# Photolytic (UVC) and photocatalyic (UVC/TiO$_2$) decomposition of pyridines

David R. Stapleton [a], Dionissios Mantzavinos [b], Maria Papadaki [c],*

[a] *Chemical Engineering, IPSE, School of Process Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*
[b] *Department of Environmental Engineering, Technical University of Crete, 73100 Chania, Greece*
[c] *Department of Environmental and Natural Resources Management, Seferi 2, 30100 Agrinio, Greece*

Available online 21 April 2007

## Abstract

The degradation of 2-chloropyridine (2-CPY) and its degradation primary product 2-hydroxypyridine (2-HPY) was studied by means of ultraviolet (UV) irradiation at 254 nm. Photolytic and photocatalytic experiments were conducted on 2-CPY and 2-HPY aqueous solutions in a batch reactor with internal recycle in laminar and turbulent conditions at 50 °C in a closed but not airtight system with and without additional aeration, at solution ambient pH and at controlled pH conditions, with use and in the absence of radical scavenger. The solution volume was 0.4 L and initial substrate concentrations were approximately 2.6 mmol/L (0.25–0.3 g/L depending on the substrate). Where applicable 1 g/L TiO$_2$ (P-25) was used, suspended in the liquid in a form of turbulent slurry or using a glass tube around the UV-lamp on which a fixed TiO$_2$ catalytic layer had been deposited. At the aforementioned conditions 2-CPY readily degrades photolytically, the catalytic path having very little influence. In all cases 2-CPY produces 2-HPY which further degrades to other products. Aeration, pH and the presence of catalyst and/or radical scavengers do not affect the rate of decomposition of 2-CPY, but have a strong influence on the further decomposition of the produced 2-HPY. 2-HPY decomposition proceeds both catalytically and photolytically following oxygen dependent and oxygen independent pathways.
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*Keywords:* 2-chloropyridine; 2-hydroxypyridine; Photolysis; Photocatalysis; UVC; Water treatment

## 1. Introduction

Remediation of water and wastewaters by advanced oxidation processes (AOP) from persistent organic pollutants that cannot be treated by conventional biological technologies becomes increasingly prominent because of increased public concern and the progressively more restrictive requirements regarding the admissible levels of organic contaminants in the aquatic environment.

Pyridine and its derivatives constitute an important class of compounds with applications in pharmaceuticals, cosmetics, pesticides, etc. Chloropyridines, in particular, are known to be hardly biodegradable and highly toxic to fresh water and marine bacteria [1]. These compounds can be found not only in the effluents of certain industrial activities but also in raw and drinking water due to spills or fugitive emissions [2].

Ultraviolet (UV) light-induced degradation processes constitute a well-established practice in water and wastewater treatment and numerous research studies have been undertaken over the past few years [3–5]. UV-driven AOP are primarily based on the generation of powerful oxidizing species, such as OH radicals, through the direct photolysis of H$_2$O or through photo-induced processes as in the photo-Fenton reactions and semiconductor photocatalysis [6].

In this work, we investigate the treatment of 2-chloropyridine (2-CPY) in water by means of UV irradiation in the presence and in the absence of TiO$_2$ catalyst. One of the primary intermediates formed during the decomposition of 2-CPY is 2-hydroxypyridine (2-HPY), which subsequently degrades further to other substances. In the current work, the formation and destruction of 2-HPY is also reported.

## 2. Materials and methods

Aqueous solutions of 2-CPY (supplied by Fluka, 98% purity) and 2-HPY (supplied by Fluka, 97% purity) were treated
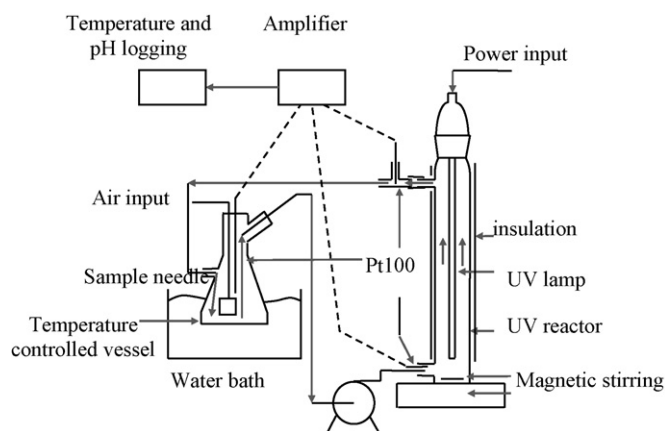
Fig. 1. Equipment schematic.

