

# Photocatalytic degradation of the diuron pesticide

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**Abstract** The occurrence of chlorinated pesticides in wellwaters is a major problem of public health in Ivory Coast and other African countries. Here, we studied the photocatalytic degradation of the pesticide diuron in aqueous solution in presence of two commercial TiO<sub>2</sub> catalysts, P25 and PC500. The capacity of diuron adsorption at the TiO<sub>2</sub> surface is lower for both photocatalysts. The efficiency of photocatalytic degradation of diuron, it is higher using P25 Degussa than PC500 Millenium TiO<sub>2</sub> catalyst.

**Keywords** Photocatalysis · TiO<sub>2</sub> · Diuron · Adsorption

## Introduction

In African agricultural areas specialized in the intensive agriculture, for example coffee, coconuts and cocoa, significant quantities of pesticides are used and rejected. In particular, the pesticide family of organochlorides are found in various natural environments such as soil, air and water. The presence of chlorinated phenols and pesticides in peasant well water is a large problem of public health in

African countries because of their great chemical stability and toxicity. It is therefore urgent to implement an efficient treatment of contaminated drinking water especially for the precarious districts of Abidjan city.

The conventional biological treatments of water slightly concentrated in chlorinated pollutants are long and moreover not very effective (Dyonisous et al. 2000). It is necessary to use an advanced oxidation process such as the heterogeneous photocatalysis. Moreover, TiO<sub>2</sub> photocatalytic reactions generally follow a pseudo first order kinetic (Mills et al. 1997). Consequently, the first 80 or 90% of water organic pollutants are rapidly degraded. The problem is for the last remaining percents, because their elimination is longer and too expensive. Our proposal is to use the adsorption on coconut activated carbon to supplement the treatment by photocatalysis. The main objective of this project is to use the natural resources of Ivory Coast for the drinking water treatment especially solar energy and active carbon from coconut shells. Diuron pesticide has been employed for the evaluation of the PhotoCatalytic/Activ-Carbon (PC/AC) coupled system performances. Diuron is a highly biorecalcitrant organic contaminant present in the hydrosphere due to industrial and intensive agricultural activities (Giacomazzi et al. 2004). This is an herbicide belonging to the urea family and the subclass of phenylurea. This compound has been chosen because it is considered as a priority hazardous substance by European commission (Hincapié 2005). According to the French Environmental Institute, diuron is detected in 28% of the samples from rivers in the national basin system.

The preliminary step of our project is to investigate the photocatalytic degradation of diuron water solution. In this paper we studied adsorption of diuron on titanium dioxide. The kinetic study of the photocatalytic degradation of diuron in aqueous solution has been performed with

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P25-TiO<sub>2</sub> from Degussa and Titania PC500 from Millennium Inorganic Chemicals. In addition we compared the influence of TiO<sub>2</sub> loading and pesticide concentration on the initial disappearance of pesticide with both catalysts.

## Experimental part

### Materials

Diuron (99.5% purity, *N*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea) was from Aldrich Company. Titanium dioxide P25 from Degussa Corporation (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of 50 m<sup>2</sup>/g) and Titania PC500 from Millennium Inorganic Chemicals (anatase > 99%, Surface area > 350 m<sup>2</sup>, crystallites mean size = 5–10 nm) were used as received.

### Adsorption experiments

All adsorption equilibrium experiments of diuron on the TiO<sub>2</sub> surface were carried out in batch mode under dark conditions. Studies were made with suspensions prepared by mixing 50 mL solution of various initial concentrations of diuron at their natural pH (5–6) and TiO<sub>2</sub> concentration of 1 g L<sup>-1</sup> (in deionized water). The equilibrium concentrations of diuron in solutions was followed after centrifugation by measuring the change in adsorption intensity at this  $\lambda_{\max}$  (248 nm) using a LIBRA S12 UV–Vis spectrophotometer.

### Photocatalytic experiments and analytical procedure

A 500 mL of diuron water solution ([Diuron] = 5, 10, 15 or 20 mg L<sup>-1</sup>) with an appropriate weight of TiO<sub>2</sub> P25 or PC500 ([TiO<sub>2</sub>] = 0.1, 0.5, 1, 1.5 or 2 g L<sup>-1</sup>) were homogenized using magnetic stirring for 45 min in deionized water, until equilibrium state was achieved. The photocatalytic processes were conducted in the Solar box ATLAS SUNTEST CPS+ simulating natural radiation (light source vapour Xenon lamp, 300 <  $\lambda$  < 800 nm). All experiments have been performed at 35°C. The mixtures of contaminants and catalysts were continuously magnetically stirred during photocatalytic tests. Under illumination and without photocatalyst, no noticeable evolution of diuron concentration was detected indicating this pesticide is not hydrolysed or degraded by photolysis.

