

Photocatalytic degradation of pyridine in water solution using ZnO as an alternative catalyst to TiO₂

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The degradation of pyridine, widely used in the synthesis of vitamins, drugs, rubber chemicals, herbicides and pesticides, can be photocatalyzed by semiconductor catalysts. Since zinc oxide promotes faster pyridine photocatalytic oxidation reactions than TiO₂, the former appears to be a suitable alternative to TiO₂ for water treatment contaminated with pyridine. The photodegradation efficiency was negligible when the photolysis was carried out in the absence of any catalyst. The formation and eventual disappearance of intermediate organic reaction products during the photocatalytic oxidation of pyridine was monitored by a combination of analytical techniques such as UV-Vis, HPLC, TOC and NMR. Based on experimental observations, an alternative mechanism is proposed for the photocatalytic oxidation of pyridine. In addition, the kinetic parameters of the Langmuir-Hinshelwood model that describe the initial reaction rate for the photocatalytic degradation of pyridine over TiO₂ and ZnO are presented.

Key words: Photocatalytic degradation, Pyridine, TiO₂, ZnO.

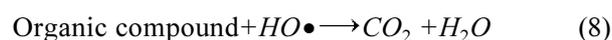
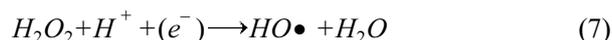
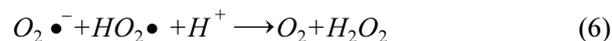
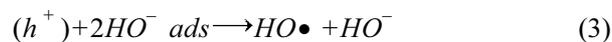
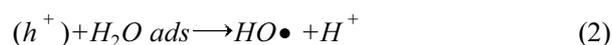
Introduction

Various chemical and physical processes, such as chemical precipitation, coagulation, adsorption on activated carbon, are applied for removal of organic pollutants from industrial effluents [1]. However, these methods are not destructive and the contaminant is only transferred from one phase to another [2]. Several advance oxidation processes (AOP) have recently gained attention for water remediation [3-9]. These methods are based on the generation of very reactive species such as hydroxyl radicals that oxidize a broad range of organic pollutants quickly and non-selectively.

AOP methods include photocatalytic degradation of organic pollutants by the use of a semiconductor catalyst (TiO₂, ZnO) and UV light [3-9]. TiO₂ has been found to be quite efficient for photocatalytic degradation of pollutants. However, widespread use of TiO₂ is not economic for large-scale water treatment operations [10]. ZnO appears to be an economical alternative since it has been reported that this catalyst also induces photocatalytic degradation of organic compounds [11-14].

When a photocatalyst like TiO₂ or ZnO is irradiated with UV light electrons move from the valence band to the conduction band (e⁻), leaving positive holes (h⁺) behind [3-9]. These highly reactive species (e⁻ and h⁺) initiate oxidation and reduction reactions on the surface of TiO₂ particles. In an aqueous suspension, h⁺ reacts with surface OH⁻ groups to give HO• radicals, which are known to be strong oxidizing species. In addition to this, (e⁻) reacts

with adsorbed molecular O₂ to produce an O₂•⁻ superoxide anion radical that can also contribute to the production of HO• radicals. It is believed that the reaction of HO• radicals with organic pollutants eventually leads to mineralization of these compounds [15]. Indeed electron spin resonance studies have demonstrated HO• to be the most abundant radical species in aqueous TiO₂ suspensions [16, 17]. The photocatalytic degradation process can be summarized by the following reactions:



Pyridine is a toxic flammable organic compound found in industrial waste waters since it is widely used in the synthesis of vitamins, drugs, rubber chemicals, herbicides and pesticides [18]. There are only few reports on the degradation of pyridine in solution phase [18-24]. In one of them, the authors [19] indicated that pyridine can be degraded by a photochemical reaction induced with UV

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light ($\lambda = 254$ nm). In a subsequent study on the pulse radiolysis of pyridine aqueous solutions, the addition of a HO• radical to pyridine ring was reported [20, 21]. Furthermore, the intermediacy of these hydroxyl radicals was demonstrated by ESR spectroscopy. The first study on the degradation of pyridine in aqueous solution by heterogeneous photocatalysis was mostly concerned with the formation of ammonium and nitrate ions [22]. The photocatalytic degradation of pyridine with UV light over TiO₂ has also been demonstrated [23, 24].

The aim of the present study is to investigate the photocatalytic degradation of pyridine, a reagent extensively used in industry, in the presence of ZnO as a suitable alternative to TiO₂ photocatalyst. The photocatalytic degradation of pyridine was monitored by a combination of analytical techniques such as UV-Vis spectroscopy, HPLC and NMR. The mineralization of pyridine in the reaction mixture was verified by total organic carbon (TOC) analysis. An alternative photocatalytic degradation mechanism and the kinetic parameters of the Langmuir-Hinshelwood model that describe the initial reaction rate for the photocatalytic degradation of pyridine over TiO₂ and ZnO are presented.

