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Journal of Photochemistry and Photobiology A: Chemistry 156 (2003) 195–200

Journal of Photochemistry and Photobiology A:Chemistry

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Heterogeneous photocatalytic degradation of 3-nitroacetophenone in TiO_2 aqueous suspension

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Received 21 November 2002; received in revised form 21 November 2002; accepted 27 November 2002

Abstract

The photocatalytic mineralization of 3-nitroacetophenone (3-NAP) by TiO_2-P25 in water suspension has been investigated as a function of pH. The reaction of 3-NAP disappearance follows first-order kinetics whatever the pH, however the order kinetic of photomineralization depends on the acidic condition. At pH 3.8, we have a pseudo-first-order kinetic, whereas at higher pH the mineralization rate follows a reaction rate of zero-order. The determination of the pathway for the photomineralization of 3-NAP is not easy, because of the presence of two substituants (NO_2 and $COCH_3$) on the aromatic ring and especially of the very small concentration of by-products in solution. However we have observed the formation of hydroxylated 3-NAP by GC-MS.

Keywords: Photocatalysis; TiO_2; 3-Nitroacetophenone; Mineralization; Detoxification

1. Introduction

The Ivory Coast is currently confronted, like the majority of west African countries, with serious problems of water pollution. In certain agricultural areas specialized in the intensive culture of coffee and cocoa, one uses significant quantities of pesticides. These products and more particularly those of the family of organochlorides are present in the various natural environments (soil, air and water). Because of their strong chemical stability and their toxicity, they constitute in the long term, a significant threat for the environment. The results of a study undertaken in 2000 [1], show the presence of residues of chlorinated pesticides belonging essentially to three groups: hexachlorocyclohexane (HCH), cyclodiennes (Aldrin, Endrin etc.) and dichlorodiphenyltrichloroethane (DDT).

Although the use of these products is prohibited in industrialized countries, they are still used in the Ivory Coast. Even if generally, the level of concentration in drinking water, of these products is below the thresholds defined by the European Union (200 ppb for and HCH and 150 ppb for pp′ DDT) several analyses made on fish show rates higher than 400 ppb for the three pollutants [1].

It is thus urgent to start an efficient treatment of contaminated drinking water and in particular the water of the peasant well water in the precarious districts of Abidjan. The conventional biological treatments of water slightly concentrated in chlorinated pollutants being long and moreover not very effective [2], it is necessary to use an advanced oxidation process such as the heterogeneous photocatalysis.

The use of the heterogeneous photocatalysis for the oxidation of organic and inorganic pollutants in water and air has been intensively studied in the last 20 years [1–8]. The irradiation of semiconductors (like TiO_2) in water suspension, induces the formation of a redox environment able to destroy the most recalcitrant pollutants. Much research [1–4] showed that the majority of chlorinated organocompounds (like pesticides, herbicides, surfactant and dyes) are completely oxidized in inorganic compounds such as carbon dioxide, hydrochloric acid and water.

We chose to begin our study on the photodegradation of a model molecule: 3-nitroacetophenone. This compound was selected because of its structure pH-NO_2, which one finds in many pesticides such as fenitrothion (*O*,*O*-Dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate) or 2-amino-4-nitroaniline (Fig. 1).

The objective of this work is: (i) to study the kinetics of photomineralization and photodisappearance of 3-nitroacetophenone; (ii) to study the effect of the experimental

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doi:10.1016/S1010-6030(02)00428-8

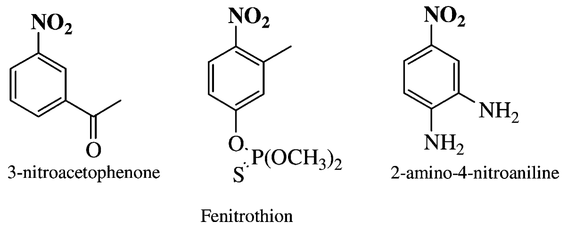


Fig. 1. Chemical structure of nitrocompounds.

conditions (concentration in TiO_2 and pH); (iii) to analyze per GC-MS the various products formed to try to determine the mechanism of photomineralization of 3-nitroacetophenone (3-NAP) in water.

2. Experimental section

2.1. Reagents

3-Nitroacetophenone was supplied by Sigma–Aldrich and the titanium dioxide P25 from Degussa (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of $50\,m^2/g$) was used as received. All chemicals were reagent grade and were used without further purification. The pH of the solution was adjusted with a NaOH or HCl solution at 3.8, 6.5 and 9.4.

