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Kinetic of adsorption and of photocatalytic degradation of phenylalanine effect of pH and light intensity

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ABSTRACT

Phenylalanine (Phe) was chosen to study the TiO_2 photocatalytic degradation of amino acids, which are at the origin of the formation of odorous compounds after chlorination. The photocatalytic degradation has been investigated in aqueous solutions containing TiO_2 suspensions as photocatalyst, in order to assess the influence of various parameters, such as adsorption, initial concentration, pH and radiant flux on the photocatalytic process. Results showed no correlation between dark adsorption and photocatalytic degradation. A multilayer kinetic was observed in the dark with a monolayer corresponding to less that 1% of OH covered, whereas Langmuir–Hinshelwood model seems to modelize the photocatalytic disappearance of Phe. However, even if the form of the curve is similar to L–H model, the degradation of phenylalanine is not a kinetic of L–H as we could plan it by considering the adsorption of the phenylalanine in the dark. The study of the mineralization of carbon and nitrogen showed that nitrogen atoms were predominantly photoconverted into NH_4^+ and a total mineralization of nitrogen and carbon seems occur. The identification of the by-products by LC–MS reveal mono- and di-hydroxylation and nitrogen–carbon (N–C) cleavage.

The effect of pH showed an increase of adsorption under acid pH but a decrease of disappearance rate. The more efficient degradation was found at basic pH. The evolution of hydroxylated compounds of phenylalanine as a function of conversion revealed the presence of more hydroxylated compounds at natural pH and at basic pH compared to acid pH suggesting a modification of mechanism with solution pH. The effect of the radiant flux evaluated under different initial concentration of phenylalanine allowed us to determine that k increases by increasing the radiant flux, whereas K decreases or remains constant from about a value of 3.5 mW/cm^2. The disappearance rate as a function of radiant flux has been showed to reach a maximal value corresponding to a maximal quantum yield of 1.6%.

1. Introduction

Amino acids concentration in drinking water range from 0.33 to 1 μg/L [1] and can vary between 0 and 30 μg/L in several drinking water plants of western France [2]. They are found behind filtration process [3] and come from the natural organic matter or from microorganisms.

Amino acids are non-toxic compounds. However, it is known that amino acids [4] can be precursors of odorous by-products. Amino acids lead to the production, under chlorination, of nitriles, chloramines and aldehydes [5], known as odorous but also to the formation of N-chloroaldimines [6] which are very stable compounds. They are stable enough to be found in tap water (their life time is around 50 h at 20 °C but hundreds of hours at 15 °C, while monochloramines' half-life time is around 1 h). Their threshold of odor is lower than 1 μg/L.

Amino acids are also interesting compounds, because they are the building blocks of proteins and can help us to understand better the mechanism of microorganisms' photocatalytic degradation. Actually, biochemical applications of TiO_2^-mediated photoxidations, under solar light, are promising for the elimination of microorganism, e.g. bacteria, fungi, mold, and virus [7–10] since the reaction occurs at ambient temperature, with addition of non-toxic semiconductor, TiO_2 which can be activated by solar light.

In the last decade, TiO_2 heterogeneous photocatalysis has proved to be one of the most powerful techniques for remediating

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environmental pollution in both liquid and gas phase reactions [11]. However, several points remain understood such as the absence of correlation between the adsorption in the dark and the adsorption determined considering Langmuir–Hinshelwood model.

Our objectives are first to contribute to a better understanding of photocatalytic treatment for removing amino acids which are the simpler molecules constituting microorganisms (DNA, RNA, proteins, etc.) by studying kinetics of adsorption in the dark under different pH, the kinetics of photocatalytic degradation at different concentrations under different pH and light intensities.

2. Experimental

2.1. Materials

Pure (99% purity) phenylalanine was provided by Janssen Chimica. The other chemicals used, HNO_3 and NaOH were purchased from Aldrich and used as received. Degussa P-25 titanium dioxide (mainly anatase, 50 $m^2\,g^{-1}$, nonporous) was used as the photocatalyst. Water used for preparation of samples was ultra-pure water, filtered through a milli-Q PLUS 185 water system.