Experimental

Materials

Pyridine, 2-hydroxypyridine, 2,3-dihydroxypyridine, 2,4-dihydroxypyridine, 2,2'-dipyridyl, 4,4'-dipyridyl, ZnO and acetic acid were purchased from Aldrich. Other organic and inorganic acids and salts used in the product studies were purchased from J. T. Baker. Spectroscopic and chromatographic grade solvents were purchased from Mallinckrodt. Double distilled water, filtered through 0.45 μm HA cellulose acetate membranes (Millipore Corp. Bedford, MA) was used throughout. Before analysis, all the reaction mixtures were filtered through 0.22 μm GV cellulose acetate membrane (Millipore Corp. Bedford, MA).

Analytical methods

For the determination of pyridine and intermediate organic compounds, the samples were analyzed by high performance liquid chromatography (HPLC) in a 600E waters instrument equipped with a UV-vis Waters 486 detector. A C18 Symmetry Column (3.9 \times 150 mm 4.91 μm) was employed for separation of reactant and product intermediates. The mobile phase was a mixture of 45% methanol/ 65% aqueous solution of the sodium salt of 1-hexasulfonic acid (Pic B6 Aldrich). The mixture was filtered through a 0.22 μm HA cellulose acetate Millipore membrane. The solution was delivered at a rate of 0.7 ml-minute⁻¹ and the wavelength of detection was set at 254 nm. For these operating conditions, the retention times for pyridine, 2-hydroxypyridine and aliphatic acids were 2.5, 1.7 and 0.98 minutes, respectively. The analytical error was controlled within 5%. Identification of intermediate organic compounds was determined by coinjection of standards.

Some of the reaction mixtures were monitored by UV-Vis spectroscopy in a Shimadzu UV-2401 PC instrument in standard quartz cells. The total organic carbon (TOC) in some samples was measured with a Shimadzu carbon analyzer model 5000 A.

To obtain ¹H and ¹³C NMR spectra a Bruker AC 200 instrument was used. Pyridine solutions (20 mg/ml) in deuterated water were prepared and photolyzed under photocatalytic reaction conditions in the presence of ZnO (2 g/l). Aliquots (2 ml) were taken at different time intervals, filtered and monitored by NMR. All ¹H NMR shifts were reported relative to TMS as an external standard. All ¹³C NMR chemical shifts are reported relative to CDCl₃ (77 ppm) as an external standard.

Photoreactor and photodegradation experiments

Photocatalytic degradation experiments were carried out in a reactor system previously described [25-27]. It is a Pyrex glass tube reactor (500 ml) irradiated with four long wave UV light lamps ($\lambda_{\text{max}} = 365$ nm, Cole-Parmer E-09815-55). For each set of experiments 250 ml of a pyridine standard solution (100 ppm) were placed inside the glass reactor and mixed with 1 g/l of ZnO. The slurry was mixed with a magnetic stirrer and pure oxygen was bubbled through the system at a constant rate of 100 ml-minute⁻¹. In order to allow adsorption of pyridine on the catalyst's surface, the reaction mixture was stirred for 30 minutes in the dark before photocatalysis experiments. The initial pH of the solution was adjusted to 6.8 \pm 0.2 with dilute solutions of NaOH and H₂SO₄ and measured by a pH meter (710 A Orion). Before analysis, each sample was filtered with a Millipore GV membrane (0.22 μm of pore diameter).

Results and Discussion

ZnO stability and photocatalytic reaction conditions

The use of ZnO in the photocatalytic degradation of organic compounds has been previously reported [11-14]. In several studies, the ZnO stability under different conditions has been investigated [11, 12]. At a pH lower than 4.0, ZnO dissolution is complete due to a classical chemical process. In contrast, at a pH higher than 10, no photocorrosion of ZnO takes place. In the dark, some dissolution of ZnO has been detected in stirred aqueous suspensions yielding a constant equilibrated concentration of Zn⁺². A larger concentration of Zn⁺² was found when the samples were irradiated. The dissolution of ZnO induced by light in a neutral solution can be explained by a simple mechanism. Absorption of light by ZnO promotes an electron (e⁻) in the conduction band creating a positive hole in the valence band (reaction 1). In the presence of oxygen, e⁻ reduces O₂ into HO₂• which disproportionates into O₂ and H₂O₂ (reactions 4-6). The formation of Zn²⁺ is attributed to the oxidation of ZnO by h⁺ as suggested by Fujishima et al. [14]. The intermediate oxygen species, O* is assumed to oxidize some organic compounds in the solution and

