Photocatalytic degradative oxidation of Diuron in organic and semi-aqueous systems over titanium dioxide catalyst

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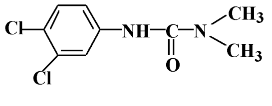
The photocatalytic degradation of Diuron in organic and semi-aqueous media is compared. The rates of disappearence fit Langmuir–Hinshelwood kinetics and the parameters k and K have been determined. A main intermediate was detected in all cases and its structure has been determined. This product is obtained by oxidation of a methyl group of the urea moiety. Several compounds [trichloroaniline, dichloronitrobenzene, *N*-(3,4-dichlorophenyl)formamide, dimethylurea . . .] were detected by GC-MS analysis in both media while hydroxylated compounds were only observed in the semi-aqueous medium.

Heterogeneous photocatalysis in TiO_2 aqueous suspensions is a technique used for the total destruction of organic pollutants in water.[1,2] (This aspect has been extensively developed by several authors in a chapter devoted to photocatalytic water treatment in ref. 2.) Titanium dioxide is particularly efficient since the formation of electron-hole pairs under illumination with sunlight is promoted by the near-UV component of this radiation, which encompasses energies higher than the corresponding band gap. The successive steps involve the oxidation of organics through reactions with the holes or with radicals generated from the solvent, from the catalyst surface and from adsorbed oxygen.

The presence of pesticides in the water supply has increased in the last few years because of the extensive use of these compounds and their high stability in solution. Their elimination is necessary, especially if the water is destined for household consumption.

As part of our research on one class of pollutants, hydroxylated biphenyl compounds,[3] we now present the study of one herbicide in particular: Diuron or *N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea for which the half-life time in soil is 372 days.[4]



The objective of this study was to compare the degradation of this compound in two different media, organic and semi-aqueous, by means of kinetic analysis, taking into account that the photocatalytic degradation of Diuron at 5×10^{-5} mol L^{-1} in water has already been reported in the literature.[5] Moreover, this molecule, which contains both an aromatic ring and an aliphatic chain, is particularly interesting as different types of photoreactions can take place. The various photochemical intermediates present in both media were also identified.

Experimental

Diuron was purchased from Sigma. TiO_2 was Degussa P-25 with a measured specific area of 57 m^2 g^{-1} and an average particle size of 27 nm.[6]

Experiments were performed at room temperature in a 500 mL open cylindrical Pyrex cell irradiated with an HPK 125 W mercury lamp (wavelength $\lambda > 310$ nm) as a central light source, surrounded with 3 similar lamps and cooled by circulating water.

Diuron in 360 mL of solvent and 150 mg TiO_2 were introduced into the reactor under oxygen bubbling. CO_2, which evolved during irradiation, was measured by conductimetry (Consort conductimeter K320) by absorption in NaOH solution. A reference curve (conductivity *vs.* weight of CO_2 dissolved in 1 M NaOH solution) was previously established. At different time intervals, aliquots of solution were taken and analyzed by high performance liquid chromatography (HPLC), using a Shimadzu UV spectrophotometer SPD-6A detector at 280 nm and controlled by a PC running an ICS software package. A Kromasil C18 column (12.5 cm, 5 μm) and an acetonitrile–water (30 : 70) mobile phase were used. Samples were also analyzed by combined liquid chromatography (Shimadzu LC-10 AT)–particle beam–mass spectrometry (Fisons Instruments Trio 1000) with the same Kromasil C18 column. The process was controlled by a Digital Venturis PC with the software package Masslab.

A GC-MS (Hewlett–Packard 5890/5970 A) was used for more sensitive analysis with an OV-1 type glass capillary column (25 m, 0.23 mm). The entire process was controlled by an HP 486 PC with the software package HP G1034C.

Results and discussion

Photocatalytic disappearance of Diuron

Because the water solubility of Diuron at ambient temperature is very low (42 ppm)[4] and our analytical technique was not suitable for detecting such weak concentrations, the

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photocatalyzed mineralization of Diuron was carried out in organic (CH_3CN) and in semi-aqueous (CH_3CN–H_2O, 2.6 : 1 by volume) media.

