Journal of Engineering and Applied Sciences 2 (4): 664-670, 2007
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Elimination of Pollutants Phenyleurea Herbicides by Advanced Oxidation Processes in Aqueous Solution

[1]R. Sayeh, [2]B. Coulomb, [2]J.L. Boudenne and [3]F. Belkadi
[1]Department of Chemistry, University of Badji Mokhtar, Annaba, Algeria
[2]Laboratory of Chemistry and Environment, University of Provence, Aix-Marseille I, France
[3]Laboratory LPCMCE, University of Sciences and Technology (UST), Oran, Algeria

Abstract: The degradation of herbicide Diuron in aqueous solution by UV/TiO_2 oxidation process was studied under various solution P^H values, light intensities and types of TiO_2. The removel of Diuron and intermediates was found to be more effective for acidic solution. Experimental results indicated the distribution of non-chlorinated and chlorinated intermediates on the photocatalytic degradation rate of Diuron were highly on solution P^H, the volume of aqueous solution and concentration of TiO_2. At the same light intensity. The adequate dosage of titanium dioxide was found to be less for alkaline solution than that for acidic solution. Increasing the light intensity would significantly increase the degradation rate of Diuron, when the two lamps vapour of mercury high pressure and low pressure are combinated at P^H 6,5. The titanium dioxide (TiO_2) was Degussa P-25 was used in this study the degradation. This research study the degradation of herbicide Diuron in aqueons solution by radical oxidation, the identification of some by- products by gaz Chromatography Coupled to Mass Spectropmetry (GC-MS) was studied (realised) on solution extract. The degradation rate of Diuron by the photocalysis is higher than 90% depending on the parameters influencing the oxidation. The mineralization process is rately complete and it is therefore importante to know both the nature and the concentration of intermediate by-products. The maingool of this research was to identify the Diuron oxidation reaction by-products in order to explain the reaction mechanisms and determine the efficiency factors of proposed treatments to the destroy these substances in drinking-water. The Diuron consentration in test solution was fixed at 5 mg L^{-1}. test solution wene prepared from a standard solution by dilution in to ultra-pur water. Contact times was 60 and 120 min.

Key words: Diuron, advanced oxidation, titanium dioxide, uv/TiO_2 process, photocatalytic degradation

INTRODUCTION

The pollution coming from agricultural practices can exist: pesticides, veterinary drugs, heavy metals but also mycotoxines. However, these contaminants are always at low or trace doses in our environment (foods, water, air, soils). The impact of this pollution on public health is not evident, in contradiction with the level fear in the population. Moreover, the distinction mode between natural and synthetic substances by the public in terms of toxicity in quite nonsense scientifically. The Phenylurea Herbicide (PUH) its chemical structure was shown in Fig. 1.

The phenylurea herbicide is largely used in field application for pre-and -post emergence weed control in a wade variety of crops. Phenyl urea herbicide in the environment is gradually biodegraded by stepwise Stepwise demethylation or demethoxylation on the urea moiety followed by generation of aromatic amines are know to be toxic and some the latter class of compounds can induce cancer (Srender, 1974; Ivens, 1992; Gosselin *et al*., 1984; Scott, 1962).

The most recent progress in the treatement of water were done in the oxidation of organic compounds biologically refectory (Andreozzi *et al*., 1999). This methods are based on the formation of very reactive hemical entity, which will decompose, the more recalcitrants biodegradation of the bimoleculars; or in mineral compounds such: CO_2 and H_2O, there are the Advanced Oxidation Processes (AOP). These processes are based on the formation of hydroxyl radicals $OH^{\cdot}$ Which have important oxidant ability than the traditional oxidants such: Cl_2, ClO_2, H_2O_2 or O_3. The radicals partially mineralize or fully mineralize the organic compounds.