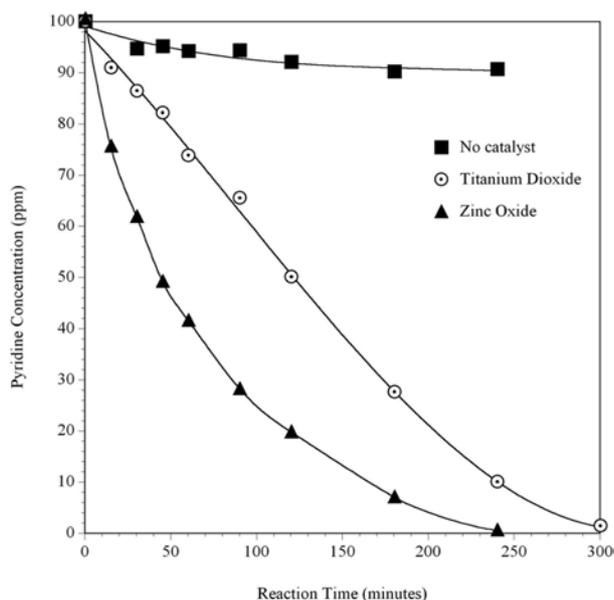
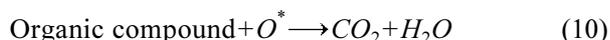


Fig. 1. Photochemical and photocatalytic degradation of pyridine in the presence of ZnO and TiO₂. ($V = 250$ ml, $C_0 = 100$ ppm, O_2 flow = 100 ml-minute⁻¹, catalysts weight = 1 g/l, $\lambda_{\max} = 365$ nm).

facilitate their degradation:



In the light of literature findings and taking into account that the pH of the suspension is an important parameter in a reaction taking place on a semiconductor particle surface, it was decided to perform the photocatalytic degradation experiments with ZnO or TiO₂ illuminated with UV light at $pH = 6.8 \pm 0.2$. The reaction samples were only analyzed by HPLC. In the presence of ZnO and UV light, 100% of pyridine was degraded after 4 hours reaction (Fig. 1). When TiO₂ was used as the photocatalyst, the 100 % degradation was reached after

5 hours reaction. These experimental results (Fig. 1) also indicate that the initial reaction rate with ZnO is at least three times faster than the initial reaction rate with TiO₂. In contrast, a negligible pure photochemical degradation of pyridine was observed when the experiments were carried out in the absence of the solid catalyst. Indeed, the partial degradation of pyridine by UV irradiation has been previously reported [18].

TOC and HPLC studies

Some experiments to study the photocatalytic degradation of standard aqueous solution of pyridine (100 ppm) with 1 g/l of catalyst (ZnO or TiO₂), UV light and a constant flow rate of oxygen (100 ml-minute⁻¹) were also carried out. The advance of the reaction was monitored by HPLC and TOC (Fig. 2). In both cases, experimental HPLC results clearly indicate that pyridine is quickly oxidized into other organic compounds. However, experimental TOC results indicate that intermediate organic compounds remain in the solution for several hours and are eventually transformed into CO₂ and H₂O. Comparing HPLC and TOC curves it is clear that the intermediates degraded at a slower rate than starting pyridine.

UV-Vis spectra changes

In order to investigate the formation and eventual disappearance of intermediate compounds in the reaction mixture, the photocatalytic reaction of pyridine in ZnO aqueous suspensions by UV light as a function of time (Fig. 3) was also monitored. Indeed, the characteristic pyridine absorption bands at 250, 255 and 262 nm were observed. Since pyridine is a heterocyclic compound, it is expected to have several electronic transitions that are combinations of $\pi-\pi^*$ and $\eta-\Pi^*$ transitions [28]. Upon pyridine photocatalytic oxidation at short times another absorption band is observed around 280 nm. It is most likely due to the formation of 2-hydroxypyridine that has a characteristic absorption band in this region for $\eta-\Pi^*$ transitions. Upon extended photolysis, the four absorption