2.2. Reactor and light source

The aqueous suspensions were irradiated in 100 mL open cylindrical reactor whose base contained an optical window with a surface area of about 19.6 cm^2. The output of a Philips HPK 125 W high mercury lamp was filtered through a circulating water cell (thickness = 2.2 cm), which avoided the solution warming by IR, and a filter Corning 0.52 mW/cm^2 allowing to cut off the wavelengths below 340 nm. The radiant flux was measured using a VLX-3W radiometer with a detector CX-365 (355–375 nm). The use of a grid permits to decrease the intensity of the light in order to obtain the intensity selected.

2.3. Photocatalytic experiments

A volume of 20 mL of phenylalanine solution with different concentrations was used. 1.25 g/L of TiO_2 is sufficient to absorb all photons entering the photoreactor [12]. The degradation was carried out at room temperature and at neutral pH (pH = 6.5) unless otherwise stated, in particular for the study of pH influence. Then, the suspension was first stirred in the dark until equilibrium adsorption. Samples taken at different times of irradiation were filtered through 0.45 μm Waters filters to remove TiO_2 particles before analyses. During the irradiation, aliquots of 200 μL of the phenylalanine solutions were collected at regular times.

2.4. Analyses

The degradation of phenylalanine and the formation of hydroxylated compounds (o, m, p hydroxyl-phenylalanine) were followed by HPLC instrument with a Waters System which was comprised a Waters 600 isocratic pump and a Waters 486 UV detector adjusted at 212 nm. A Hypersil BDS C18 reverse phase column (125 mm long, 4 mm diameter), was used. The mobile phase was consisted of 3.8 g ammonium acetate acidified with acetic acid at pH = 5. The flow rate was 0.3 mL/min

The HPLC–MS identification of photoproducts was performed with electrospray ionization (ESI) in positive and negative mode using a Hewlett-Packard HP 1100 series LC–MSD using a column Hypersyl BDS C18 (125 mm × 4 mm, particle size 5 μm). The mobile phase composition was H_2O buffered at pH = 5 with CH_3–COO–NH_4/acetonitrile at a ratio 5/95. The flow rate was 0.3 mL/min. The parameters of nebulization were the following: capillary potential = 4000 V, auxiliary gas = N_2, flow rate = 12 L/min, pressure = 55 psig.

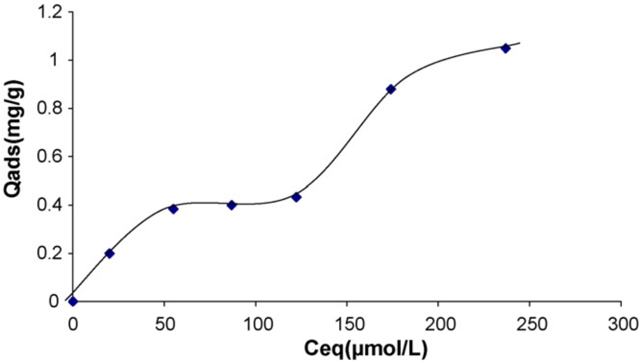


Fig. 1. Amount of phenylalanine adsorbed per gram of catalyst as a function of Phe concentration remaining in solution at the equilibrium.

The formation of carboxylic acids has been analyzed by LC using a Waters 600 pump, a Waters 486 UV detector (detection at 210 nm), and a Sarasep CAR-H (300 mm × 4.6 mm) column. The flow rate was 0.7 mL/min. The injection volume was 100 μL and the mobile phase was H_2SO_4 (5×10^{-3} mol/L).

The formation of nitrate ions has been followed using ionic chromatography with a Dionex DX-120 pump and conductivity detector, and an IonPac AS14A (250 mm × 4 mm) column. The flow rate was 1 mL/min and the mobile phase was an alkaline buffer ($NaHCO_3$ (1.0 mmol/L) + Na_2CO_3 (8.0 mmol/L)).

The formation of ammonium ions has also been followed using ionic chromatography with a Dionex DX-120 pump and conductivity detector. In this case a CS 12A (250 mm × 4 mm) column. The flow rate was 1 mL/min and the mobile phase was H_2SO_4 solutions containing 610 μL of pure sulfuric acid).

3. Results and discussion

3.1. Adsorption

In order to ensure that the adsorption process had reached equilibrium, the mixture (TiO_2/water/phenylalanine) ([phenylalanine = 121 μmol/L]) was stirred in the dark and analysed as a function of time. The phenylalanine adsorption reached equilibrium after about 30 min. The amount of Phe adsorbed at equilibrium corresponds to less than 3% of the initial phenylalanine concentration which was measured from the remaining solution. This amount corresponds to an area density of adsorbed Phe of 0.031 molecules/nm^2. By considering that adsorption of phenylalanine occurs on OH group present on the TiO_2 solid surface, which represent about 5 OH/nm^2 [13], less than 1% of OH covered.