both photolytically and photocatalytically at an initial substrate concentration of 2.6 mmol/L (0.25–0.3 g/L depending on the substrate), volume 0.4 L and temperature 50 °C. Experiments were performed with and without addition of air, in the solution ambient pH and at controlled pH, with and without catalyst (TiO$_2$, P-25), with and without radical scavenger *tert*-butanol. The concentration of catalyst employed was 1 g/L except for sreening experiments, where concentration varied from 0.02 to 1 g/L. Where applicable, radical scavenger was used in a molar proportion of 6.5:1 *tert*-butanol:2-CPY and 8:1 *tert*-butanol:2-HPY.

The experimental system used is shown in Fig. 1. It consists of a tubular flat bottom glass photoreactor (length 315 mm, diameter 27 mm, volume 300 ml) with recycle. Experiments were performed under agitated conditions using magnetic stirring. A recycle vessel was placed in a temperature controlled water bath. Air sparging was conducted in the vessel at a rate of 17 ml/s through a diffuser. The reaction was performed in a batch mode with the reaction solution continuously recirculating between the recycle vessel and the reactor at a flow-rate of 200 ml/min. Three very thin RTD-100 thermometers with accuracy better than 0.1 °C were employed for the measurement of the temperature at the reactor inlet, outlet and recycle vessel. The average of the inlet and outlet reactor temperature values (which was less than 0.5 °C) was taken as the nominal temperature of the experiment. A low pressure mercury lamp with an output wavelength of 90%, 254 nm (supplied by Ultra-Violet Products Ltd, UK) provided the light source.

Photocatalytic experiments were performed employing the same reactor and using 1 g/L TiO$_2$, P-25 (Degussa) as suspended slurry, in all but the screening experiments where different concentrations ranging from 0.2 to 1 g/L were employed. The catalyst was mixed with the substrate aqueous solution in the dark where it was then left for one hour under continuous agitation before UV irradiation was applied. A few fixed-bed photocatalytic experiments were also performed. In this case, the lamp was closely surrounded by a three-layer TiO$_2$ coated glass-tube.

Samples periodically drawn from the vessel were analysed by means of high performance liquid chromatography (HPLC, manufactured by Hitachi) to follow concentration profiles of

the original organic substrate and, where applicable, its primary degradation product. The samples were analysed using a Sielc Primesep A, 4.6 × 250 mm, 5 μm particle size, 100 Å pore size column. A 5:95 acetonitrile:water solution was used as an isocratic mobile phase at 1 ml/min flow-rate and 30 °C. The injection volume was 20 μl and detection was through a UV detector set at 250 nm. A calibration curve was established using external standards at various concentrations and was used for quantification. HPLC analyses were run in duplicate and mean values of two separate measurements are quoted as results. Total organic carbon (TOC) was analysed by means of catalytic combustion/non-dispersive infrared gas analysis on a Shimadzu 5050 TOC analyser. pH was continuously measured employing a Hanna Instruments pH211 pH meter with a Hanna Instruments HI1131 probe.

## 3. Results and discussion

Fig. 2 shows the rate of aerated and nonaerated photolytic and photocatalytic degradation of 2-CPY. The catalytic curves shown here correspond to measurements taken with a fixed layer of catalyst on glass tube surrounding the lamp at a radial distance of 1 mm. As can be seen in Fig. 2, the rate of 2-CPY degradation is not practically affected by the presence or absence of air in the reactor either during photolysis or photocatalysis. Additionally, the deposit on the glass tube TiO$_2$ catalyst has no positive effect on its rate of degradation. Similar experiments were performed employing 1 g/L of TiO$_2$ (P-25) powder catalyst in a form of a turbulent suspension. Again, the catalyst did not result in any improvement of 2-CPY degradation rate. On the contrary, as is shown later, it appeared to have the opposite effect, presumably due to the inhibition of light caused by the catalyst powder. This result is consistent with other researchers' work [7] with similar substances.