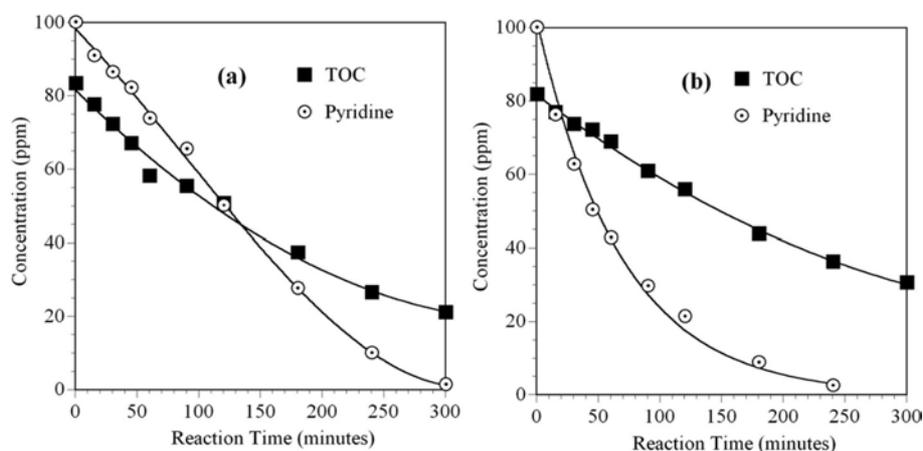


Fig. 2. Photocatalytic degradation of pyridine in the presence of (a) TiO₂ and (b) ZnO. ($V = 250$ ml, $C_0 = 100$ ppm, O_2 flow = 100 ml-minute⁻¹, catalysts weight = 1 g/l, $\lambda_{\max} = 365$ nm).

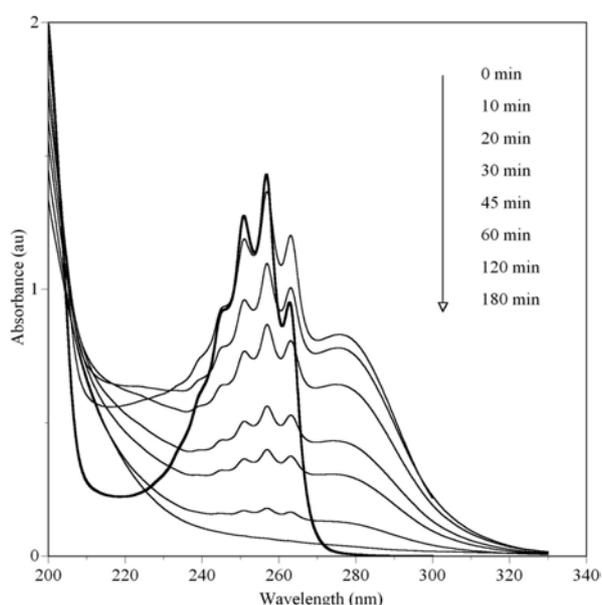


Fig. 3. Photocatalytic degradation of pyridine using ZnO as catalyst. Samples for UV analysis were taken at different reaction times. ($V = 250$ ml, $C_0 = 40$ ppm, O_2 flow = 100 ml-minute $^{-1}$, catalysts weight = 1 g/l, $\lambda_{max} = 365$ nm)

bands are observed to disappear. The mineralization of aromatic compounds in the reaction mixture is evident in the UV-vis spectrum of the sample since most of their characteristic absorption bands disappear after several hours of irradiation.

Identification of degradation intermediates

The photocatalytic degradation of pyridine was monitored by HPLC to monitor the organic intermediates formed.

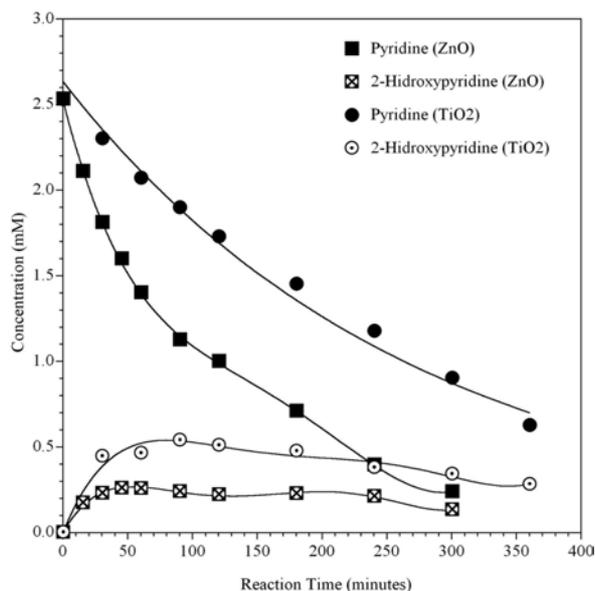


Fig. 4. Formation and disappearance of intermediate organic products during the photocatalytic degradation of pyridine in the presence of TiO_2 and ZnO. ($V = 250$ ml, $C_0 = 200$ ppm, O_2 flow = 100 ml-minute $^{-1}$, catalysts weight = 1 g/l, $\lambda_{max} = 365$ nm).