Effect of initial concentration in organic medium. The photocatalytic degradation of Diuron in acetonitrile solution was studied for three initial concentrations: 6×10^{-4}, 6×10^{-3} and 3×10^{-2} mol L^{-1}, corresponding to an initial mass m_0 of 50, 500 and 2500 mg, respectively. The disappearance of Diuron *vs.* time (Fig. 1) follows apparent first-order kinetics, at a low coverage resulting from the low concentration of Diuron (6×10^{-4} mol L^{-1}):

$$v = -\mathrm{d}[\mathrm{Diuron}]/\mathrm{d}t = k_a[\mathrm{Diuron}]$$

with the apparent pseudo-first-order rate constant k_a. The linear transformation Ln [Diuron] = $-k_a\ t$ + Ln $[\mathrm{Diuron}]_0$ is given in Fig. 2. The slope of the straight line gives the value of $k_a = 0.53\ h^{-1}$. At high concentration (3×10^{-2} mol L^{-1}), the reaction becomes zeroth-order [the disappearance of Diuron *vs.* time is linear: [Diuron] = $k't$ with $k' = 0.0017$ mol $L^{-1}\ h^{-1}$ (Fig. 3)], indicating saturation of the TiO_2 surface. These results are consistent with a Langmuir–Hinshelwood model, which is a manifestation of the more general case of saturation-type kinetics.

Fig. 4 shows the variation of the initial rate of Diuron disappearance *vs.* initial concentration. The experimental data fit Langmuir–Hinshelwood-like kinetics, which is generally found for photocatalytic degradations:[7–9]

$$v_0 = \frac{kK[\mathrm{Diuron}]_0}{1 + K[\mathrm{Diuron}]_0}$$

where v_0 is the initial rate of Diuron disappearance, k the rate constant and K the adsorption coefficient. The linear transformation of the Langmuir–Hinshelwood-type relationship, by plotting $1/v_0$ against $1/[\mathrm{Diuron}]_0$ (Fig. 5), allows the values of the kinetic parameters k and K to be determined from the intercept and the slope of the straight line. The values $k = 1.4 \times 10^{-3}$ mol $L^{-1}\ h^{-1}$ and $K = 446$ L mol^{-1} were obtained. These values are discussed further below.

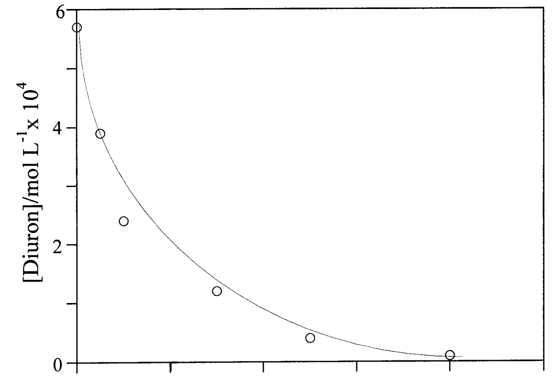


Fig. 1 Photocatalytic disappearance of Diuron (m_0 = 50 mg) *vs.* time with 150 mg TiO_2.

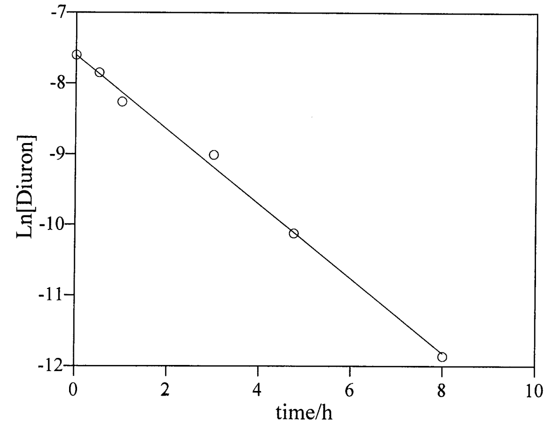


Fig. 2 Linear transform of the disappearance of Diuron (m_0 = 50 mg) *vs.* time.

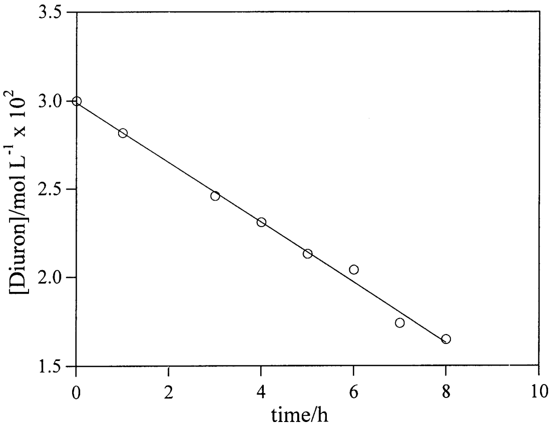


Fig. 3 Photocatalytic disappearance of Diuron (m_0 = 2.5 g) *vs.* time with 150 mg TiO_2.

