

Kinetics of photocatalytic decomposition of Fenuron over TiO₂ in aqueous solution

Ouarda Brahmia,¹ Abdelaziz Boulkamh,¹ Tahar Sehili,¹
Jean-Pierre Aguer,² and Claire Richard^{2,†}

¹ *Laboratoire des Sciences et Technologie de l'Environnement, Faculté des Sciences,
Université Mentouri, Constantine 25000, Algérie*

² *Laboratoire de Photochimie Moléculaire et Macromoléculaire (UMR 6505)
Université Blaise Pascal, F-63177 Aubière Cedex, France*

ABSTRACT. The kinetics of the photocatalytic degradation of Fenuron (3-phenyl-1,1-dimethylurea) in aqueous suspension of several semiconductors irradiated at 365 nm has been investigated. The kinetics of the reaction is well described by the Langmuir-Hinshelwood model showing that the degradation reactions occur on the semiconductors particles surface. The primary photoproducts were identified by RMN and GC/MS. The main initial reaction is hydroxylation in *ortho* and *para* position with respect to the urea function. The rate of the photocatalytic degradation increases upon addition of small amounts of hydrogen peroxide, but is slightly reduced by chloride ions.

1. INTRODUCTION

The pollution of the aquatic environment by harmful organic chemicals, insecticides and herbicides, was of great concern in the last years all over the world. In recent years, photochemical methods for the destruction of organic pollutants in wastewater have been developed. The hydroxyl radical, the active species which attacks and destroys the undesired organic compounds [1], can be produced by heterogeneous processes. Photocatalytic methods present a high applicative potential [2–4] and also economical advantages in comparison with other methods.

The herbicide Fenuron is a compound largely used in agriculture owing to its inhibiting effect on the photosynthesis, but unfortunately it is a very persistent pollutant in the environment. This compound does not absorb at wavelength longer than 300 nm and consequently does not undergo direct photolysis in solar light. However, Aguer and Richard showed that the transformation of Fenuron can be photoinduced by humic substances [5]. The photocatalytic degradation of Monuron (3-(4-chlorophenyl)-1,1-dimethylurea), *i.e.* the chlorinated derivative of Fenuron, in aqueous suspensions of TiO₂ has been reported [6, 7]. The main photoproducts identified at pH = 5.7 were produced to be 4-chlorophenylisocyanate, 2-chlorophenol, 1,2-dihydroxybenzene, 1,2,3-trihydroxybenzene and 1,2,4-trihydroxybenzene.

The aim of the present work is to compare the photocatalytic reactivity of several commercial TiO₂ toward Fenuron. Product studies were performed in order to

identify the photoproducts and to propose a reaction mechanism. The effects of hydrogen peroxide and chloride ions on the photocatalytic degradation of Fenuron were also evaluated.

2. EXPERIMENTAL DETAILS

2.1. Chemicals. Fenuron (3-phenyl-1,1-dimethylurea) was purchased from Aldrich (98%). Titanium dioxide TiO₂ Degussa P25 was 70 : 30 anatase : rutile according to the manufacturer's specifications [8], with specific area 50 m² · g⁻¹. TiO₂-Tiona PC 100, TiO₂-Tiona PC 105 and TiO₂-Tiona PC 500 were all provided by Millennium Inorganic Chemicals, with respective specific areas (BET method) 100 ≥ S ≥ 80 m² · g⁻¹, 95 ≥ S ≥ 75 m² · g⁻¹ and S > 250 m² · g⁻¹, respectively. Millennium TiO₂ were mainly anatase.

2.2. Irradiation. Irradiations of aqueous suspensions of TiO₂ at wavelengths longer than 300 nm were carried out in an experimental device previously described [9]. The fluorescent lamp (Philips TLAD 15 W/05) emitted within the wavelength range 300–450 nm with a maximum of emission at 365 nm. The reaction mixture consisted of 20 mL of Fenuron (5 × 10⁻⁵ M) and 2 g · L⁻¹ of the oxide. It was stirred under oxygen bubbling for 30 minutes prior to irradiation.