This low coverage of OH could partially be explained firstly (i) by taking into account the work of Tran et al. [14] which suggest that effective adsorption for phenylalanine should be only on basic terminal OH on the solid surface and secondly (ii) by the small concentration of Phe used in our experimental observation (120 μmol L^{-1}). It is why we determined the effect of the initial concentration of phenylalanine on the adsorption. In all cases, the initial reaction mixture was maintained in the dark for 30 min under stirring to reach equilibrium adsorption as reported in the first part. The amount of Phe adsorbed per gram of TiO_2 as a function of the Phe concentration presenting in solution (Ceq) indicates that Langmuir model is not applicable for this type of molecule (Fig. 1).

The curve suggests that adsorption of Phe was a multilayer model. A first plateau corresponding to the monolayer was observed at a value of about 0.43 mg of phenylalanine per gram

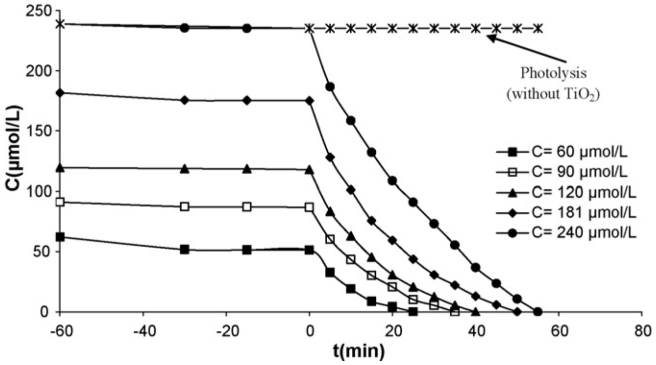


Fig. 2. Kinetics of phenylalanine disappearance for different initial concentrations.

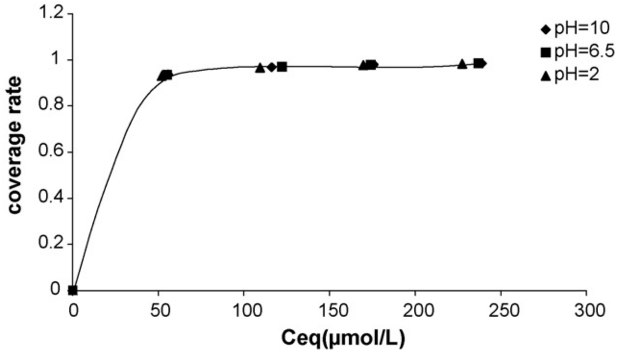


Fig. 4. Evolution of coverage rate as a function of Phe equilibrium concentration.

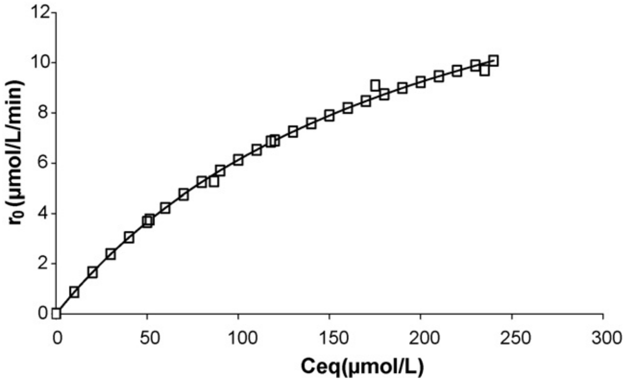


Fig. 3. Evolution of initial rate of disappearance of phenylalanine as a function of the concentration of phenylalanine remaining in solution (Ceq).

of TiO_2, that is to say 0.031 molecules/nm^2. As the Phe adsorption is not modelized by Langmuir equation, we can assume that a molecule of Phe is not adsorbed on one OH site but on several OH groups or that OH groups are not the adsorption site.