2.2. Photocatalysis experiments

Photocatalysis experiments were carried out in a Solar box ATLAS SUNTEST CPS+ simulating natural radiation. The light source was a vapor xenon lamp ($300\,nm < \lambda < 800\,nm$). In order to determine the photocatalytic mineralization kinetic, the initial concentration of 3-NAP amounted to 20 mg/l (120 μmol). Homogeneous mixing was provided by sonication of the slurry for 5 min with titanium dioxide. The solution was mixed by a magnetic stirrer in the dark for 30 min in order to obtain an equilibrium state. Time zero was the beginning of irradiation. For all experiments the photocatalyst concentration was 1 g/l except the experiment where the influence of TiO_2 loading (from 0.1 to 2 g/l) was studied. The volume of the reaction solution was 300 ml and illuminated surface $80\,cm^2$. The process was conducted at 20 °C.

2.3. Analytical procedures

The mineralization of 3-NAP was analyzed without filtration by direct injection in the TOC analyzer. The TOC values at different irradiation times were determined with a Shimadzu TOC Analyzer (TOC-5050-A). The concentration measurements in 3-NAP and by-products were made by high performance liquid chromatography (HPLC waters 600 pump and 996 photodiode array detector, C-18 apolar column and acetonitrile (10%) water (90%) mixture as mobile phase). Before injecting, the solutions were filtered through micropore filters (0.45 μm of diameter).

All GC-MS measurements were performed with an Agilent 5973 mass-selective detector combined with an agilent 6890 gas chromatograph fitted with an HP-5MS-5% phenylmethylsiloxane capillary column (30 m × 250 μm i.d., 0.5 μm film thickness).

3. Results and discussions

3.1. Study of the disappearance and mineralization kinetics of 3-NAP

The disappearance of the 3-NAP from the reaction mixture was monitored as a function of time of irradiation with a xenon lamp. Fig. 2 shows the plots of the observed 3-NAP concentration changes as a function of time at natural pH = 6.5. This reaction follows a first-order kinetics:

$$\log\,[\text{3-NAP}]_t = -kt + \log\,[\text{3-NAP}]_0 \qquad (1)$$

where $[\text{3-NAP}]_0$ represents the concentration (ppm) of the substrate in solution at time zero and $[\text{3-NAP}]_t$ at time t; k the apparent rate constant (min^{-1}). The inset diagram is a plot of the data in the main diagram after the integration of Eq. (1) to show the rate law. We find a good approximation ($R^2 = 0.97$). With an initial 3-NAP concentration of 20 ppm the first-order reaction rate constant was $k = 0.02\,min^{-1}$. We have verified that the direct photolysis (without TiO_2) of 3-NAP is very weak.

The photocatalytic mineralization of organic carbon into CO_2 has already been reported for nitrobenzene derivatives [9,10]. Regarding the 3-NAP (Fig. 3), it seems that the reaction follows a kinetic of zero-order rates. This zero-order kinetics could be attributed to a rate determining the oxidation of an intermediate en-route to carbone dioxide. Mineralization is a complex process and more sophisticated models taking into account intermediates, have been developed to describe the results [11–14].

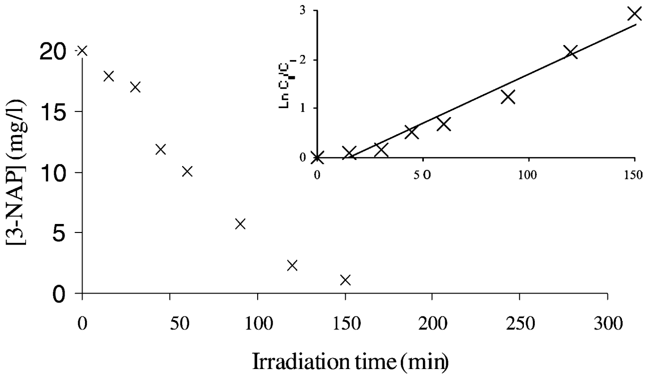


Fig. 2. Photocatalytic disappearance of [3-NAP] = 20 mg/l with $[TiO_2] = 1$ g/l.