TOC and pH measurements were performed during the reaction. Fig. 3 shows the effect of aeration (at a constant flow-rate of 17 ml/min), liquid flow pattern (liquid flow-rate of 200 ml/min with agitation or no agitation), the combined use of aeration and agitation and presence of P-25 turbulent aerated suspension on the rate of TOC removal and the pH of the solution. TOC removal at the end of the original substrate complete degradation was
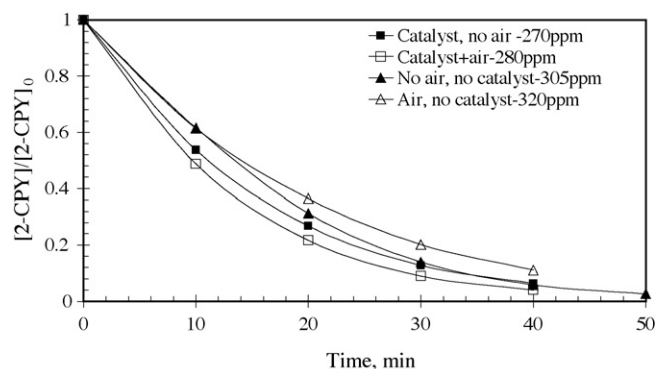


Fig. 2. Rate of aerated and nonaerated photolytic and fixed-bed photocatalytic degradation of 2-CPY.
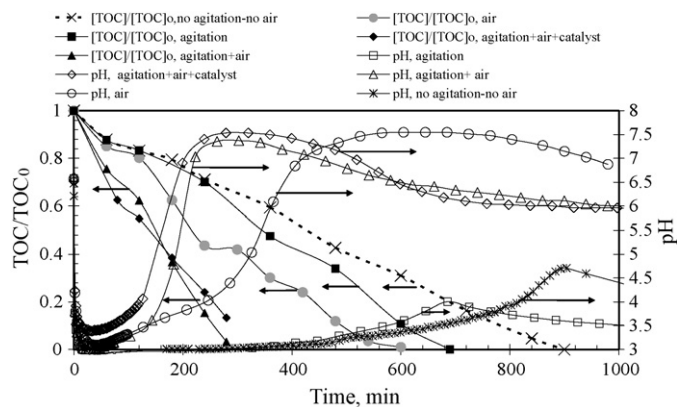
Fig. 3. Effect of aeration, agitation and suspension of P-25 powder on TOC removal and solution pH during 2-CPY degradation.

of the order of 20%. However, prolonged irradiation resulted in almost complete mineralisation of the organic load. As can be seen in Fig. 3, nonagitated nonaerated photolytic destruction results in the slowest rate of TOC removal with the pH remaining fairly acidic. The addition of some agitation slightly increases TOC removal with the pH remaining acidic. Aeration noticeably accelerates the rate of TOC removal and shifts the pH to higher values. The simultaneous use of agitation and air circulation results in a dramatic increase of the rate of TOC removal and a sharp change of the pH to higher values. Furthermore, addition of P-25 does not clearly show to cause a further increase in the rate of TOC removal.

HPLC measurements provided the concentration history of the original substrate 2-CPY as well as its primary photodecomposition product 2-HPY. The normalised concentration profiles of these two substances that resulted from three typical experiments (nonaerated photolytic, aerated photolytic and photocatalytic conditions) are shown in Fig. 4. All concentrations have been normalised via division by the initial 2-CPY concentration. As can be seen in Figs. 2 and 4, 2-CPY is readily susceptible to photolytic degradation with over 95% disappearance observed within 40 min. The rate of photolytic degradation is not enhanced with aeration, indicating that there are no measurable reaction paths involving dissolved oxygen. As can be seen in Fig. 4, the rate of decomposition of 2-CPY
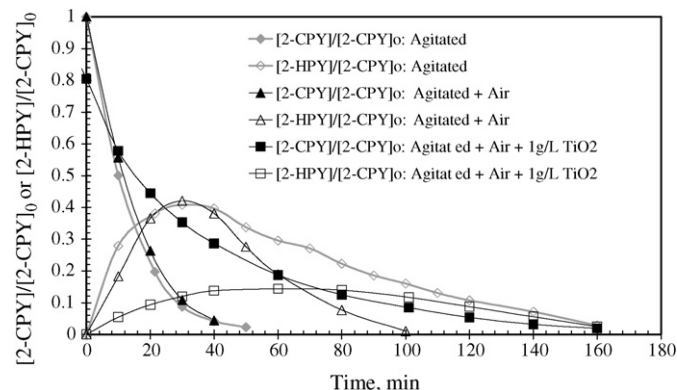