3.2. Phenylalanine disappearance

The complete disappearances of Phe in aqueous solutions at initial concentrations of 60, 90, 120, 181 and 240 µmol/L were obtained upon illumination at $\lambda > 340$ nm and a radiant flux Φ equals to 3.5 mW/cm^2 at 25, 35, 40, 50 and 55 min respectively (Fig. 2). The direct photolysis at $\lambda > 340$ nm was negligible indicating that disappearance observed in the presence of TiO_2 and UV at this wavelength is only due to photocatalytic process.

The initial rate of disappearance of phenylalanine is reported as a function of the concentration of phenylalanine remaining in solution (Ceq) (Fig. 3). Until a concentration of about 120 µmol/L, the initial rate is proportionnal to the Phe concentration in solution ($r = kK\text{Ceq}$). Then, the initial rate became independent of Phe concentration. This phenomenon is expected from a Langmuir–Hinshelwood type kinetic, $r = kKC/1 + KC$, since the product of the adsorption constant, K, by the concentration, cannot be neglected with respect to one in the denominator of r at higher concentrations.

From this curve we can determine the rate constant k and the adsorption constant K and determine the coverage rate ($\theta = KC/1 + KC$) under UV.

The values of k and K are respectively 0.38 µmol/min and 0.26 L/µmol. It is important to note that k is very important compared to the value determined at a concentration of 240 µmol/L whereas the disappearance rate is already nearly independent of the concentration and that coverage rate is near 100% (Fig. 4). In these conditions $k \approx r_0$ ($k \approx 0.2$ µmol/min).

This result shows that even if the form of the curve is similar to L–H model, the degradation of phenylalanine is not a kinetics of L–H as we could plan it by considering the adsorption of the phenylalanine in the dark. This result shows the importance to study the adsorption of pollutant in the dark to check that the adsorption obey to Langmuir model as recommended by Ohtani et al. [15]. However, we do not have to forget that under irradiation the surface of solids can be modified leading to the modifications of adsorption.

An interesting value in photocatalysis is the quantum yield (ρ). It is defined as the ratio of the initial rate (number of molecules transformed per second (r)) divided by the number of incident efficient photons absorbable by titania (φ_n) per second.

$$\rho = \frac{r}{\varphi_n}, \quad \varphi_n = \frac{(\Phi/E)S}{N_A}$$

with the radiant flux Φ in W cm^{-2} (J s^{-1} cm^{-2}), the radiant flux energy E in J photons^{-1}, N_A the Avogadro's number (N_A) and the surface of optical window S (19.6 cm^2).

In the experimental conditions the quantum yield increases until about 1.6%. At low concentration of Phe adsorbed on TiO_2, active species formed on TiO_2 surface cannot react and recombine leading to a lower quantum yield.

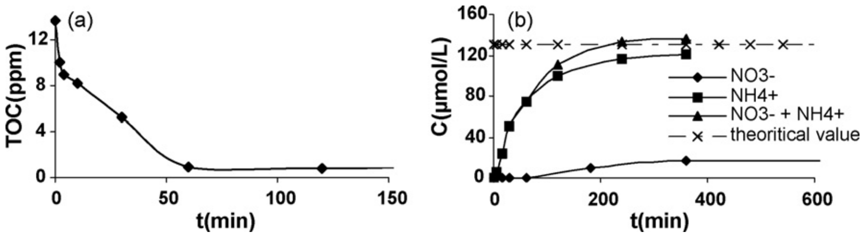
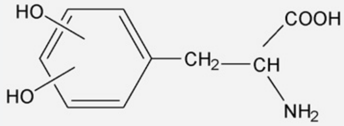
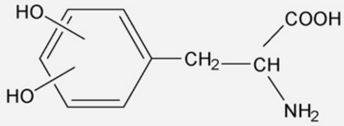
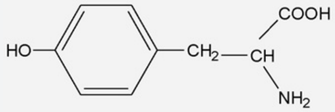
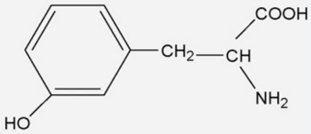
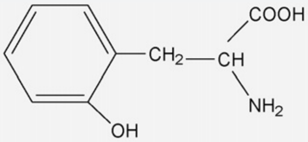
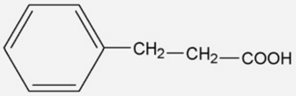


Fig. 5. TOC disappeared (a) and evolution of nitrate and ammonium (b) as a function of irradiation time.

Table 1
Structure of Phe by-products identified by LC–MS with electrospray (ES).