2.3. Analyses. UV spectra were recorded on Secomam 1000 PC.

Semi-conductors particles were removed after irradiation by filtration on a Millipore filter (0.45 μm). HPLC analyses were performed on a Waters chromatograph equipped with a μ Bondapak 250 mm × 4.6 mm C₁₈-type

[†]E-mail: Claire.RICHARD@univ-bpclermont.fr

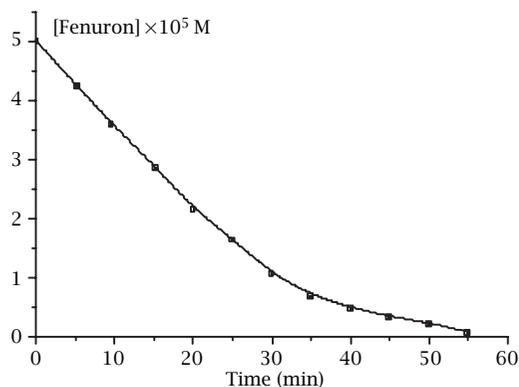


Figure 1. Kinetics of disappearance of Fenuron (5×10^{-5} M) in the presence of TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$).

column. The eluent was a mixture $\text{MeOH}/\text{H}_2\text{O}$ (30–70, v/v). The L.C. Spectrometer Lambda-Max 481 detector was set at 210 nm. Isolation of photoproducts was performed using a preparative HPLC Gilson equipped with a C_{18} Microsorb Column ($3 \mu\text{m}$, $100 \times 24 \text{ mm}^2$).

3. RESULTS AND DISCUSSION

3.1. Kinetic study. The irradiation of an aqueous solution of Fenuron (5×10^{-5} M) at 365 nm in the presence of TiO_2 Degussa P25 ($2 \text{ g} \cdot \text{L}^{-1}$) led to the total consumption of the substrate in 55 minutes (see Figure 1). The initial rate of the reaction and the half-life were equal to $1.5 (\mu \cdot \text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1})$ and 18 minutes respectively.

Adsorption-desorption equilibrium is an important preliminary step in the photocatalytic degradation process. Therefore, it is necessary that this equilibrium is attained before irradiating the solution. Assuming a Langmuir-Hinshelwood type kinetics, the initial rate of Fenuron consumption V_0 can be written:

$$V_0 = \frac{-dC}{dT} = K\theta = \frac{kK_F[F]_0}{1 + K_F[F]_0}, \quad (1)$$

where k , K , θ and $[F]_0$ are the rate constant of the reaction, the adsorption equilibrium constant, the surface coverage and the initial concentration of Fenuron, respectively. A linearised form of equation (1) has been employed:

$$\frac{1}{V_0} = \frac{1}{k} + \frac{1}{kK_F[F]_0}, \quad (2)$$

All experimental data were reported in Figure 2 as plots according to equation (2). Values of k and K were calculated by linear regression analysis of the experimental data. The results are summarized in Table 1.

3.2. Analytical study. Two main photoproducts were detected by HPLC. These products were separated

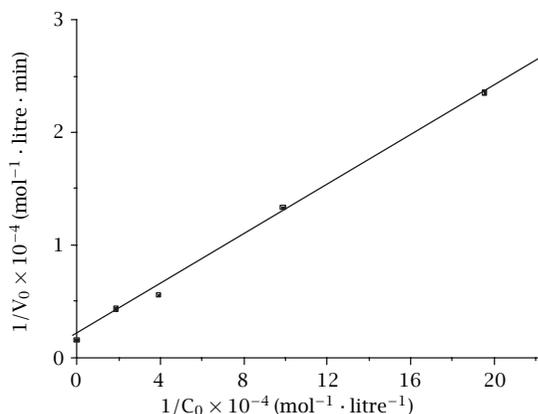


Figure 2. Linearised plots of equation (1) for transformation of Fenuron.

Table 1. Rate constant of photocatalytic transformation, adsorption constant and surface coverage (θ) for Fenuron (5×10^{-5} M) over TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$).

	k ($\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$)	K_F ($\text{mol}^{-1} \cdot \text{L}$)	θ
TiO_2	2.1×10^8	3440	0.146

by preparative HPLC and analyzed by NMR and mass spectrometry.