HPLC analysis with appropriate detectors allowed monitoring the formation and eventual degradation of some reaction intermediates (Fig. 4). Only 2-hydroxypyridine and traces of aliphatic acids were detected in the reaction mixture. 2-hydroxypyridine was fully identified and quantified by the co-injection technique during the HPLC analysis. This intermediate product remains in solution during most of the reaction time. But, the small amount of 2-hydroxypyridine detected clearly indicated its further oxidation. In these experiments, dihydroxypyridine and dipyridyl derivatives were not detected in the reaction mixture. These compounds were not detected even in trace amounts.

NMR studies

A standard pyridine (20 mg/ml) solution in deuterated water was prepared and degraded in the presence of ZnO (1 g/l) and UV irradiation. Before photolysis, the 1H NMR of the solution (Fig. 5) presented the characteristic signals due to pyridine (8.6 , bs, $2H$); (7.64 , m, $1H$); (7.25 , m, $2H$). Upon photolysis, the three signals decreased in intensity as a function of irradiation time. Eventually, after 20 hours of irradiation all the pyridine signals completely disappeared. In the reaction mixtures, only one strong sharp signal was observed to growth at 2.2 ppm. Signals in this region are due to hydrogens alpha to carbonyl groups. The photocatalytic degradation of pyridine was also monitored by ^{13}C NMR. In this case, the standard solution of pyridine (Fig. 6) gave the three signals expected (150.9 , 140.0 and 126.8 ppm). Upon photolysis, all the signals were observed to decrease (Fig. 6). In addition to this, a medium intensity signal was observed in the 25 ppm region. An intense signal was

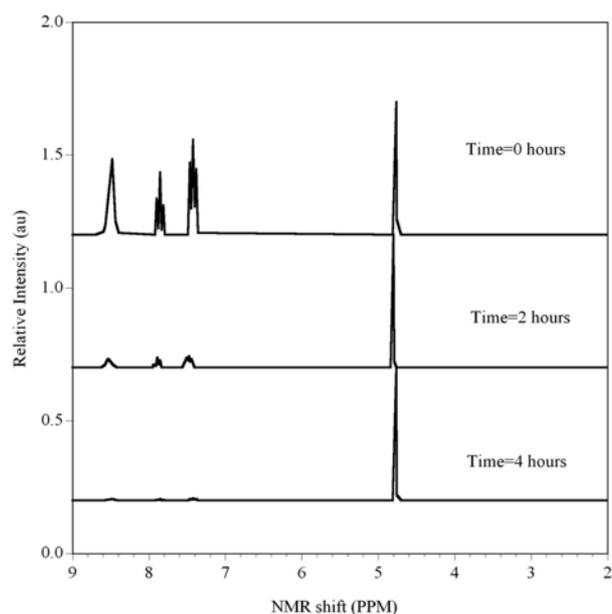


Fig. 5. Photocatalytic degradation of a pyridine solution in D_2O using ZnO as catalyst. Samples for 1H NMR analysis were taken at different reaction times. ($V = 100$ ml, $C_0 = 20$ ppm, catalysts weight = 2 g/l, $\lambda_{max} = 365$ nm).

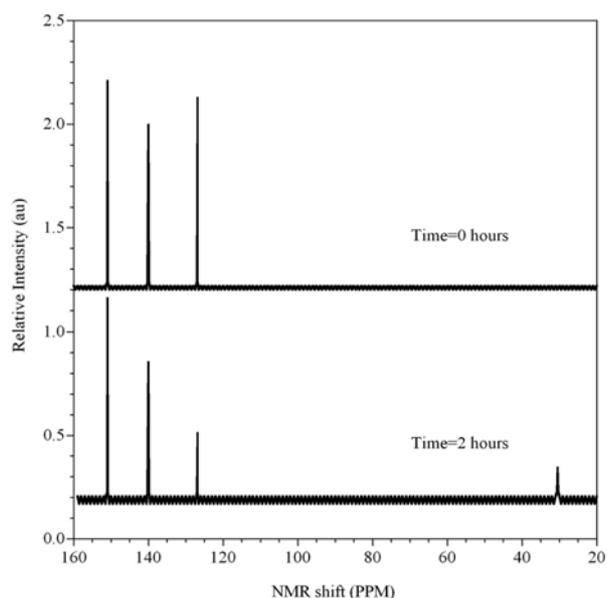


Fig. 6. Photocatalytic degradation of a pyridine solution in D₂O using ZnO as catalyst. Samples for ¹³C NMR analysis were taken at different reaction times. (*V* = 100 ml, *C*₀ = 20 ppm, catalysts weight = 2 g/l, λ_{max} = 365 nm).