Compounds (*m*/*z*)	Fragments positive mode	Fragments negative mode	t_R (min)	Structure
A-197	198/159/152/119/104/97	(MS): 196 (MS/MS): 196/157	4.3	
B-197	198/159/152/119/104/97	(MS): 196 (MS/MS): 196/157	6.2	
C-181	(MS): 182/165/147/136/180 (MS/MS): 182/165/147/136/123/119/95/ 91	(MS): 180 (MS/MS): 182/163/119/93	6.8	
D-181	(MS): 182/136 (MS/MS): 182/136/91	(MS): 180 (MS/MS): 182/163/119	8.9	
E-181	(MS): 182/164/136 (MS/MS): 182/164/147/136/119/91	(MS): 180 (MS/MS): 180/186/119/107	11.9	
F-150	151/150/119/111/97		16.9	

3.3. *Mineralisation and transformation products*

Total mineralization is the ultimate step of the photocatalytic degradation of organic molecules. In order to quantify this process, total organic carbon (TOC) and the evolution of nitrate and ammonium ions are followed as a function of time.

The TOC disappearance (TOC measured) and the evolution of nitrate and ammonium are represented in Fig. 5.

TOC disappeared from the beginning of irradiation indicating initial decarboxylation reaction. After complete elimination of Phe (40 min), around 65% of the value of TOC expected from total mineralization was obtained and 1 h is necessary to mineralize about 95% of carbon. The presence of about 0.5 ppm of TOC at the end is not significant due to the precision of TOC measure. We can consider a total mineralization of carbon.

NH_4^+ ions appear from the beginning of the degradation and are the major one. The formation of nitrates occurred only after total disappearance of Phe indicating that nitrate ions are not primary oxidation by-products and come from intermediate compounds Fig. 5(b). After an irradiation time of 4 h, total mineralization of nitrogen was observed.

The more important formation of NH_4^+ ions is in agreement with the work of Hidaka et al. [17] on different amino acids and with our previous work [16]. Actually, oxidation degree of amine group and ammonium are both equal to +3. The formation of ammonium can be explained considering the reaction of e^- on protonated amine (in our pH conditions, more than 99% of Phe is present under amphoteric structure) as mentioned below and suggested by Möning et al. [19].

$$R-CH\begin{matrix}COO^-\\NH_3^+\end{matrix} + e^- \longrightarrow R-\overset{\circ}{C}H-COO^- + NH_3$$

The difference between Phe disappearance and its mineralization reflects the presence of several intermediate compounds during its oxidation.

Main intermediate products detected were identified by LC–MS and are listed in Table 1.

These different structures correspond to the following reactions:

(i) Hydroxylation on the aromatic ring (compounds C–E),
(ii) dihydroxylation (compounds A and B),
(iii) deamination of heterocycle (compound F).

No decarboxylation compound has been evidenced whereas the decarboxylation seems to be important regarding the evolution of TOC. The absence of decarboxylation products could be explained considering that amine intermediates formed could have important interaction with residual OH of the C18 column and not be eluted in our experimental conditions.

Five linear organic acids have also been identified i.e., oxalic, oxamic, lactic, acetic and propanoic acids. Lactic and oxamic appear

Table 2
Molecular fraction of different forms of phenylalanine.

Phenylalanine	R-CH-COOH NH_3^+	R-CH-COO- NH_3^+	R-CH-COO$^-$ NH_2
pH = 10	0%	14%	86%
pH = 6.5	0%	100%	0%
pH = 2	80%	20%	0%

from the beginning of degradation suggesting that they come from direct break of aliphatic chain. The three other acids are not primary intermediates.

3.4. Influence of pH

The pH influences both the surface state of titania and the ionized state of Phe (Table 2).

For pHs higher than the PZC (point zero charge) of titania, which is around 6.5 for TiO_2 Degussa P-25, the surface becomes negative charged. At pH < PZC the surface is positive charged according to the following equilibrium:

$$pH < PZC : Ti-OH + H^+ \Leftrightarrow TiOH_2{}^+,$$

$$pH > PZC : Ti-OH + OH^- \Leftrightarrow TiO^- + H_2O,$$

Considering the p*K*a values of Phe ($pKa_1 = 2.6$ and $pKa_2 = 9.2$) the percentage of molecular fraction of cationic, amphoteric and anionic forms are reported in Table 1 with three different pH values (pH = 2, 6.5 and 10).