The remaining concentration of diuron was determined after separation of photocatalyst by centrifugation, by high performance liquid chromatography (HPLC waters 600 pump and 996 photodiode array detector, C-18 apolar

column and acetonitrile (70%) water (30%) mixture as mobile phase).

The concentration of ammonia (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) ions was measured after 120 min of degradation. NO<sub>3</sub><sup>-</sup> was determined by the spectrophotometric method using sulfosalicylic and sulphuric acid after alkali treatment. As for ions NH<sub>4</sub><sup>+</sup>, they are measured with the indophenol blue. NH<sub>4</sub><sup>+</sup> reacts with phenol and hypochlorite in the presence of nitroprussiate as a catalyst. Measurements are made with a 630 nm wavelength.

## Results and discussion

### Diuron adsorption on TiO<sub>2</sub> P25 and PC500 without illumination

Preliminary experiments, performed up to 14 h under constant magnetic stirring, have demonstrated that the equilibrium is reached after 1 h. As shown in Fig. 1, the amount of diuron adsorbed at equilibrium in the dark increases with the equilibrium concentration for both titanium dioxide samples. Adsorption results of diuron on TiO<sub>2</sub> exhibit a typical IUPAC type II isotherm shape, usually attributed to non-porous and macroporous substances. This probably corresponds to the transition from a monolayer to a multilayer adsorption suggested by Parra et al. (2002). In the case of diuron a second plateau is not reached because of its low solubility in water ( $S_{\max}$  = 35 mg L<sup>-1</sup> in pure water). Consequently, it is not possible to linearize this isotherm.

### Photocatalytic degradation of diuron with TiO<sub>2</sub> catalysts

Studied concentrations (5–20 mg/L) are huge in front of the environmental ones, even in contaminated areas (rarely superior to 0.1 mg/L). This can be understood because of

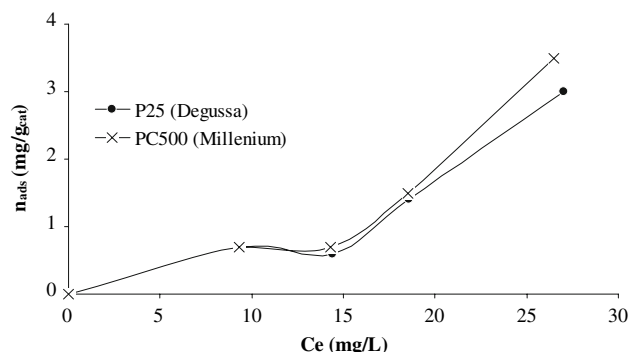


Fig. 1 Adsorption isotherms of diuron on TiO<sub>2</sub> P25 and PC500

technical constraints (analysis of intermediates products, adsorption study, etc.).

#### Effect of initial diuron concentration

The photodegradation kinetics of many organic compounds in TiO<sub>2</sub> dispersions under UV irradiation have been often modelled to the Langmuir–Hinshelwood equation (Turchi and Ollis 1990). In this model, the rate of reaction ( $r$ ) is proportional to the fraction of surface covered by the substrate ( $\theta$ ) (Eq. 1):

$$r = -\frac{dC}{dt} = k\theta = \frac{kKC}{1 + KC} \quad (1)$$

where  $C$  is the concentration in substrate,  $t$  the irradiation time,  $k$  the true rate constant (depends on experimental parameters) and  $K$  the constant of adsorption equilibrium of L–H (empirically obtained). When the solution is highly diluted, the term  $KC$  can be neglected. In this case the reaction is essentially an apparent first order reaction and after integration, Eq. (1) can be simplified in Eq. (2):

$$\ln(C_0/C) = k_{ap}t \quad (2)$$

where  $k_{ap}$  is the apparent rate constant of a pseudo first-order reaction.

Figure 2 presents  $\ln(C_0/C)$  versus  $t$  (the illumination time) at different initial concentration with 1.0 g/l of P25 or PC500 TiO<sub>2</sub> at natural pH. The apparent rate constant ( $k_{ap}$ ) can be determined from the slope of the curve obtained (Table 1). These curves describe a linear behaviour and the linear regression coefficients are comprised between 0.9904 and 0.9997. This clearly indicates that the photodegradation reaction of diuron obeys a first order kinetics.