Fig. 4. Concentration history of 2-CPY and 2-HPY during photolytic nonaerated, photolytic aerated and photocatalytic experiments.

in the presence of 1 g/L suspended $TiO_2$ catalyst is significantly decreased. Ninety-five percent removal of 2-CPY was achieved after 120 min of irradiation while in pure photolytic conditions only 40 min of irradiation were sufficient to achieve the same degree of conversion. However, as shown in Fig. 2, the use of fixed (almost transparent) catalyst on glass does not reduce appreciably the rate of 2-CPY photolytic decomposition. The primary path of decomposition of 2-CPY when irradiated at 254 nm is photolytic. The addition of catalyst in the form of suspended slurry obstructs the light. This was not however the case with the fixed catalyst. It is thus believed that the retardation of the reaction is because of the turbidity of the solution induced by the suspended catalyst. These results agree with the findings of Abramovic et al. [8] for the degradation of 2-amino-5-chloropyridine.

After mixing the substrate and catalyst in the dark for one hour, a 19% drop in concentration was observed which was attributed to adsorption. Malllard-Dupuy et al. [9] have found only 9% disappearance of substrate when treating pyridine using P-25. The increased adsorption in the case of 2-CPY indicates that adsorption is facilitated by the presence of chlorine on the *ortho*-position. (As will be shown later, control experiments employing 2-HPY as the original substrate resulted in 6.5% substrate adsorption for similar initial concentrations).

On the other hand, the effect of both aeration and catalyst presence on the formation and/or destruction of 2-HPY is appreciable, which probably justifies the increased TOC removal. The observed maximum concentration of 2-HPY under nonaerated photolytic conditions was reached at approximately 30 min when 90% of 2-CPY had been destroyed, 42% of which was present at that time in the reactor as 2-HPY. For the first 30 min of reaction, both nonaerated and aerated photolytic experiments display the same concentration profiles for both substances of consideration. Neither the magnitude nor the time that it was reached was measurably affected by the use of aeration. The degradation profile of 2-HPY after the maximum has been reached is significantly faster in the aerated experiment compared to the nonaerated one, indicating that 2-HPY decomposition is strongly dependent of the presence of dissolved oxygen. The nonaerated experiment was performed in a closed but not airtight system with some dissolved oxygen present. It is possible that the similarity in the concentration history of 2-HPY during the first 30 min of the reaction was due to the sufficiency of oxygen in the solution, which was later depleted. The effect of residual dissolved oxygen and diffused oxygen was tested in control experiments where the reaction medium was purged with helium for two hours before and during the reaction. The results showed no significant effect on 2-CPY disappearance and a slight drop in rate of 2-HPY disappearance, supporting the above argument. However, as 2-HPY degrades in both cases, it is believed that 2-HPY decomposition follows both oxygen dependent and oxygen independent reaction pathways.