Corresponding Author: R. Sayeh, Department of Chemistry, University of Badji Mokhtar, Annaba, Algeria

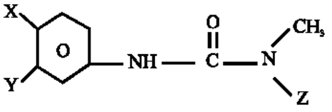

Fig. 1: Chemical structure of phenylurea (PUH)

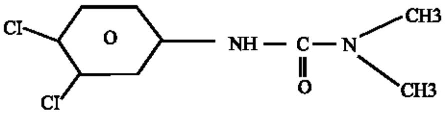

Fig. 2: Chemical structure of diuron

The presence of phenylurea herbicides in aquatic bodies has been known to cause sever pollution problems because of their carcinogenicity. The major source of phenylurea herbicides include the agriculture and the improper discharge of industrial wastewater (Bellar *et al*., 1974). Public concern over the contamination of drinking in water supplies and the aquatic environment has stimulated investigation involving the development of various treatment technologies to remove organics from water. For instance, several photocatalytic semiconductors such as TiO_2, CdS, ZnS, etc., were illuminated with UV light to generate highly oxidative holes on the solid surface, initiale the oxidation of organic pollutants in waters by converting dissolved oxygen, water or hydroxyl ions to hydroxyl and other free radicals. Semiconductor photocatalysis may be more effective than the conventional chemical oxidation methods because semiconductors are inexpensive and capable of mineralizing various recalcitrants organic compounds. The photocatalytic activity and stability are the majors concerns regarding the solution of semiconductors as a photocatalyst.

The degradation rates of organics by photocatalytic reactions are influenced by the active site and the photon absorption of the catalyst used, the volume of the aqueous solution and the solution P^H. several reports have evaluated the effect of photocatalyst concentration and light intensity on the photocatalytic reactions.

Auguliaro *et al*. (1991) indicated that at low photocatalyst loadings, the removal of organic compounds increased linearly with the catalyst loading, however, the presence of excess photocatalyst in the aqueous solutions could cause a shielding effect on the penetration of light. Al-Sayyed *et al*. (1991) reported that the dégradation rate of Diuron increased lineary with the amount of titanium the dioxide up to a level of 3-4 g L^{-1} at solution P^H 3. Tseng and Huang (1991). demonstrated that the oxidation rate of chlorophenols increased with the concentration of TiO_2, reached a maximum level at 3 g L^{-1} then decreased to a constant value up on further increase in TiO_2 at a neutral condition. Kuy and Hsieh (1992) depicted that the removal increased with increasing TiO_2 amount, there by approaching a limiting value at a loading of about 1,4 g L^{-1} for a solution containing about $3\,10^{-4}$ M 2, 4- dichlorophenol at initial solution PH 6,5. Thus on the basis of previous findings, suitable amounts of TiO_2 for the photocatalytic reaction were about 1- 4 g L^{-1} loadings at acidic solution and were assumed to be dependent on experimental conditions. However, the light intensity also significantly affected the rate of organic compounds photodegradation.the photocatalytic degradation rate of phenols was found in several investigation to be between half- and first-order to light intensity (D'olivera *et al*., 1990; Okamoto *et al*., 1985).

The photocatalysis is a new method air and water purification, is advantageous to the treatment of refractory pollutant in low concentration. Application of photocatalysis to pesticide degradation has been studied intensively (Hoffman *et al*., 1995; Muszkat and Feigson, 1995; Kerzhentsey *et al*., 1996; Doong and chang, 1997; Hermann *et al*., 1998; Malato *et al*., 1999; Reddy *et al*., 1999). Because most pesticides are refractory and occurs in low concentration in the natural water body.Recently many pesticides are suspected to be endocrine disruptess as well as the cause of other health problems. The heterogeneous photocatalysis in TiO_2 aqueous suspensions is a technique used for the total destruction of organic pollutants in water (Smatthewr, 1991; PPTWA, 1993). This aspect has been extensively developed by several authors in a chapter devoted to photocatalytic water treatment in ref.10.Titanium dioxide is particularly effient since the formation of electron-hole pairs under illumination with lamp light Ultraviolet (UV) of vapour mercury is promoted by the 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 absorbed oxygen.

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

As part of our research on one class of pollutants, phenylurea herbicides compounds. We now present the study of one herbicide in particular: Diuron or (3-(3, 4-dichlorophenyl -1, 1-dimethylruea) and it's chemical structure was shown in Fig. 2. For which the half- life time in soil is 372 days (ARS). The objective of this study was to detail the investigation of the photocatalytic degradation of Diuron in the presence and the absence of suspended Titanium dioxide particles is discussed under various solution PH values, volume of the aqueous solution of the pollutant Diuron, light intensities of UV and amounts of photocatalyst.