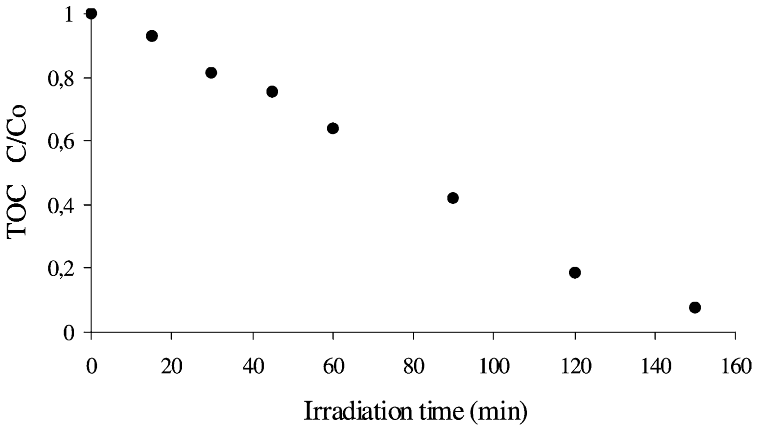


Fig. 3. Photocatalytic mineralization of [3-NAP] = 20 mg/l with $[TiO_2]$ = 1 g/l.

Table 1
Effect of $[TiO_2]$ on the disappearance and mineralization kinetics of [3-NAP] = 20 ppm

$[TiO_2]$ (g/l)	Photodisappearance rate constants (pseudo-first-order kinetic)		Photomineralization rate constants (pseudo-zero-order kinetic)	
	k (min^{-1})	R^2	k ($ppm\,min^{-1}$)	R^2
0.1	0.008	0.98	0.0036	0.99
0.5	0.022	0.99	0.0056	0.99
1	0.020	0.97	0.0065	0.99
2	0.025	0.97	0.0066	0.98

3.2. Effect of catalyst concentration

The influence of the photocatalyst concentration on the disappearance and mineralization kinetics of 3-NAP has been investigated employing different concentrations of Degussa P25 varying from 0.1 to 2 g/l (Table 1).

For higher concentrations of TiO_2, the removal efficiencies decreased with an increasing amount of TiO_2. These results show that there is an optimum amount of TiO_2. Above this concentration level (between 0.5 and 1 g/l), the suspended particles of TiO_2 block the UV-light passage and reduce the formation of electron/hole pairs and active sites [15]. Most likely, the turbidity and color of treated solution, along with the effect of TiO_2 blocking in solution, made the decomposition less effective. It is a classical phenomenon in photochemical processes [3–6]. This effect is less important for photomineralization.

3.3. Effect of pH

It is well known that the surface of TiO_2 is amphoteric and consequently the charge of surface is pH dependent [16]. For the TiO_2-P25, the pH_{zpc} (the point of zero charge) is close to 6.3.

The evolution of pseudo-first-order rate constant for photocatalytic disappearance of 3-NAP are given in Table 2. We noted that the kinetic of 3-NAP disappearance is affected by the pH. At acidic pH (3.8), the degradation rate is greater than in neutral or alkaline conditions. We didn't make a precise study of the 3-NAP adsorption at catalyst surface, but we know that about 30% of the 20 ppm 3-NAP solution is adsorbed by TiO_2 at acidic pH (this value is lower at neutral or basic pH). Xu et al. [17] report that in the case of acetophenone, there seem to be two adsorption regions

Table 2
pH effect on the 3-NAP disappearance constant rate

pH	$k_{3\text{-NAP}}$ (min^{-1})	$t_{1/2}$ (min)
3.8	0.034	20.38
6.5	0.02	34.65
9.4	0.018	38.50

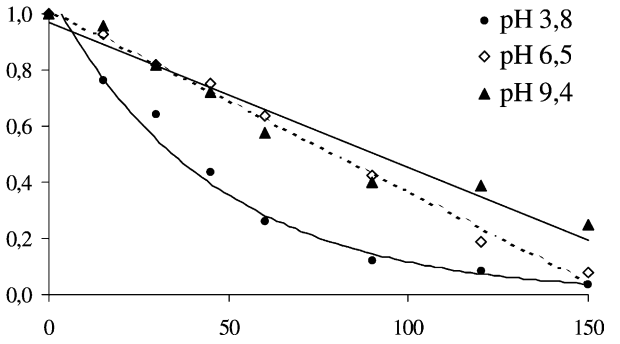


Fig. 4. Influence of the pH on the mineralization kinetics of [3-NAP] = 20 ppm.

displayed in the adsorption isotherm: one at lower concentration ($C < 3.10^{-4}$ mol dm^{-3}) appearing of the Langmuir type (monolayer coverage) and another at $C > 3.10^{-4}$ mol dm^{-3} probably taken as the multilayer adsorption. At lower pH value, the TiO_2 surface is positively charged, which induces an increase of the adsorption by free electron pairs of oxygen atoms of 3-NAP carbonyl and nitro groups [18,19].