I and II have the following characteristics:

I: m/z 180; $[\text{H}^1]$ NMR (CD_3OD) δ (ppm) 7.30 (d, 2H, $J = 8.8 \text{ Hz}$), 6.89 (d, 2H, $J = 8.7 \text{ Hz}$), 3.19 (s, 6H).

II: m/z 180; $[\text{H}^1]$ NMR (CD_3OD) δ (ppm) 7.67 (dd, 1H, $J = 7.9 \text{ Hz}$, $J = 1.5 \text{ Hz}$), 7.11 (td, 1H, $J = 7.9 \text{ Hz}$, $J = 1.5 \text{ Hz}$), 7.02 (dd, 1H, $J = 8 \text{ Hz}$, $J = 1.5 \text{ Hz}$), 6.97 (td, 1H, $J = 7.8 \text{ Hz}$, $J = 1.5 \text{ Hz}$), 3.25 (s, 6H).

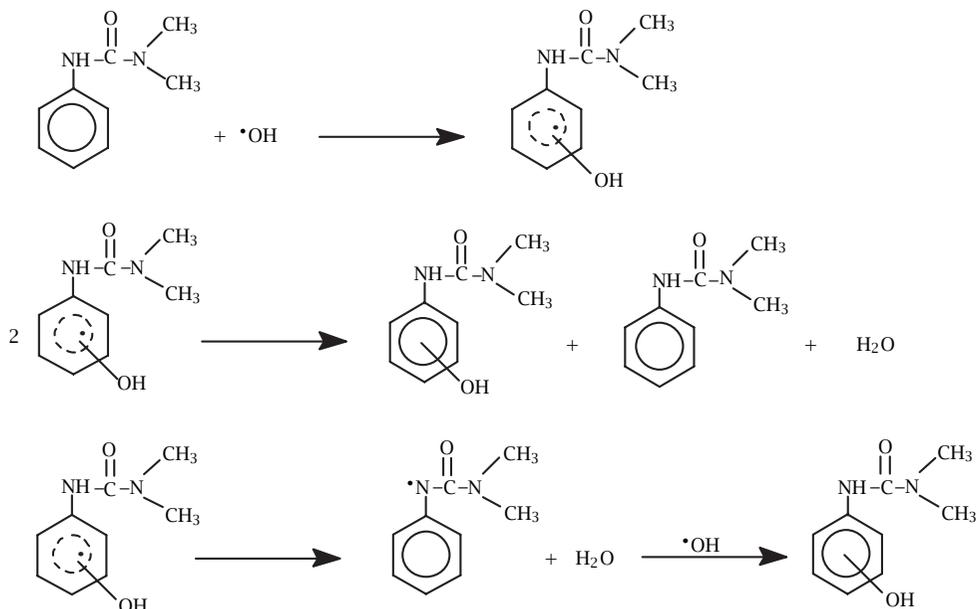
These two photoproducts can be assigned to the isomeric hydroxylation products:

I: 3-(4-hydroxyphenyl)-1,1-dimethylurea.

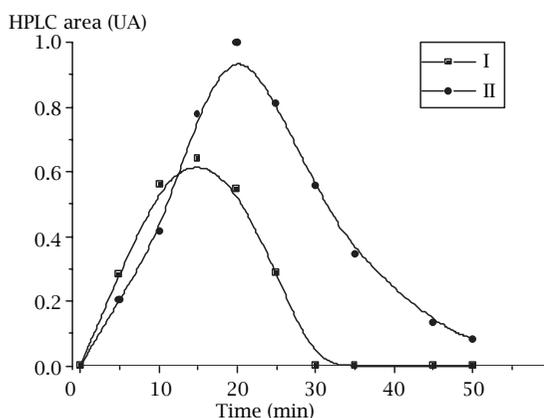
II: 3-(2-hydroxyphenyl)-1,1-dimethylurea.