MATERIALS AND METHODS

Reagents and chemicals: The Diuron used in this experiment is standard Pestanal, Riedel de Haen and the Titanium dioxide (TiO_2) used was Degussa p-25 with a measured specific area of 51-55 m^2 g^{-1} and an average particle size of 27 nm.

Experimental equipment: Show Fig. 3. We have used a peristaltique pump IPC Ismatec used in circulating a sample in aqueous solution in two directions: upward and downward.

We have also used a UV. Spectrophotometer Secomam S750 this serves for analysing the sample, because the degradation is followed by a state of continuous circulation, which is not the case of full condition each time the sample is analysed in the cuve.

Ring reactor: Having the shape of ring which is used to have a circular movement to produce a pressure, this reactor is in quartz, that is the quartz is more transparent than glass for allowing radiations, this reactor have two filters for minimising the passage of TiO_2 grians.

Two mercury vapour lamps; this serves for irradiation of our sample in the reactor: One of the two lamps, a mercury vapour lamp is a low pressure (UVP Lamp), principal ray of 254 nm; the other lamp is High Pressure (HPK Lamp), principal ray of 320 nm.

The photolysis and the photocatalysis were realised by a dispozitif (device) which is shown in Fig. 3 to summon above instruments.

Sample preparation: The solution of pesticide Diuron formulation was prepared by direct mixing with water in the required proportion. The experiments were performed at room temperature. The Diuron consentration in test solutioins fixed at 5 mgl L^{-1}. Test solutions were prepared from a standard solution by dilution into ultra-pure water, contact times is 60 and 120 min

Illumination procedure: The samples were contained in a reactor from the Pyrex glass cylindrical bottle. The photocatalytic experiment was carried out with the dose of 0.1-1g L^{-1} from the catalyst TiO_2 suspended in 50 mL of 5 mg L^{-1} from pesticide solution by stirring magnetically. The suspension in a pyrex bottle cylindrical was illuminated or irradiated with a high-pressure mercury lamp HPK (wavelength λ = 320 nm) and also a low pressure mercury lamp UVP (wavelength λ = 250 nm). shown in Fig. 3 the sample was circulated during the experiment in the dispozitif by the pump peristaltique and filtered by a Millipore membrane filter of 0.2um pore size. shown in Fig. 3 the filtrate was subjected to the analyses. Before illumination the solution was stirred in dark for 15 min to ensure the adsorption to TiO_2. Photolysis experiment was performed in a similar manner but in the

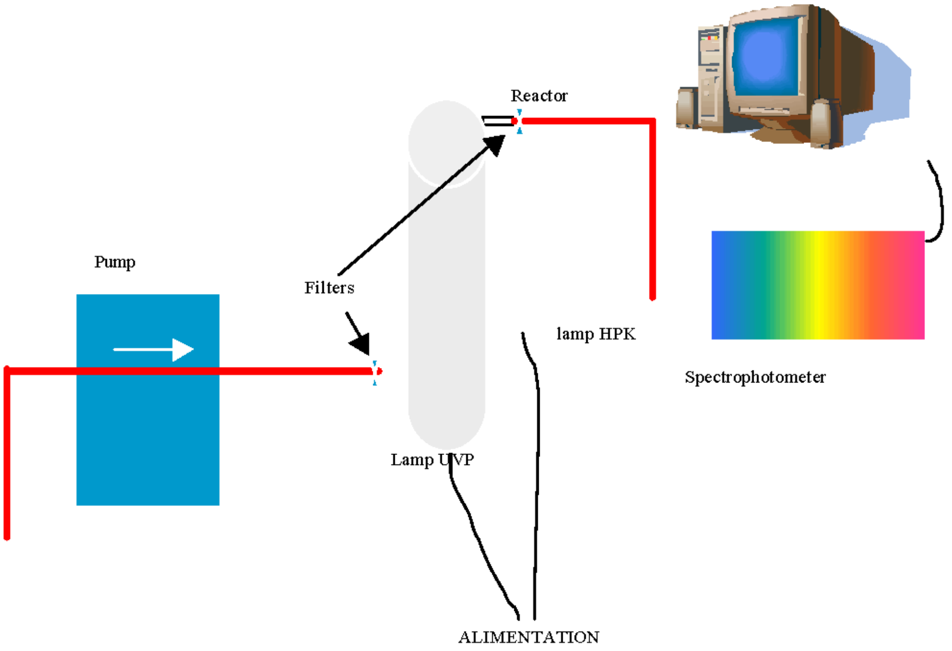

Fig. 3: Experimental dispozitif of the photocalitic oxidation of diuron

absence the catalyst TiO_2 Degradation rate was estimated by measuring the remaining pesticide with High Performance Liquide Chromatography (HPLC). Aromatic intermediate was identified and quantified using a HPLC and multiwavelength UV-Vis detector.