Scheme 1 shows the suggested reaction mechanism for the conversion of 2-CPY to 2-HPY. It is postulated that the excited 2-CPY causes polarisation of the C–Cl bond which facilitates bond scission within the water matrix producing the hydroxyl group on the pyridine ring and the formation of HCl. This type
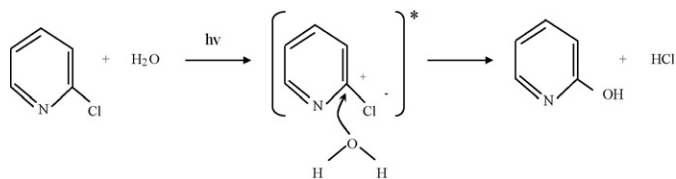
Scheme 1. Proposed reaction mechanism for the photo-destruction of 2-CPY.

of reaction has been observed for chlorinated phenols [10–14] and other aromatic compounds [14]. The presence of HCl was confirmed by a sharp drop in pH (from around neutral to 2.9 within 10 min of irradiation) and by chloride ion titration of the final solution as reported in our previous work [15]. The independence from the presence or absence of oxygen as well as pH independence of 2-CPY destruction (see Fig. 3) rule out oxidation or reaction with $OH^-$ ions [16].

In the case of photolysis/photocatalysis, on the other hand, there was a significant decrease in the observed maximum concentration of 2-HPY compared with photolysis alone (maximum 2-HPY concentration reached only 14% of the original substrate concentration).

The degradation of 2-CPY can be described by a pseudofirst order rate on 2-CPY concentration [17]. The effect of catalyst concentration, pH and presence of *tert*-butanol as radical scavenger on apparent reaction rate constant, $k_{app}$, is shown in Fig. 5. As $TiO_2$ concentration increases from 0 to 50 mg/L an increasingly detrimental effect on the reaction rate is observed with $k_{app}$ being almost halved at concentrations around 50 mg/L. Further addition of catalyst (up to 1 g/L) continues having a detrimental effect on the reaction rate, however, not as pronounced as at lower concentrations.

Under natural pH conditions, the formation of HCl causes a reduction in pH from 8 to 2.9 within 10 min. Experiments were performed with a dropwise addition of NaOH in order to maintain the solution pH in the range 6.5–8. As can be seen in Fig. 5, controlled pH resulted in higher reaction rates but in the case of photolysis (i.e. 0 g/L catalyst) the rate was unaffected by the pH change. However, the presence of catalyst resulted in reduction in the measured $k_{app}$, apparently slowing down the reaction. In the system under study, both direct photolysis and

photocatalysis occur simultaneously and this reduction in overall rate with catalyst addition could be explained by the light blocking effects of the $TiO_2$ powder. It is therefore postulated that photocatalysis of 2-CPY is less effective than direct photolysis. At the higher catalyst concentration tested, the rate constant was 0.023 and $0.037\,s^{-1}$ respectively for the natural and pH-controlled runs. This is attributed to the fact that adsorption of 2-CPY onto $TiO_2$ surface seems to be enhanced around the zero charge point according to Bhatkhande et al. [18]. Experiments were performed in the presence of a known hydroxyl radical scavenger *tert*-butanol (10 times mass excess, 6.5:1 molar ratio), with the addition of 1 g/L $TiO_2$. The presence of *tert*-butanol had an insignificant effect on the rate of the decomposition reaction of 2-CPY. Under both natural and controlled pH conditions $k_{app}$ was only marginally reduced as can be seen in Fig. 5, thus suggesting that the reaction is scarcely affected by the presence of hydroxyl radicals. This is consistent with the findings of Sun and Pignatello [19]. The degradation cannot be solely explained by direct photolysis as this route is essentially pH independent and the results show significant pH dependency. This suggests that the photocatalytic path of the reaction proceeds largely by the direct hole oxidation route when adsorbed on the $TiO_2$ surface and not by hydroxyl radical attack [19,20]. This indicates that the higher $k_{app}$ under controlled pH conditions is owing to greater substrate adsorption.

The addition of $TiO_2$, *tert*-butanol and the controlled pH conditions not only affect the rate of 2-CPY destruction but also have a significant influence on the value of the maximum observed concentration of the intermediate, 2-HPY, as seen in Fig. 6. Direct photolysis yields significantly higher maximum 2-HPY concentrations than combined photolysis/photocatalysis, indicating that 2-HPY either undergoes reduced formation in the presence of $TiO_2$ or/and degrades at a faster rate. In controlled pH conditions (i.e. higher pH), increased concentrations of 2-HPY were observed in photolytic and combined photolytic/photocatalytic cases.