The evolution of the two main photoproducts I and II as a function of the irradiation time is given in Figure 3. The concentration of the two products reached a maximum after 15 and 20 minutes of irradiation respectively. Then, photoproducts disappeared in turn in less than one hour. These kinetics show that the intermediary products disappear approximately in the same time scale as the parent compound. It favours the total mineralization.

3.3. Mechanism. The formation of hydroxylated photoproducts let assume the involvement of hydroxyl radicals in the primary oxidation step. The *ortho* and *para* orientation of the hydroxylation is in a good agreement with the hydroxyl radicals electrophilic behavior.



Scheme 1.

Figure 3. Evolution of the photocatalytic degradation products (TiO_2 Degussa P25).

The first stage of Fenuron photocatalytic degradation in the presence of TiO_2 is most probably the formation of an intermediate adduct, (complex radical : Fenuron ... HO^\bullet) as it has been observed with phenol [10], 4-nitrophenol [11] and chlorophenols [12].

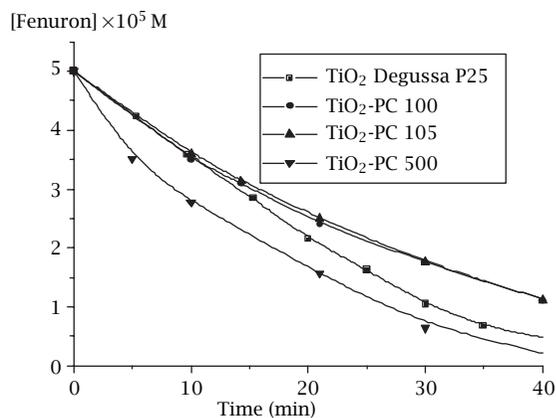
This complex undergoes either dismutation or dehydration followed by a second hydroxylation yielding the identified photoproducts according to the following reaction mechanism (Scheme 1).

The oxidation of the anilino radical or its reaction with the superoxide anion could also yield to the formation of hydroxylated products.

3.4. Comparative study of four different types of TiO_2 semiconductor. The photocatalytic activity of the TiO_2 Degussa P25 has been compared to that of

three other types of TiO_2 : Tiona PC 100, Tiona PC 105 and Tiona PC 500.

The kinetics of consumption of Fenuron (5×10^{-5} M) at 365 nm in the presence of the different TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$) is shown in Figure 4. It can be noticed that the induced photocatalytic degradation rates over the TiO_2 -PC 100 and TiO_2 -PC 105 were almost identical, and both smaller than the one observed over Degussa P25 in spite of the fact that these two photocatalysts have a surface area twice larger than that of Degussa P25. On the other hand, TiO_2 -PC 500, with a specific surface 5-fold larger degraded Fenuron slightly more quickly than TiO_2 Degussa P25. The increase of the surface area of the photocatalyst did not lead to the results hoped for. An improvement of the photocatalytic activity of TiO_2 was only observed with PC 500. But even in that

Figure 4. Comparison of the photocatalytic degradation of Fenuron in presence of four different types of TiO_2 .

case, the improvement was rather moderate in regard to the very large increase of the specific surface area.

Other factors, all related to the surface state, seem to affect equally the activity of the catalyst. It is possible that PC 100, PC 105 and PC 500 samples possess a higher density of superficial defects that contribute to the recombination of electron and positive hole h^+ . This could unfavour the photocatalytic activity of the semiconductor. A similar phenomenon has already been observed by D'Oliveira [13]. The possible presence of micropores in which Fenuron cannot penetrate and which provide in some ways an inactive surface may be mentioned too.

3.5. Chloride ions effect. Chlorides are inorganic ions frequently present in industrial waters and rivers. It is therefore interesting to consider their effect on the Fenuron degradation rate. This effect is shown in Figure 5. It was found that the presence of chloride ions (10^{-2} M) slightly reduced the photocatalytic oxidation rate. Nevertheless, this phototransformation still remained fast and led to the total disappearance of Fenuron within 60 minutes.