Parametric study

Volume parameter: Photocatalysis system without TiO_2 suspension, in this case the experiment was carried out by the following: Once with circuled our sample in a solution by rotation with the aid of a peristaltique pump upward, the reactor is full having a 50 mL volume which we call in this case the large volume.

The next time the rotation sens in the photocatalysis system is inversed which we call in this case downward sens, which system is having a small volume of 10 mL always with the peristaltique pump.

UV lamps parameter: the mercury vapour lamp having a principal ray 254 nm and the one having high pressure its ray having 320 nm.

The catalyst TiO_2 parameter concentration: once we carried out in absence TiO_2 and another time with TiO_2 with a quantity between 0.1 and 1g L^{-1}.

The solution PH parameter: once the experiment was carried out in an acidic aqueous solution and the next time in the same solution which basic having P^H solution between 1 and 11.

RESULTS AND DISCUSSION

Volume effect and lamps: Once the experiment was carried out with a small volume inversing the circulation of our sample with the mercury vapour lamp at low pressure (UVP) we obtain a result higher than 80% of pollutant Diuron degradation show in Fig. 4.

Another time the experiment was carried out having small volume (10 mL) with a high pressure mercury vapour lamp (HPK) we obtain the degradation result lower compared to the one obtained with UVP lamp which is about 70% degradation shown in Fig. 4.

Now, for the case of the two lamps associated to gather (high and low pressure, UVP+HPK). We obtain a better result of pollutant degradation compared to the above isolated cases (UVP+HPK).

Now if the experiment carried out at high volume with an upper circulating sens of the sample, we obtain a reduced result compared to the one with a small volume shown in Fig. 4. But of we associate the two lamps, we see that the result is improved compared to the case when we operate with two isolated lamps, this result is about 30% shown in Fig. 4.

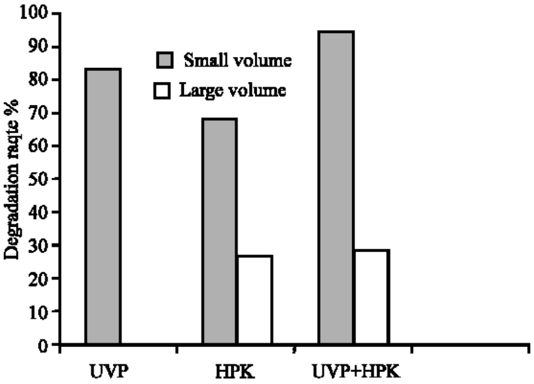

Fig. 4: The effect of volume and lamps in the photocatalytic degradation of diuron

Comparatively,if we operate at small volume having an inversed downward circulation sens and an upward circulation sens.We see that the result is better than for the case of small volume and in operating with the two lamps, the output is better than the case with separated lamps Fig. 4.

The effect of titanium dioxide (TiO_2) catalyst: The presence of the titanium dioxide suspensions in the solution allows to significanteley improuve the result of the degradation of the pollutant ever if we operate with a large solution volume as Fig. 5a and 5b.

The degradation rate as a function of an irradiation time is shown in Fig. 6 for different concentrations; using two lamps (UVP+HPK). It can be seen that the degradation increases with the concentration of the catalyst TiO_2.

Experimental results shown in Fig. 6 and 5 indicate that the degradation rate increased with increasing TiO_2 subsided when the UV light absorbance of TiO_2 suspensions in the case for two lamps associate to gather we obtain a better result of pollutant degradation rate.

The effect of solution P^{hon} the degradation rate of diuron: When we operate with a large volume and a concentration of TiO_2 of 0.8 g L^{-1} and an irradiation time of 120 mn using tow lamp (UVP + HPK), with a P^H between 1.5 and 10.1, we noted that the P^H has a weak effect on the final degradation rate of the pollutant. However an acidic P^H seems to accelerate the degradation kinetics of the pollutant in the aqueous solution as shows in Fig. 7.