As 2-HPY is an intermediate in a series reaction scheme, its concentration in the reaction solution at any time depends on both its production and decomposition rates. In order to investigate the rate of its decomposition alone experiments at controlled conditions were performed using 2-HPY as the orig-
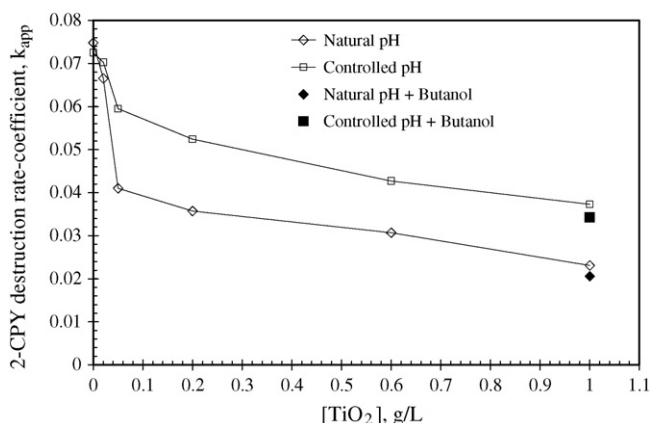


Fig. 5. Effect of $TiO_2$ concentration, pH control and *tert*-butanol addition on pseudofirst order reaction rate constant for 2-CPY photocatalytic degradation.
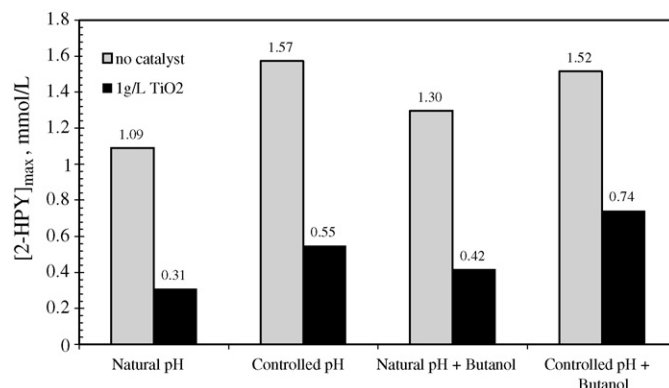


Fig. 6. Effect of $TiO_2$, pH control and *tert*-butanol addition on the maximum measured 2-HPY concentration during 2-CPY degradation.
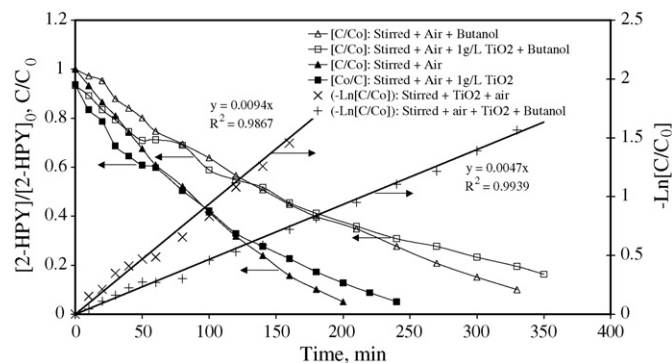
Fig. 7. 2-HPY concentration-time profiles during its degradation at various conditions.

inal substrate and the results are shown in Fig. 7. Addition of *tert*-butanol resulted in a decrease of the pseudofirst order photocatalytic rate constant from 0.0094 (without scavenger) to $0.0047 \, s^{-1}$. This indicates that OH radicals play an important role on the destruction of 2-HPY. This is consistent with the experiments involving 2-CPY as the starting material where the addition of *tert*-butanol generally resulted in an increase of 2-HPY maximum concentration (Fig. 6) observed as the scavenger is likely to inhibit further decomposition of 2-HPY. The presence of 1 g/L $TiO_2$ showed a negligible net rate change, although light blocking effects were expected to retard direct photolysis. From Figs. 5 and 7, one can see that 2-CPY degrades appreciably faster than 2-HPY under similar reaction conditions (by about an order of magnitude). As 2-HPY degradation rate is strongly affected by OH radicals, but OH radicals do not affect its concentration in solutions involving 2-CPY as original substrate it is possible that in the presence of catalyst the photocatalytic path of 2-HPY destruction predominates. This view is further endorsed by the fact that the light obstruction caused by the catalyst, which has a significant effect on the decomposition of 2-CPY does not have a measurable effect on 2-HPY destruction. Moreover, 2-HPY decomposition strongly depends on the presence of dissolved oxygen. It is worth mentioning here that the rate reduction of 2-HPY destruction under photolytic conditions cannot be attributed to the UV absorbance of *tert*-butanol as a solution, where *tert*-butanol and 2-HPY were present in a molar proportion of 8:1, the 254 nm absorbance of *tert*-butanol was measured to be only 0.34% of that of 2-HPY. It is therefore plausible that in the presence of the catalyst, 2-HPY is essentially destructed by photocatalysis. Supporting evidence is also provided by experiments performed with the addition of HCl as explained next.