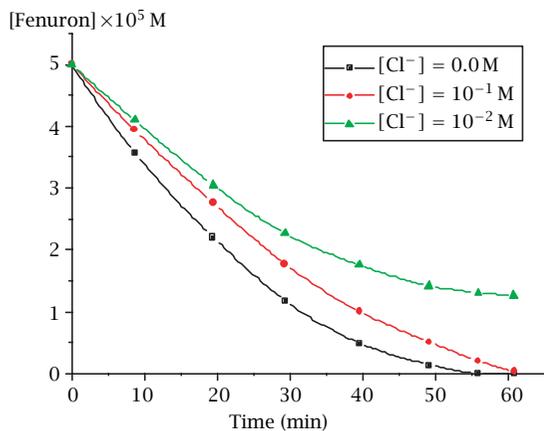


Figure 5. Influence of chloride ions concentration on the Fenuron photocatalytic degradation rate.

In photocatalysis, the inhibiting effect of inorganic ions is generally attributed either to their adsorption over the semi-conductor surface that blocks the active adsorption sites or by their quenching reaction with the most reactive oxidizing species (especially HO^* and h^+). For example, chloride ions add onto hydroxyl radicals with $k = 4.3 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ [14].

To determine by which of the two mechanisms mentioned above chloride ions inhibit the reaction, we made the following calculations. The chloride adsorption constant over TiO_2 Degussa P25 was obtained using the Langmuir-Hinshelwood model, taking into consideration the adsorption competition between the two different species present in the medium. We can express the surface coverage of Fenuron and chloride ions

Table 2. Fenuron (5×10^{-5} M) and chloride ions surface coverage fractions over TiO_2 ($2 \text{ g} \cdot \text{L}^{-1}$).

$[Cl^-]$ (M)	θ_F (%)	θ_{Cl^-} (%)
0	14.6	0
10^{-2}	13.8	6
10^{-1}	9	39

respectively as to be:

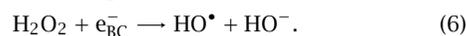
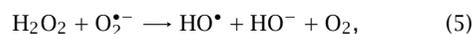
$$\theta_F = \frac{K_F [F]_0}{1 + K_F [F]_0 + K_{Cl^-} [Cl^-]_0}, \quad (3)$$

$$\theta_{Cl^-} = \frac{K_{Cl^-} [Cl^-]_0}{1 + K_F [F]_0 + K_{Cl^-} [Cl^-]_0}. \quad (4)$$

In the presence of chloride ions, the rate of Fenuron loss is expressed by: $V_0 = k\theta_F$ and the plot of $1/V_0$ vs $[Cl^-]_0$ gives the ratio $K_{Cl^-}/kK_F[F]_0$ as slope. Using the values of k and K_F given in Table 2, we found $K_{Cl^-} = 7.5 \text{ mol}^{-1} \cdot \text{L}$.

For a chloride concentration of 10^{-2} M, Fenuron surface coverage is only slightly reduced (from 14.6% in the absence of chloride to 13.8% in their presence). It can be concluded that the observed photoinhibition resulted from the quenching of hydroxyl radicals rather than from competitive adsorption. For the higher chloride concentration (10^{-1} M), Fenuron adsorption decreased by 38%. The observed inhibition can be due to the combined effect of the HO^* radical quenching with the competitive adsorption of chloride ions.

3.6. Hydrogen peroxide effect. H_2O_2 can be converted into the very oxidizing OH^* radicals by reduction. In photocatalysis, such a reduction may involve superoxide ions or electrons [15].



To check this hypothesis, we added H_2O_2 to the reactional mixture. As seen in Figure 6, the initial rate of

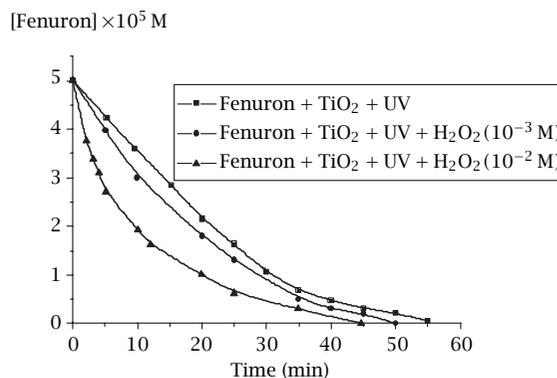


Figure 6. Influence of H_2O_2 on the photocatalytic degradation of Fenuron (5×10^{-5} M) over TiO_2 Degussa P25.

the Fenuron disappearance was increased by a factor of three using H₂O₂ (10⁻² M). This acceleration may be attributed to the above mentioned reactions. Therefore the TiO₂/H₂O₂/UV process is more efficient than the TiO₂/UV process.