As for Piccinini et al. [10] for nitrobenzene, a remarkable pH effect is observed on TOC profiles (Fig. 4). We can see that the order of the reaction changes with the pH. At pH 3.8, we have a pseudo-first-order kinetic, whereas at higher pH the mineralization rate follows a reaction rate of zero-order. It seems that at pH 9.4, the evolution of the reaction intermediates is considerably slowed. Piccinini et al. [10] and Kormann et al. [20] explain that in the case of nitrobenzene the formation of organic species bearing a negative charge as the result of acid-base equilibrium is likely to reduce drastically the photocatalytic rate of degradation, since these species at basic pH are repelled by the negatively charged TiO_2 surface.

3.4. *Tentative determination of 3-NAP photodegradation mechanisme*

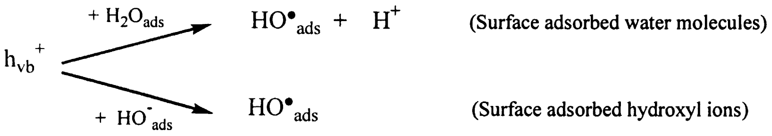
The basic process of photocatalysis consists in ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO_2 semi-conductor creating a hole (h^+) in the valence band. This is due to the UV irradiation of TiO_2 with an energy equal or superior to the band gap energy (>3.2 eV).

The generally accepted first steps in photocatalytic processes are:

(1) electron-hole pair generation by illumination of TiO_2

$$TiO_2 \xrightarrow[E>E_g]{hv} e_{cb}^{-} + h_{vb}^{+}$$

(2) possible traps for holes (generation of hydroxyl radicals $OH^•$)



(3) oxidation of organic compound by hydroxyl radical

$$HO_{ads}^{•} + 4\text{-}NAP_{ads}$$
$$\rightarrow (3\text{-}NAP\text{-}OH^{•})_{ads} \rightleftharpoons 3\text{-}NAP_{ads}^{•+}OH_{ads}^{-}$$

(4) recombination

$$e_{cb}^{-} + h_{vb}^{+} \rightarrow TiO_2 + \text{energy}$$

In a TiO_2 suspension, the electron donating species are water molecules, hydroxyl ions and 3-NAP molecules. HPLC analyses indicated the formation of organic intermediate products (Fig. 5). The analysis of these by-products by GC-MS formed in the degradation of 3-NAP revealed the formation of 3-hydroxy-5-nitroacetophenone (3-OH-5-NAP).

The formation of 3-OH-5-NAP can be explained by initial hydroxylation of 3-NAP. This reaction is a classical step