Effect of initial concentration in acetonitrile–water solution. Fig. 6 shows the kinetics of disappearance of Diuron in organic and semi-aqueous media. These experiments show that Diuron degradation is faster in CH_3CN than in CH_3CN–H_2O; after about 8 h of irradiation in acetonitrile, the disappearance of Diuron is complete, whereas in acetonitrile–water, it is not totally achieved even after 48 h. This result seems surprising since it is well-known that in

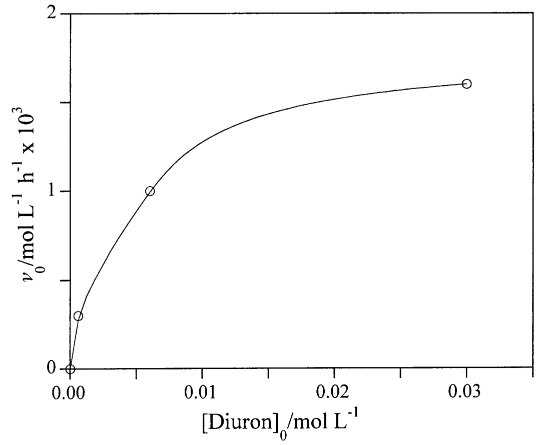


Fig. 4 Initial rate of Diuron disappearance *vs.* initial concentration.

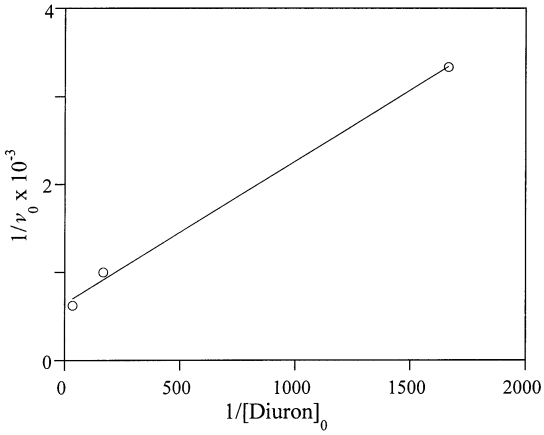


Fig. 5 Relationship between reciprocal initial rate and reciprocal concentration.

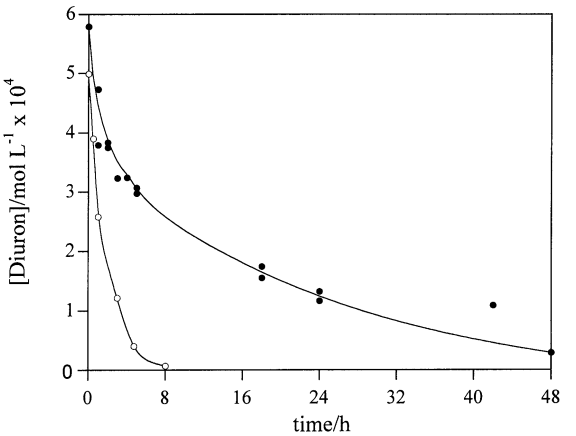


Fig. 6 Kinetics of disappearance of Diuron (m_0 = 50 mg) in CH_3CN (○) and 2.6 : 1 CH_3CN–H_2O (●) with 150 mg TiO_2.

water, ˙OH are formed and these radicals are very efficient in promoting various degradation processes.

As described above, the two Langmuir parameters in the semi-aqueous medium were calculated to be $K = 4700$ L mol^{-1} and $k = 6.6 \times 10^{-4}$ mol L^{-1} h^{-1}. This value of K is 10 times greater than that in acetonitrile and is consistent with the reported values for other aromatic compounds in water; for example, $K = 4860$ L mol^{-1} for 4-chlorophenol, chlorobenzene and benzoic acid.[7]

From the traditional derivation of Langmuir–Hinshelwood kinetics, K represents the equilibrium adsorption constant of the reactant while k is the measure of the intrinsic reactivity at the surface. The fundamental meaning of the model parameters is unclear for photocatalytic degradations and the value of K derived from a photocatalytic kinetic study is not directly equivalent to the Langmuir adsorption constant (determined in the dark).[10,11] As expected, K varies with the medium, as seen above, while k decreases when K is increasing. More data are required to give an interpretation of these phenomena.

Reaction intermediates

Diuron clearly offers two sites for oxidation: the aromatic ring and the aliphatic side chain. It seems that, according to the literature, experimental conditions determine which portion of the molecule, aromatic or aliphatic, is attacked.[9]

The temporal course of the degradation was followed by high performance liquid chromatography. In both organic and semi-aqueous media, one intermediate primary product was detected by HPLC, which very slowly underwent further transformation and mineralization. Its maximum concentration was reached after 50 h irradiation time. The evolution *vs.* time curve is given in Fig. 7. After 120 h irradiation time, this intermediate product was still detected (30%). We cannot rule out that other parallel Diuron degradation pathways might exist, whose products could not be detected due to their low concentration in the solution and their instability, up to total mineralization. However, a good mass balance was found between the quantity of Diuron consumed and the total amount of intermediate and CO_2 evolved.

