatalytic stages and a great number of intermediates. On the basis of our experimental results and some pertinent suggestions of other researchers concerning the pyridine photooxidation [30,31], as well as the photodecomposition of various carboxylic acids [22,34–37], we attempted to propose qualitatively for the Triclopyr photooxidation the dual hole-radical mechanism, in which direct h⁺ oxidation of the oxyacetic group takes place, under liberation of CO₂, in competition with the OH· attack of the pyridine molecule.

At low pH, the positively charged TiO₂ offers a suitable surface for adsorption of pyridinyloxyacetic anion. Preference for the carboxylate group may stem from the ability to coordinate directly with Ti⁺⁴. This bond has a relatively high covalent character, and the oxygen atoms of the oxyacetic group, being relatively strong electron donors, are able to directly interact with valence band holes thus facilitating direct electron transfer. According to the current literature carboxylate groups are preferentially attached by holes. On the other hand, the OH· radicals produced due to the reaction of the photogenerated holes with the adsorbed water molecules, attack the carbon atoms in the pyridine ring and as a result we have the formation of various chlorohydroxypyridine isomers, in a similar manner with that of dichloro- and trichlorophenols [38]. Finally after dechlorination, the rapid addition of O₂ leads to a series of amides, oxalic and formic acid and at longer irradiation time to CO₂, Cl⁻, NH₄⁺ and NO₃⁻.

Increasing the pH reduces adsorption and gradually increases the electrostatic repulsion between the pyridinyloxyacetic anion (pK = 2.93) and the oxide surface. The increased distance between the reactants no longer allows direct charge transfer. With only limited Triclopyr adsorption occurring, most of the decomposition is probably mediated by OH· formed at other semiconductor surface sites. This implies that oxidant attack is shifted away from the carboxyl group towards the ring.

The drastic decrease in photodecomposition rates up to pH = 8 is probably due to Coulombic repulsion between the anions and the highly negative charged oxide surface. Decomposition would thus depend on diffusion of surface-generated OH· towards the double layer to the low concentration of pyridinyloxyacetic anion, a slower process than direct charge transfer. Additionally the increase of pH causes a cathodic displacement of the valence band position of TiO₂

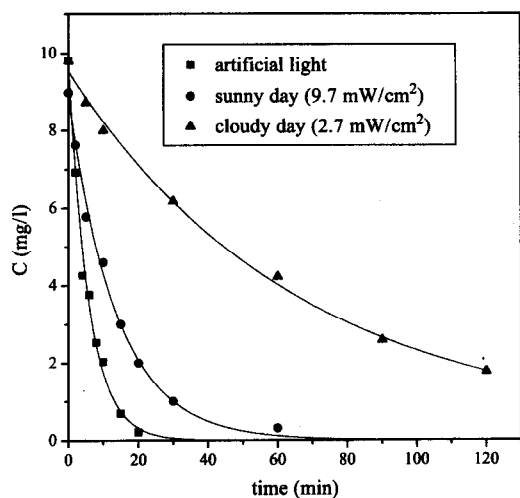


Fig. 8. Photocatalytic degradation of 10 mg l^{-1} Triclopyr under artificial and natural illumination.

of 59 mV/pH and results to the weakening of the oxidation ability of the holes.

3.5. Solar experiments

For the solar exposure experiments the same open Pyrex cell, as for the previous measurements under artificial light, is adapted. The photodegradation of Triclopyr under solar illumination on a sunny day (9.7 mW cm^{-2}) and on a cloudy day (2.7 mW cm^{-2}) is shown in Fig. 8. In the same figure, we also present the photodegradation of Triclopyr when artificial light was used. In the presence of solar light, it is observed that the degradation of Triclopyr is equally effective. The time required for 90% degradation of 10 mg l^{-1} Triclopyr under the given experimental conditions was 30 min in the case of the sunny day, approximately 3 times smaller than with the blacklight fluorescent tubes, and more than 15 times smaller in the case of the cloudy day. Consequently, Triclopyr can be effectively degraded to non-toxic ions in a TiO_2 suspension under solar exposure.

4. Conclusions

In this work the photocatalytic oxidative degradation of Triclopyr, a pyridine analogue of the phenoxy herbicides, has been studied. It was observed that quantitative degradation of the organic molecule occurs within 1 h with TiO_2 P-25 as photocatalyst. The chlorine and nitrogen of the organic compound were recovered in the form of chloride and ammonium ion. Nitrogen was found only as NH_4^+ because of the low intensity of UV radiation and the short illumination time, which are necessary for higher oxidation states of nitrogen. The comparison of various commercial catalysts showed that TiO_2 P-25 does not only decompose Triclopyr faster, but it is the only one which oxidizes completely the organic compound to CO_2 . The rate and extent of photodecomposition as

a function of H_2O_2 and pH, indicates that the most possible oxidation mechanism of Triclopyr is the dual hole-radical mechanism, in which direct h^+ oxidation of the oxyacetic part takes place, under liberation of CO_2 , in competition with OH^\cdot attack of the pyridine molecule.

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