It can be seen that the predominant forms are varied with three pH values.

3.4.1. Influence of pH on sorption isotherm

Firstly, we observed the evolution of Phe adsorbed on TiO_2 in the dark with three pH values as (Fig. 6). Even if the pH values are different, the forms of these curves suggest a multilayer adsorption.

The more important adsorption is observed at acid pH. At basic pH, the adsorption of phenylalanine is about 30% higher than this one found at neutral pH.

This behaviour is not understandable considering the surface state of titania and the ionization state of phenylalanine if we consider that phenylalanine adsorbed in the same way at three pH.

This behaviour could suggest that considering the pH of the solution, the part of phenylalanine adsorbed on TiO_2 could be different. At acid pH, the adsorption will be made mainly by carboxylic groups whereas at basic pH adsorption predominantly will occur by NH_2 groups.

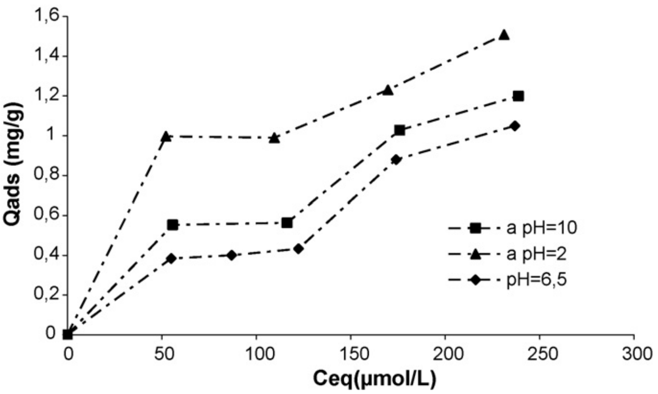


Fig. 6. Amount of phenylalanine adsorbed per gram of catalyst as a function of Phe concentration remaining in solution at the equilibrium.

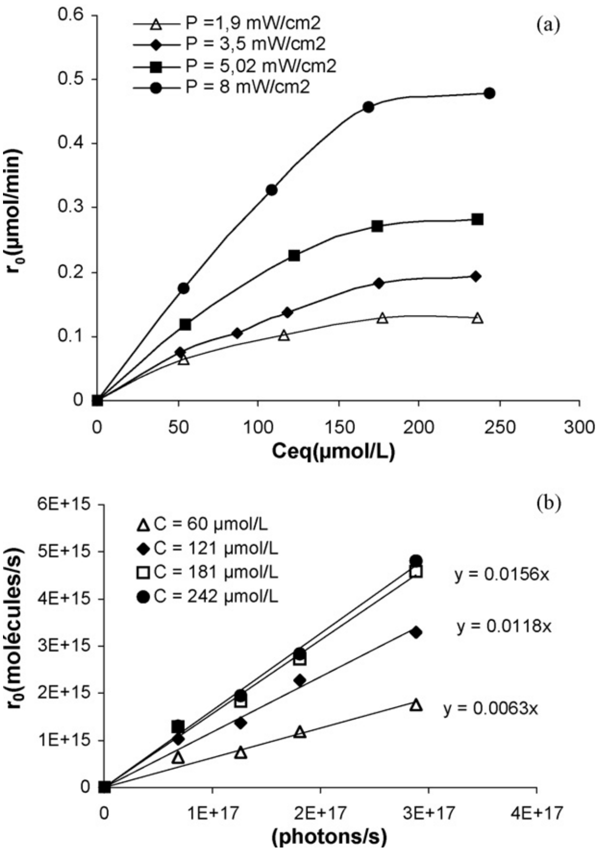


Fig. 7. Evolution of initial rate of Phe as a function of (a) Phe concentration and (b) radiant flux.

3.4.2. Influence of pH on the disappearance

Initial disappearance rates of Phe at acid, neutral and basic pH were determined at different initial concentration of phenylalanine. The order of reactivity of phenylalanine under three pH values is the following:

$$r_0(pH = 10) > r_0(pH = 2) > r_0(pH = 6.5)$$

Considering Table 1, Phe seems to be more easily degraded under anionic or cationic forms but not under amphoteric form.