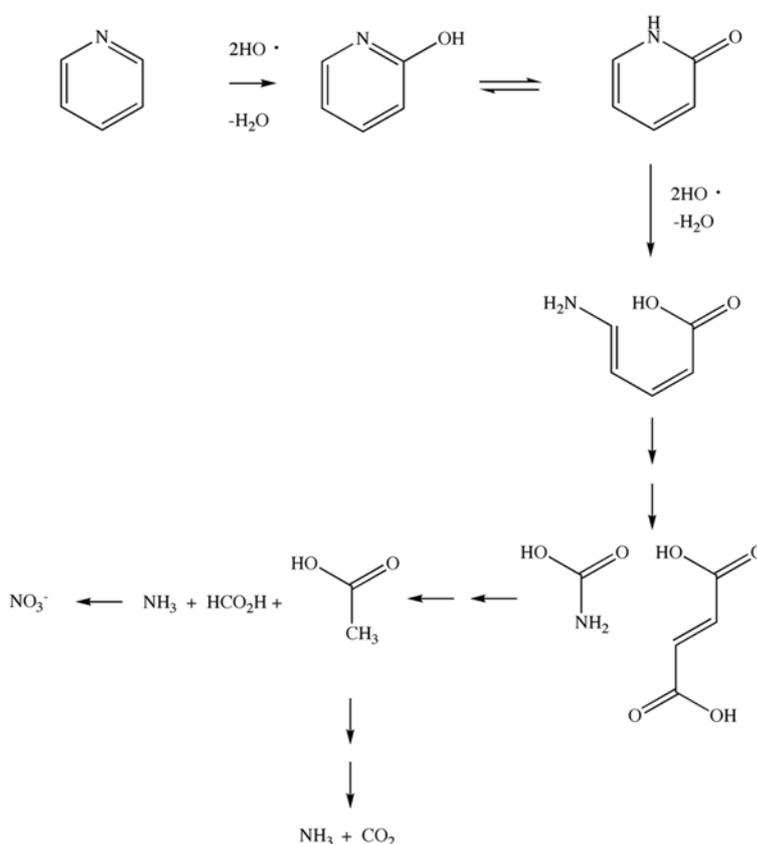
observed at 185 ppm. This signal was detected in the reaction mixture after several hours and eventually disappeared. These signals were assigned to a H₃CC = O group in acetic acid in the reaction mixture. To further

confirm this, a pure sample of acetic acid was added to the reaction mixture. This latter sample gave the same but stronger ¹H and ¹³C NMR signals.

Mechanism

In the first report by Low et al. [22] on the photocatalytic oxidation of pyridine a mechanism for this oxidation was proposed. In spite of the fact that they did not monitor intermediate compounds they suggested that the mechanism is analogous to the oxidation of benzene where the formation of a hydroxycyclohexadienyl radical and hydroxymucondialdehyde intermediates were observed. The reaction is initiated by the addition of the hydroxyl radical to pyridine to give a 3-hydro-3-hydroxypyridine radical followed by a rapid addition of oxygen an HO₂• radical to give N-(formylimino)-2-butenal. This latter compound decomposes in water to give dialdehyde and formamide. In a latter study by Maillard et al. [23] another mechanism for pyridine photocatalytic oxidation was proposed. In this case, the reaction was suggested to proceed by the formation of 2-hydroxypyridine then dihydroxypyridine and trihydroxypyridine in a similar oxidation mechanism previously presented for the oxidation of aromatic phenols. However, in the photocatalytic oxidation of pyridine only 2-hydroxypyridine has been detected.

In this experimental study, it was clearly observed that pyridine is first transformed into 2-hydroxypyridine. This



Scheme 1. Pyridine photocatalytic degradation reaction mechanism.

is explained in terms of pyridine absorption on the ZnO surface by the nitrogen lone pair since this favors hydroxylation next to nitrogen. The fact that 2-hydroxypyridine is the only aromatic intermediate monitored in HPLC is probably due to its tautomeric stability to give 2(1H)-pyridinone. Furthermore, this intermediate could be easily degraded by an oxidation mechanistic pathway (Scheme 1). Indeed, amido groups R-NH-CH=O are

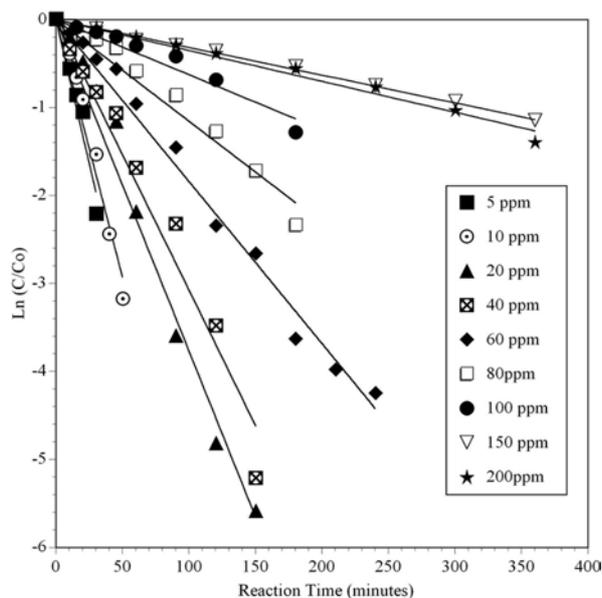


Fig. 7. Logarithmic plots of the relative pyridine concentration (C/C_0) as a function of time for the photocatalytic degradation of pyridine using TiO_2 . ($V = 250 \text{ ml}$, O_2 flow = $100 \text{ ml}\cdot\text{minute}^{-1}$, catalysts weight = 1 g/l , $\lambda_{\text{max}} = 365 \text{ nm}$)