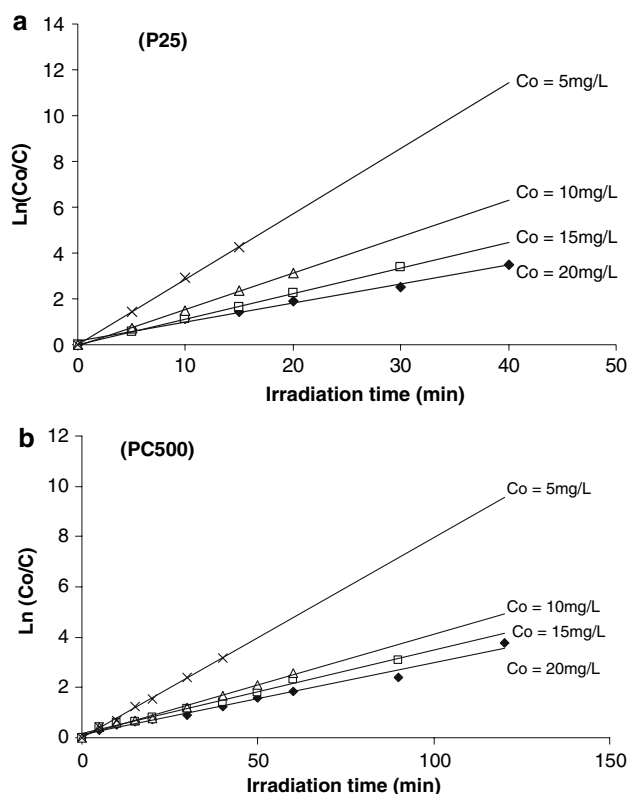
In Fig. 3, it is shown that the initial degradation rate  $r_0$  increases at the beginning with the diuron concentration, to then attain a plateau at around 10 mg L<sup>-1</sup>, indicative of Langmuir-type saturation kinetics. This is confirmed by the linear plots of  $1/r_0$  versus  $1/C_0$  with an intercept on the ordinate in accordance with Eqs. (3) and (4).

$$r_0 = -\frac{dC}{dt} = \frac{kKC_0}{1 + KC_0} \quad (3)$$

Hence

$$\frac{1}{r_0} = \frac{1}{kKC_0} + \frac{1}{k} \quad (4)$$

where  $C_0$  is diuron initial concentration,  $k$  is often interpreted in the literature (Cunningham and Srijaranai 1994) as a pseudo-first-order Langmuir–Hinshelwood-type rate coefficient relating to TiO<sub>2</sub> sensitized primary oxidation



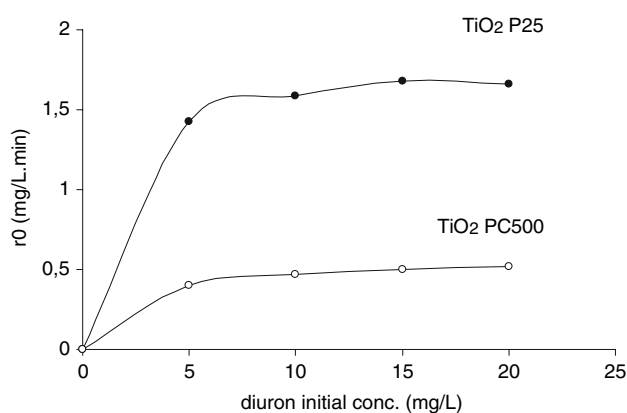
**Fig. 2** First-order linear transforms of the photodegradation of various diuron solutions by **a** TiO<sub>2</sub>–PC500 and **b** TiO<sub>2</sub>–P25

events in a surface monolayer ( $k = 0.576 \text{ mg L}^{-1} \text{ mn}^{-1}$  and  $k = 1.787 \text{ mg L}^{-1} \text{ mn}^{-1}$  respectively for TiO<sub>2</sub> PC500 and P25) and  $K$  is a pseudo-equilibrium constant related to monolayer adsorption ( $K = 0.451 \text{ L mg}^{-1}$  and  $K = 0.801 \text{ L mg}^{-1}$ , respectively, for TiO<sub>2</sub> PC500 and P25).

This Langmuir-type relationship between the initial degradation rate and concentration, reported also by other authors (Parra et al. 2002), indicates that adsorption intervenes in the photocatalytic reaction.