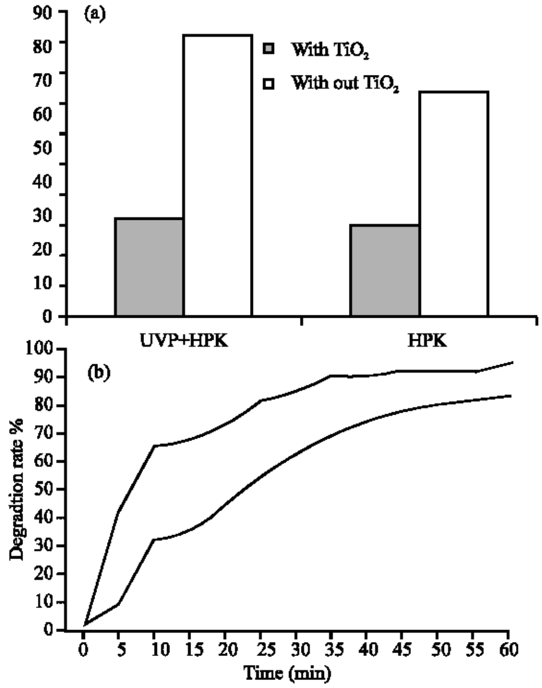

Fig. 5 : The effect of TiO_2 catalyst on the degradation rate of diuron

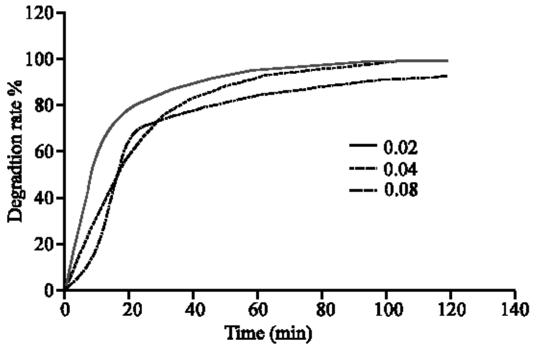

Fig. 6: The effect of TiO_2 concentration on the photocatalytic degradation rate of Diuron with two lamps (UVP + HPK)

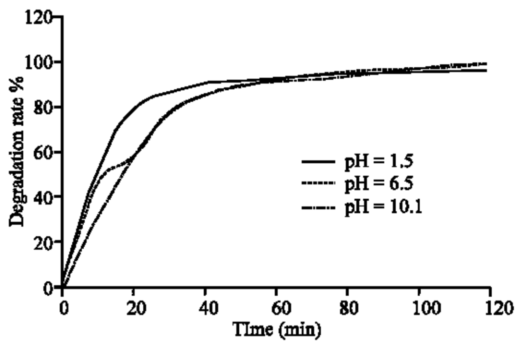

Fig. 7: The effect of the solution PH on the photocatalytic degradation rate of duiron

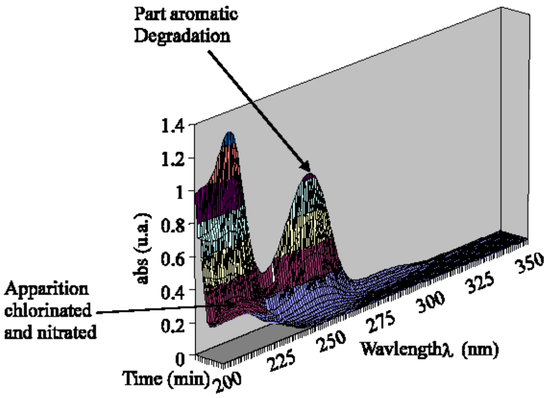

Fig. 8: The intermediates products during the photocatalytic oxidation of Diuron TiO_2 at 0.4 g L^{-1} large volume 120 mn an irradiation K with lamps associated UVP+HPPH 6.5

The purpose of this study was to explore and select the best conditions for carrying out the UV-Light, TiO_2-photocatalyzed mineralization of low concentration or trace organic compounds in polluted water.