Experiments employing 2-HPY as a starting material do not become acidic as reaction progresses. Thus, the effect of the acidic environment on the decomposition of 2-HPY was examined. Control experiments using 2-HPY as the initial substrate showed that HCl addition reduces the rate of its destruction under both photolysis and combined photolysis/photocatalysis. However, unless photolysis is practically insignificant, this dependency contradicts the previous findings. When 2-CPY was employed as a starting material, the concentration of 2-HPY under controlled higher pH conditions was increased. As 2-CPY

photolysis –and therefore the rate of 2-HPY formation– is practically unaffected from the pH, this indicates that the higher pH values (controlled conditions) obstruct the rate of 2-HPY destruction and that the observed increase of 2-HPY concentration in the photolysis of 2-CPY was due to reduced rates of 2-HPY destruction alone. In the case of photocatalysis both 2-HPY formation and destruction are favoured by higher pH so 2-HPY concentration can either increase or decrease depending on the relative rates of formation and destruction.

## 4. Conclusions

The degradation of 2-CPY and its degradation primary product 2-HPY was studied by means of UV irradiation at 254 nm with and without $TiO_2$. It was found that:

- The decomposition of 2-CPY is very fast and progresses via photolytic and photocatalytic paths.
- The photolytic paths are not oxygen or pH dependent, while the rate of the photocatalytic path depends on pH.
- The independency of 2-CPY photolysis from the presence or absence of oxygen as well as its pH independency rule out oxidation or reaction with $OH^-$ ions as is also claimed by Boule et al. [16].
- The rate of decomposition of 2-CPY in the presence of $TiO_2$ reduces due to the inhibition of light caused by the catalyst thus reducing the effectiveness of photolytic paths.
- 2-CPY decomposition is hindered by the presence of suspended only catalyst, but for any given catalyst concentration the degradation is faster at higher pH values. Thus the 2-CPY degradation cannot be solely explained by direct photolysis as this route is essentially pH independent and the results show significant pH dependency. This suggests that the photocatalytic path of the reaction proceeds largely by the direct hole-oxidation route when adsorbed on the $TiO_2$ surface and not by hydroxyl radical attack as is also supported by Sun and Pignatello [19] and Marugan et al. [20]. This indicates that the higher destruction rates, under controlled pH conditions are owing to greater substrate adsorption. The measured adsorbance of 2-CPY on $TiO_2$ after one hour of mixing in the dark was 19%, significantly higher than that of 2-HPY (6.5%) and than the 9% that Malllard-Dupuy et al. [9] found when treating pyridine with P-25.
- 2-HYP is the first important intermediate substance formed by the substitution of chlorine atoms by hydroxyls.
- The decomposition of 2-HPY is strongly dependent of the presence of dissolved oxygen and OH radicals play an important role on the destruction of 2-HPY.
- In controlled pH conditions (i.e. higher pH) increased concentrations of 2-HPY were observed in photolytic and combined photolytic/photocatalytic cases. At the same time, decreased pH values resulted in reduced rates of 2-HPY destruction.
- Under photolytic conditions lower pH values do not affect 2-HPY formation but they reduce the rate of its decomposition. Higher pH values favour both the photocatalytic formation and the photocatalytic destruction of 2-HPY.

## Acknowledgement

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