**Table 1** Kinetic parameters obtained

$C_0$ (mg L <sup>-1</sup> )	$r_0$ (mg L <sup>-1</sup> min <sup>-1</sup> )	$k_{ap}$ (min <sup>-1</sup> )	$k$ (mg L <sup>-1</sup> min <sup>-1</sup> )	$K$ (L mg <sup>-1</sup> )
TiO <sub>2</sub> P25				
5	1.428	0.2856		
10	1.586	0.1586	1.787	0.801
15	1.682	0.1121		
20	1.662	0.0831		
TiO <sub>2</sub> PC500				
5	0.399	0.0798		
10	0.472	0.0472	0.576	0.451
15	0.500	0.0333		
20	0.520	0.026		



**Fig. 3** Variation of diuron initial degradation rates as a function of its initial concentration

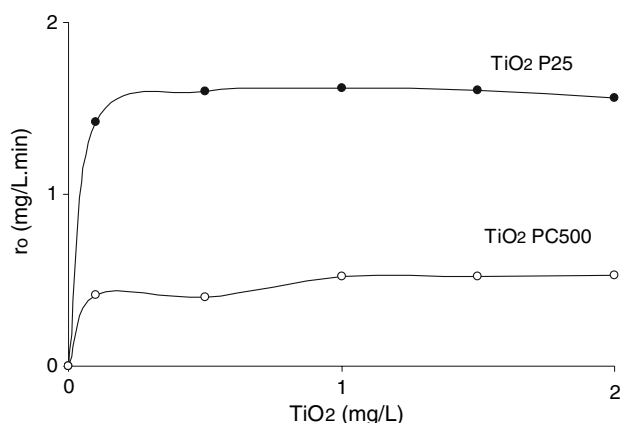
As it may be observed, the initial degradation rate ( $r_0$ ) of diuron increased with the initial concentration ( $C_0$ ) (Table 1). A better analysis of this result can be done if considered Eq. (3). So, for low initial concentrations of diuron, the product  $KC_0$  becomes  $\ll 1$  and the denominator of this equation turns  $\sim 1$  and it can be represented as :

$$r_0 = kKC_0 = k_{ap}C_0 \quad (5)$$

that describes the degradation rate for a first order reaction (Mehrotra et al. 2005).

#### Effects of $TiO_2$ loading

The mass of catalyst is a very important parameter in heterogeneous photocatalysis because the apparent rate constants of reaction were found to be directly proportional to the mass until a certain value a plateau is reached (Fig. 4). According Jean Marie Herrmann (1999) this limit depends on the geometry and the working conditions of the



**Fig. 4** Evolution of the degradation rate according to the mass of photocatalyst ([Diuron] = 20 mg/l)

photoreactor. This plateau fits with to the maximum amount of  $TiO_2$  in which all the particles are totally illuminated, after this limit a screening effect of excess particles occurs. In our condition the optimum mass of catalyst is 1 and 0.5  $mg/cm^3$ , respectively, for PC500 and P25. On Fig. 4, we observed also that the  $TiO_2$  P25 is more efficient than PC500 in the same working conditions. Madani et al. (2006) explained this difference in reactivity by a better light absorption by P25 than by PC500.

Another reason for the better photocatalytic activity of P25 could be attributed to the fact that P25 is composed of small nanocrystallites of rutile being dispersed within an anatase matrix. The band gap energy of anatase is slightly higher than that of rutile (Haque et al. 2006).

#### Mineralization of nitrogen

We followed the mineralization of the organic nitrogen atom of the diuron. Table 2 shows the simultaneous formation of ammonia  $NH_4^+$  and nitrate  $NO_3^-$  ions after 120 min of photocatalytic degradation. Malato et al. (2003) proposed the following stoichiometric equation for the complete oxidation of diuron:



As these authors, we noticed that nitrogen released has been measured as a combination of ammonia and nitrate. Ammonia is an intermediate compound that can be oxidized to nitrate after a long irradiation time (Bonsen et al. 1997). In the Table 2, for both photocatalysts the quantities of  $N-NO_3^-$  and  $N-NH_4^+$  has been noted. We observed that the nitrogen mass balance of diuron is not complete because

**Table 2** Concentration of  $N-NO_3^-$  and  $N-NH_4^+$  after 120 min of irradiation

$TiO_2$ P25	$C_0$ (mg/l)			
	5	10	15	20
$N-NO_3^-$	0.082	0.147	0.385	0.352
$N-NH_4^+$	0.194	0.396	0.436	0.739
$N_{Exp}$	0.276	0.543	0.821	1.091
$N_{Th}$	0.3	0.6	0.9	1.2
%N	92	90.5	91.22	90.92
$N-NO_3^-$	nd	0.055	0.352	0.387
$TiO_2-PC500$				
$N-NH_4^+$	nd	0.474	0.451	0.677
$N_{Exp}$	nd	0.529	0.803	1.064
$N_{Th}$	nd	0.6	0.9	1.2
%N	nd	88.17	89.22	88.67

nd no-determined

only 90% of the initial N was detected as ammonia or nitrate after 120 min of irradiation time. Different authors explain this incomplete conversion by the formation of other nitrogen organic compounds (like hydroxylamine) or  $N_2$  (Low et al. 1991 and Pramauro et al. 1993).