Duiron herbicide degraded by illumination with UV Light in the absence of TiO_2 and in the presence of TiO_2 Fig. 4. We have encountered the last case when examining the photodegradation of polluted best water. The photocatalytic degradation of Diuron is compared with the direct photodegradation (non-catalytic, direct excitation), emphasising the decisive contribution of TiO_2 catalysis to the degradation process show Fig. 4. However, the degradation is much faster in the presence of TiO_2. The adsorption to TiO_2 was not observed possibly because of the detection limit. Generally photocatalytic degradation rate is determined by Hammett's constant (Sangchkr *et al*., 1995) and absorbability to TiO_2 as suggested in the literatures (Thrchi *et al*., 1990; Minero *et al*., 1992).

Duiron clearly offers two sites for oxidation: The aromatic ring and the aliphatic side chain show Fig. 2. It that according to the literature, excremental conditions determine which portion of the molecule, aromatic or aliphatic, is attacked (Vidal *et al*., 1994).

Many reports on the photocatalytic degradation of organic compounds in aqueous solution have suggested the action $OH^{\bullet}$ Radicals (Jaeger and Bard, 1979; Matthews, 1984; Maillard *et al*., 1992). This radicals can be produced by the surface reaction of photoproduced holes with adsorbed water. the formation of Hydroxylated compounds would seem therefore reasonable. Possible Hydroxylated, mono-and di-hydroxy-3. 4- diclorophinilisocyanate intermediates were identified by GC-MS were compounds might arise from Diuron by oxidative process involving $OH^{\bullet}$ Radicals, followed by the previously noted thermal degradation in the gas chromatography injector, it is not possible yet.From the data, to elucidate the mechanism of the decomposition. Since it is very difficult to identify all the other intermediates.

The heterogeneous photocatalytic process is mainly based on the excitation of TiO_2 rayon by luminous of wavelength lower than 384 nm during the processes of irradiation of semiconductor with an energy luminous (uv.light) an electron will pass from the valence band to the conduction band, creating a site of excitation, that is a hole h^+ and a site of reduction of electron e^-.

An h^+ hole may react with an adsorbed hydroxide groupement at the surface of a semiconductor to from $OH^{\bullet}$ Radical's very oxidant. These later will react with pollutant to degrade it in carbon dioxide and water. Electron react's with electron acceptorlike dioxide to form superoxyde radicals. This reaction limits the charge recombination. In fact, in the absence of acceptors and of appropriate electron donors, we will assist. At the annihilation hole/ electron wich is a very quick reaction.

The pair of electron-hole producted by photoexcitation of TiO_2 will produce hydroxyle radicals, superoxyde and hydroperoxyde and also hydrogeneous peroxide and liquide water.

The higher removals of Diuron by photocatalysis at acid conditions were possibly attributed to the increased amounts of Diuron species adsorbed on the TiO_2 surface similar results were reported by David and Hung (1991).

Various organic intermediates shown in Fig. 8 were reported to be produced from the degradation of pollutants by Advanced Oxidation Processes (AOP) in aqueous solution (Korman *et al.*, 1991; Al Pruden and Ollis, 1983; Thurchi and Ollis, 1989). Some intermediates be more toxic than the Original pollutants (Rice, 1980). Therefore, making the completeness of mineralization of pollutants chould be of primary concern.

In this study, the organic intermediates show Fig. 8 formed during the degradation of Diuron by irradiation in the presence of photocatalyst are subdivided into two categories. One is the nom-chlorinated intermediates, another is the chlorinated and nitrated intermediates shown in Fig. 8 the difference or negative charges density on the benzene ring of Diuron species adsorbed on TiO_2 surface might alter $OH^{\bullet}$ Electrophilic attack and further influence the formation of non-chlorinated and chlorinated organic intermediates under various solution P^H.

CONCLUSION

This research shows the beneficial effect of the mercury vapour lamps when associated and the concentration of TiO_2 catalyst on the degradation of the pollutant Diuron. It also shows that it is easy to degrade the Diuron but the complete mineralization is not evident. The influence of certain parameters (sample volume, TiO_2 concentration mercury vapour lamp, solution $P^{H)}$ on the degradation process is important. The production of free radicals OH In the medium allows degradation of the Diuron in aqueous solution.

The photocatalytic degradation of Diuron has been demonstrated in aqueous medium a primary intermediate corresponding to the oxidation of a methyl group was detected the solvent; the further degradation of this compound is slow. In aqueous medium, traces of hydroxylated products can be assumed but the degradation scheme is complexes.

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