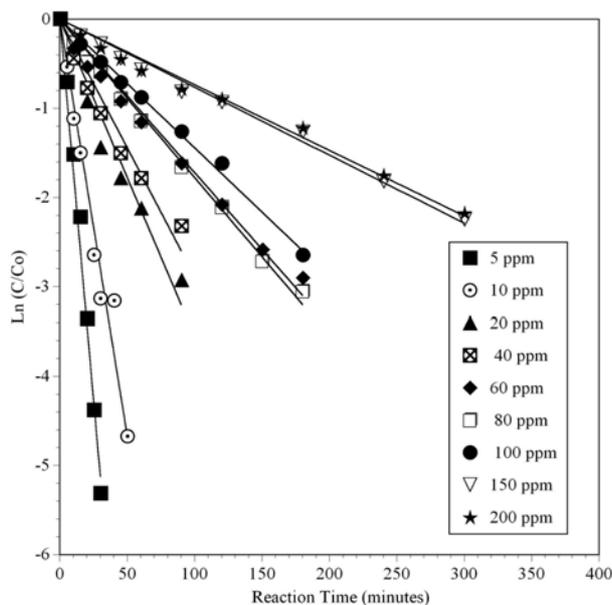


Fig. 8. Logarithmic plots of the relative pyridine concentration (C/C_0) as a function of time for the photocatalytic degradation of pyridine using ZnO . ($V = 250 \text{ ml}$, O_2 flow = $100 \text{ ml}\cdot\text{minute}^{-1}$, catalysts weight = 1 g/l , $\lambda_{\text{max}} = 365 \text{ nm}$)

known to oxidize very easily in the presence of $\text{HO}\cdot$ radicals or HO^- anions [29]. There are several observations that indicate pyridine photocatalytic oxidation on ZnO (or TiO_2) does not proceed via dihydroxypyridine. First of all, this intermediate has never been detected by HPLC or GC-MS in the reaction mixture. Furthermore, in the case of di- or tri-hydroxylated aromatic compounds the photocatalytic oxidation is faster due to a better adsorption of these compounds on the catalyst's surface (TiO_2 or ZnO). Several authors [29] have indicated that electron transfer takes place very quickly after adsorption of di- or tri-hydroxylated aromatic compounds on the surface of the photocatalyst. In spite of this, in most of the degradations of aromatic phenols several polyhydroxylated intermediates have been detected. In these particular degradation experiments, the oxidation of the organic chain becomes a rather slower process as evidenced by TOC experiments. Therefore the oxidation of pyridine must undergo a different mechanism than the one reported for phenol degradation.

Kinetic studies

Since the reaction rate for the photocatalytic degradation of any organic compound is a strong function of catalyst type and reactant concentration, several kinetic experiments were carried out to investigate the effect of the initial pyridine concentration on the reaction rate using TiO_2 and ZnO as catalysts. Previous studies (30, 31) have demonstrated that the first step in the photocatalytic reaction follows a pseudo first order kinetic law of the following form:

$$-r_p = \frac{dC}{dt} = K_{app}C \quad (11)$$

Therefore the raw data for pyridine concentration were normalized (C/C_0) and plotted in a natural logarithm scale as a function of reaction time on Fig. 7 and Fig. 8. The apparent rate constants presented in Table 1 were determined by linear regression (30).

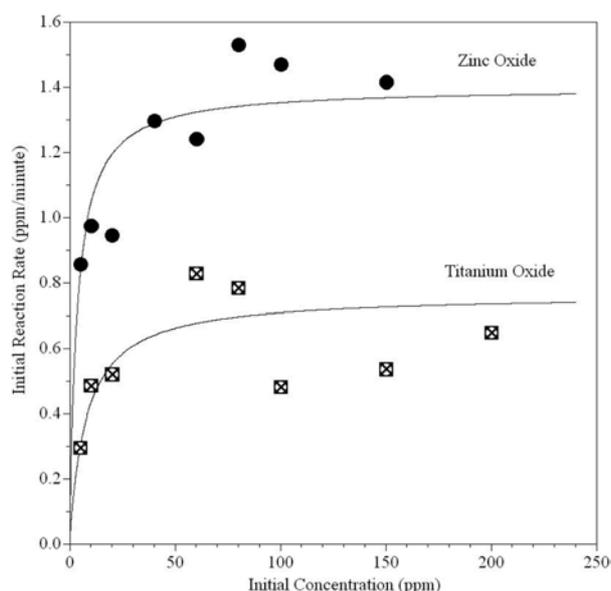
The value of the apparent rate constant decreases with initial pyridine concentration indicating that the pyridine reaction follows a Langmuir-Hinshelwood mechanism (30, 31). At very short reaction times, the pyridine concentration