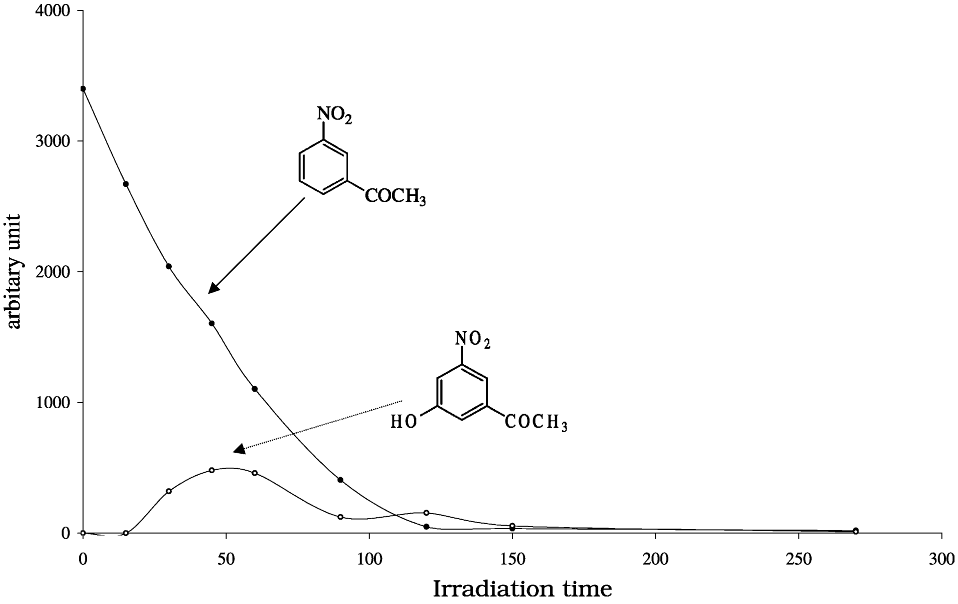
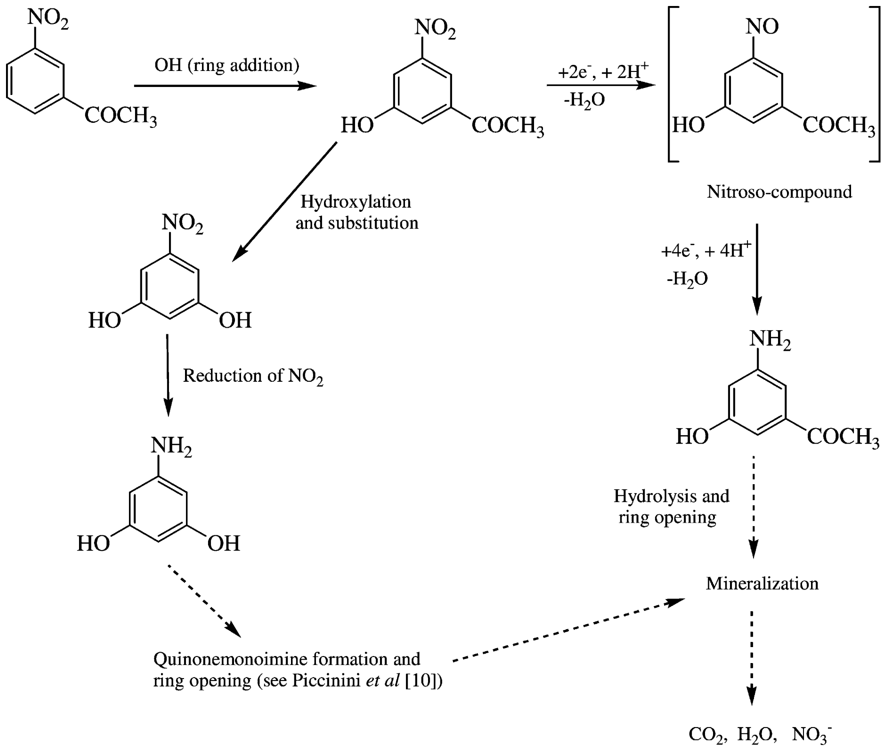


Fig. 5. HPLC analysis during the photodegradation of [3-NAP] = 20 ppm by $[TiO_2]$ = 1 g/l.



Scheme 1. Possible ways for the mineralization of 3-NAP.

during the photocatalysis of aromatic ring (e.g. [10,17]). The GC-MS analysis does not allow to determine the position of the OH group. However the presence of a strongly deactivating group (NO_2) and a moderately deactivating group ($COCH_3$) in meta, influences the hydroxylation position. We can propose one of the possible ways for the photocatalytic mineralization of 3-NAP (Scheme 1).

Maldotti et al. [21] have reported the formation of aniline by photoreductive processes of nitrobenzene. The nitroso-derivative R–NO is a possible intermediate deriving from the photoinduced reduction of nitrocompounds. In our condition, we cannot determine the presence of R–NO or amino compounds because their concentrations are very weak in the slurry. According to Piccinini et al. [10], the formed aniline derivatives are transformed into imides and hydrolyzed in quinones. Finally, there is a ring opening and formation of oxo-organocompounds easily degraded in CO_2, H_2O and other mineral nitrogen compounds.

4. Conclusion

The present study for the photocatalytic degradation of 3-nitroacetophenone has shown that the reaction follows a first-order kinetics. The kinetic of 3-NAP disappearance is affected by the pH. It is preferable to work at acidic pH (3.8), because the degradation rate is greater than in neutral or alkaline conditions. The pH affects the mineralization kinetic, we have shown that the order of the reaction changes according to the pH condition. At acidic pH, we have a pseudo-first-order kinetic, whereas at higher pH the mineralization rate follows a reaction rate of zero-order.

The determination of the pathway for the photomineralization of 3-NAP is not easy, because of the presence of two substituents (NO_2 and $COCH_3$) on the aromatic ring and especially of the very small concentration of by-products in the solution. However we have carried out the formation of hydroxylated 3-NAP by GC-MS.

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