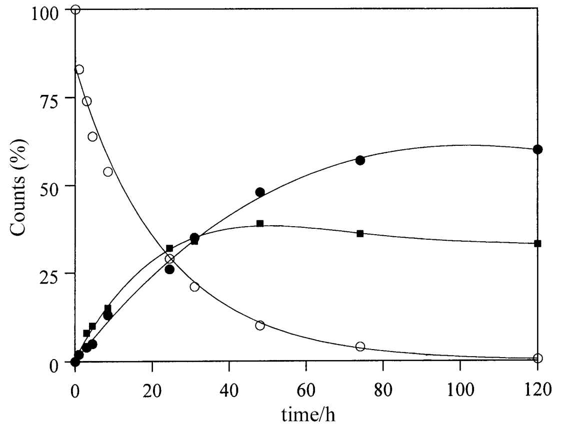
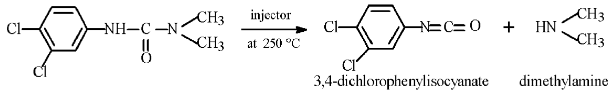


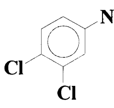
Fig. 7 Kinetics of the disappearance of Diuron (○) (m_0 = 500 mg) and of the resulting appearance/disappearance of intermediate (■) as well as the resulting formation of carbon dioxide (●) in acetonitrile medium with 150 mg TiO_2.

The nature of this intermediate, clearly determined by IR, ^{13}C and ^1H NMR, and LC-MS, is consistent with an *N*′-[3,4-dichlorophenyl]-*N*-methyl-*N*-formylurea structure. The oxidation thus occurred on one methyl group to give the corresponding aldehyde. This result is in good agreement with that described by Jirkovsky *et al.*[5] Photocatalytic transformations of two compounds of the same family, Monuron[12] and Fenuron,[13] have also been reported in the literature. In aqueous solutions, Monuron is degraded into several hydroxylated aromatic products and 4-chlorophenylisocyanate from the selective attack of oxidizing species on the alkyl urea group. The photocatalytic transformation of Fenuron depends on the pH of the aqueous TiO_2 suspension; in neutral media, both the aromatic and the methyl groups are oxidized. In acidic solution, the main reaction is the oxidation of the methyl groups and attack on the aromatic ring is a very minor process. The specific oxidation of the methyl groups in acidic media can be explained by the way in which Fenuron is adsorbed at the surface of TiO_2.[13] Our results are in accord with those on Fenuron in acidic media.

GC-MS analysis of the Diuron filtrate after 48 h of irradiation revealed traces of several other compounds depending on the solvent. It is worth noting that Diuron itself is not detected by GC because it is thermally degraded in the GC injector to give 3,4-dichlorophenylisocyanate (**1**) following the reaction:



In organic solvent. In acetonitrile, traces of trichloroaniline (**2**), dichloronitrobenzene (**3**), *N*-(3,4-dichlorophenyl)formamide (**4**) and *N*,*N*-dimethylurea (**5**) were detected by GC-MS. *N*,*N*-Dimethylurea results from the cleavage of the side chain. The presence of trichlorinated compounds is difficult to explain and such a phenomenon (increase in the Cl atom number) has not been reported in the literature for similar substrates,[12,14] but has been reported once in the case of Lindane.[15]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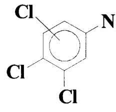
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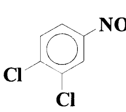
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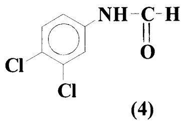
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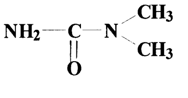
(5)

$NH_2{-}C(=O){-}N(CH_3)_2$

In semi-aqueous medium. Many reports on the photocatalytic degradation of organic compounds in aqueous solutions have suggested the action of ˙OH radicals.[16–18] These radicals can be produced by the surface reaction of photoproduced holes with adsorbed water. The formation of hydroxylated compounds would seem therefore reasonable. In fact, possible hydroxylated intermediates were identified by GC-MS and, in particular, the peaks at m/z = 203 and 219 can be attributed to mono- and di-hydroxy-3,4-dichlorophenylisocyanate. These compounds might arise from Diuron by an oxidative process involving $^{\bullet}OH$ radicals, followed by the previously noted thermal degradation in the GC injector. It is not possible yet, from the present data, to elucidate the mechanism of the decomposition, since it is very difficult to identify all the other intermediates.

Conclusion

The photocatalytic degradation of Diuron has been demonstrated in organic and semi-aqueous medium. It follows Langmuir–Hinshelwood kinetics. A primary intermediate corresponding to the oxidation of a methyl group was detected in both solvents; the further degradation of this compound is slow. In semi-aqueous media, traces of hydroxylated products can be assumed but the degradation scheme is complex.

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