4. CONCLUSION

The primary reaction observed upon the excitation of titanium dioxide suspensions in a solution containing Fenuron involves an oxidation by hydroxyl radical in the *ortho* and *para* positions with respect to the urea function. The major intermediates formed are: 3-(4-hydroxyphenyl)-1,1-dimethylurea and 3-(2-hydroxyphenyl)-1,1-dimethylurea.

The kinetic study of Fenuron disappearance in the presence of TiO₂ shows that the reaction occurs mainly in the adsorbed phase where the substrate undergoes an oxidation before it gets desorbed. The Fenuron adsorption constant on TiO₂ was evaluated as 3440 (mol⁻¹ · L).

The addition of hydrogen peroxide accelerates the Fenuron photocatalytic degradation rate by increasing the rate of formation of the hydroxyl radicals. Hydrogen peroxide reacts either with electrons ejected from the semiconductor surface upon illumination or with O₂⁻ photoadsorbed on the semiconductor surface.

The disappearance rate of Fenuron is reduced by the presence of chloride ions in moderate concentrations (10⁻² M).

With Fenuron, TiO₂-PC 500 is more efficient than Degussa P25. However, the TiO₂ specific surface area is not the only parameter influencing the TiO₂ photocatalytic activity.

Acknowledgements

The authors acknowledge the Ministère de l'Enseignement Supérieur et de la Recherche Scientifique for its

financial support. We are grateful to Millenium Inorg. Chem. for providing several titanium dioxides and to Dr P. BOULE of the University of Blaise Pascal (France), for his kind interest in this work and help.

References

- [1] W. R. Haag and C. C. D. Yao, *Environ. Sci. Technol.* **26** (1992), 1005.
- [2] M. Trillas, J. Peral, and X. Doménech, *Appl. Catal. B: Environmental* **3** (1993), 45.
- [3] A. Scalfani, L. Palmisano, and M. Schiavello, *J. Phys. Chem.* **94** (1990), 829.
- [4] A. Mills, S. Morris, and R. Davies, *J. Photochem. Photobiol. A: Chem.* **70** (1993), 183.
- [5] J. P. Aguer and C. Richard, *Pestic. Sci.* **46** (1996), 151.
- [6] V. Augugliaro, G. Marci, and L. Palmisano, *Res. Chem. Intermed.* **19** (1993), 839.
- [7] E. Pramauro, M. Vincenti, V. Augugliaro, and L. Palmisano, *Environ. Sci. Technol.* **27** (1993), 1790.
- [8] Degussa Corporation (1990) Technical Bulletin pigments, No. **56**, Degussa G, Frankfurt, 5th edition.
- [9] K. Djebbar and T. Sehili, *Pestic. Sci.* **54** (1998), 269.
- [10] E. J. Land and M. Ebert *Trans. Faraday Soc.* **63** (1967), 1181.
- [11] B. Cercek and M. Ebert, *Adv. Chem. Ser.* **81** (1968), 210.
- [12] N. Getoff and S. Solar, *Radiat. Phys. Chem.* **28** (1986), 443.
- [13] J.-C. D'Oliveira, C. Guillard, C. Maillard, and P. Pichat, *J. Environ. Sci. Health. A28* (4) (1993), 941.
- [14] N. Kouachi and T. Sehili, *Toxicol. Environ. Chem.* **68** (1997), 141.
- [15] J. Weinstein and H. J. Bielski, *J. Am. Chem. Soc.* **101** (1979), 58.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