## Conclusion

The photocatalytic degradation of the herbicide diuron by two commercial titanium dioxide has been considered. The results of our kinetic study show that the kinetic model for diuron photocatalytic degradation follows the L–H model. The adsorption capacity of diuron is lower and similar for P25 and PC500. The rate of degradation is proportional to the initial concentration. Then a plateau is reached. For a maximum yield, reaction should be performed with initial concentration equal to the threshold of the plateau.

In our condition the optimum mass of catalyst are 1 and  $0.5 \text{ mg/cm}^3$ , respectively, for PC500 and P25. The determination of  $N\text{-NO}_3^-$  and  $N\text{-NH}_4^+$  concentration after 120 min of irradiation indicates that the nitrogen mass balance is incomplete and 10% of nitrogen is in organic form or  $N_2$ .

## References

- Bonsen EM, Schroeder S, Jacobs H, Broekaeet JAC (1997) Photocatalytic degradation of ammonia with  $\text{TiO}_2$  as photocatalyst in the laboratory and under the use of solar radiation. *Chemosphere* 35:1431–1445
- Cunningham J, Srijaranai S (1994) Adsorption of model pollutants onto  $\text{TiO}_2$  particles in relation to photoremediation of contaminated water. In: Helz GR, Zepp RG, Crosby DG (eds) *Aquatic and surface photochemistry*. Lewis Publishers, Boca Raton, pp 317
- Dionysiou DD, Khodadoust AP, Kern AM, Suidan MT, Baudin I, Lainé JM (2000) Continuous-mode photocatalytic degradation of chlorinated phenols and pesticides in water using a bench-scale  $\text{TiO}_2$  rotating disk reactor. *Appl Catal B: Environ* 24:139–155
- Giacomazzi S, Cochet N (2004) Environmental impact of diuron transformation: a review. *Chemosphere* 56:1021–1032
- Haque MM, Muneer M, And Banhemann DW (2006) Semiconductor-mediated photocatalyzed degradation of a herbicide derivative, chlorotoluron, in aqueous suspensions. *Environ Sci Technol* 40:4765–4770
- Herrmann JM (1999) Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal today* 53:115–129
- Hincapié M, Maldonado MI, Oller I, Gernjak W, Sanchez-Perez JA, Ballesteros MM, Malato S (2005) Solar photocatalytic degradation and detoxification of EU priority substances. *Catal Today* 101:203–210
- Low GK, McEvoy SR, Matthews RW (1991) Formation of nitrate and ammonium ions in titanium dioxide mediated photocatalytic degradation of organic compounds containing nitrogen atoms. *Environ Sci Technol* 25:460–467
- Madani ME, Guillard C, Pérol N, Chovelon JM, El Azzouzi M, Zrineh A, Herrmann JM (2006) Photocatalytic degradation of diuron in aqueous solution in presence of two industrial titania catalyst, either as suspended powders or a deposited on flexible industrial photoresistant papers. *Appl Catal B: Env* 65:70–76
- Malato S, Caseres J, Fernandez-Alba AR, Piedra MD, Hernando MD, Aguera A, Vial J (2003) Photocatalytic treatment of diuron by solar photocatalysis: evaluation of main intermediates and toxicity. *Environ Sci Technol* 37:2516–2525
- Mehrotra K, Yablonsky GS, Ray AK (2005) Macro kinetic studies for photocatalytic degradation of benzoic acid in immobilized systems. *Chemosphere* 60:1427–1436
- Mills A, Le Hunte S (1997) An overview of semiconductor photocatalysis. *J Photochem Photobiol A: Chem* 108:1–11
- Parra S, Olivero J, Pulgarin C (2002) Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous  $\text{TiO}_2$  suspension. *Appl Catal B: Environ* 36:75–85
- Pramauro E, Vicenti M, Augugliaro V, Palmisano L (1993) Photocatalytic degradation of Monuron in aqueous  $\text{TiO}_2$  dispersions. *Environ Sci Technol* 27:1790
- Turchi CS, Ollis DF (1990) Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack. *J Catal* 122:178–185