Table 1. Pseudo first order rate constants for the photocatalytic degradation of pyridine using TiO_2 and ZnO as catalysts

Pyridine concentration (ppm)	$K_{app} \cdot 10^3 \text{ (minute}^{-1}\text{)}$	
	TiO_2	ZnO
5	58.40	170.80
10	48.30	97.30
20	25.90	47.13
40		32.35
60	13.75	20.64
80	9.76	19.09
100	4.79	14.67
150	3.55	9.42
200	3.23	

Table 2. Kinetic parameter of the Langmuir-Hinshelwood model for the photocatalytic degradation of pyridine using TiO₂ and ZnO as catalysts

TiO ₂	TiO ₂	ZnO	ZnO
Kinetic constant	Adsorption constant	Kinetic constant	Adsorption constant
K ₁ (minute ⁻¹)	K ₂ (ppm ⁻¹)	K ₁ (minute ⁻¹)	K ₂ (ppm ⁻¹)
0.9929	0.1301	0.408	0.2917

**Fig. 9.** Initial reaction rate as a function of the initial concentration for the photocatalytic degradation of pyridine using ZnO and TiO₂ as catalysts. (*V* = 250 ml, O₂ flow = 100 ml·minute⁻¹, catalysts weight = 1 g/l, λ_{max} = 365 nm).

is almost equal to its initial concentration and the Langmuir-Hinshelwood model can be represented by equation 2:

$$-r_{p0} = -\left. \frac{dC}{dt} \right|_{t=0} = \frac{K_1 C_0}{1 + K_2 C_0} \quad (12)$$

The kinetic parameters of the Langmuir-Hinshelwood model for the photocatalytic degradation of pyridine (Table 2) were evaluated by non-linear regression of the experimental results presented in Fig. 9. They indicate that ZnO has an adsorption constant (*K*₂) two times more than TiO₂. Therefore, zinc oxide promotes a faster photocatalytic degradation reaction than TiO₂ as indicated by the values of the kinetic constant (*K*₁) for each of the catalysts.

Conclusions

A combination of UV light and ZnO could be efficiently used to oxidize pyridine. Furthermore, the degree of pyridine degradation is affected by the irradiation time and the amount of catalyst. Only 1 g/l of catalyst was enough to promote the complete mineralization of the parent organic compound. The photocatalytic oxidation is quite efficient at pH = 6.8 ± 0.2. HPLC studies of the reaction mixture indicated the degradation of pyridine to take place in two

hours. However, TOC studies indicated the degradation of intermediate compounds to be a rather slower process with the formation of more recalcitrant compounds. Eventually, total mineralization of pyridine was evidenced by TOC experiments. NMR analysis monitoring ¹H and ¹³C signals also confirmed total oxidation of pyridine. By means of this analytical technique, pyridine degradation was monitored in situ. In addition to this, the formation and eventual disappearance of acetic acid in the reaction mixture was observed. Based on the intermediate compounds monitored in the reaction mixture, an alternative degradation mechanism for the catalytic oxidation of pyridine on ZnO is presented. In addition, the kinetic parameters of the Langmuir-Hinshelwood model that describe the initial reaction rate for the photocatalytic degradation of pyridine over TiO₂ and ZnO are presented. They clearly indicate that zinc oxide induces faster photocatalytic degradation reactions because it has better adsorption properties than TiO₂.

Acknowledgments

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Nomenclature

<i>C</i>	Pyridine concentration	ppm (mg/l)
<i>C</i> ₀	Pyridine initial concentration	ppm (mg/l)
<i>K</i> ₁	Pyridine degradation reaction rate constant	minute ⁻¹
<i>K</i> ₂	Pyridine adsorption constant	ppm ⁻¹
<i>K</i> _{app}	Apparent reaction rate constant	ppm·minute ⁻¹
- <i>r</i> _p	Pyridine reaction rate	ppm·minute ⁻¹
- <i>r</i> _{p0}	Initial pyridine reaction rate	ppm·minute ⁻¹
<i>t</i>	Time of reaction	minutes
TOC	Total organic carbon	ppm (mg/l)

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