It can be suggested that different types of mechanisms occur depending the ionic form of Phe. At acid pH $NH_3{}^+$ are reduced by e^- as proposed by Horikoshi et al. [18] whereas decarboxylation will be the main reaction at basic pH. Actually, decarboxylation reaction (photo-kolbe reaction) is favoured in the presence of carboxylate group which will be less important at acid pH. This hypothesis is in agreement with the work of Möning et al. [19].

$$R\text{–}COO^- + h^+ \rightarrow R^\circ + CO_2$$

Hydroxylation reactions should also be considered to explain the higher efficiency at basic pH.

$$OH^- \xrightarrow{h^+} OH^\circ$$

At acid pH the number of OH° should be lower due to the presence of hydronium ions favouring the presence of hole.

$$H_2O + h^+ \rightleftarrows OH^\circ + H^+$$

Considering these two types of reaction, we can explain the higher efficiency observed at basic pH. Actually, carboxylate group are present and the number of OH° will be more important.

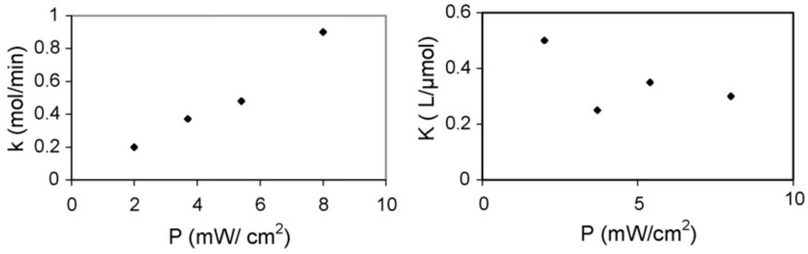


Fig. 8. Evolution of rate constant k and adsorption constant K as a function of radiant flux.

The hypothesis of a modification of the number of OH° radicals depending of the pH is in agreement with the quantification of hydroxylated compounds. Actually a more important concentration of hydroxylated compounds is formed at basic pH compared to this one detected at acid pH. However, it is at neutral pH that the more important amount of hydroxylated compounds is detected. This result could be explained considering repulsion between OH^- and the surface of TiO_2 which is negatively charged. However, carboxylate group should also repulse from TiO_2 surface leading to less decarboxylation reaction. More studies should be done to understand better this behaviour.

An other important point to underline is the absence of correlation between adsorption in the dark and disappearance. This result is in agreement with a modification of adsorption under UV light.

3.5. *Influence of radiant flux*

The effect of radiant flux has been studied by considering different concentrations of phenylalanine. The initial disappearance rate of Phe as a function of remaining concentration in solution (Fig. 7(a)) and a function of radiant flux (Fig. 7(b)).

Whatever the initial concentration of amino acid, a Langmuir–Hinshelwood curve can modelize the kinetic observed. At low Phe concentration the curve is linear and tends towards a plateau. The proportionality occurs when the Phe concentration is varied with the radiant flux.

This phenomenon can be explained by considering that the number of active species (e^-, h^+) formed increases as a function of radiant flux, but these species recombined themselves if no organic molecule is present to react.

From Langmuir–Hinshelwood curves, the value of rate constant k and adsorption constant K can be determined. These both values are represented as a function of radiant flux in Fig. 8. The rate constant proportionally increases with radiant flux while the opposite effect is observed on adsorption constant.

The proportionality observed between k and Φ means that the number of active species linearly increases with radiant flux, in other word that in our experimental conditions, photocatalytic regime occurs. This result can also be seen in Fig. 8(b).

The decrease of adsorption constant K by increasing radiant flux means that the rate of adsorption (K_{ads}) decreases or that desorption rate increases (K_{des}) under UV ($K = K_{ads}/K_{des}$).

$$\mathrm{Phe} + \mathrm{TiO_2} \xrightarrow{K_{ads}} \mathrm{Phe_{ads}}$$

with $r_{ads} = k_{ads}\,[\mathrm{Phe}]\,[\mathrm{TiO_2}]$

$$\mathrm{Phe_{ads}} \xrightarrow{Kdes} \mathrm{Phe} + \mathrm{TiO_2}$$

with $r_{des} = k_{des}\,[\mathrm{Phe_{ads}}]$

This result is in agreement with a modification of adsorption under UV underlined in Section 3.2.

From Fig. 8(b), it is interesting to notice that above 180 µmol/L, the slope r/Φ remains constant. This slope is directly proportional to quantum yield (ρ) which corresponds to the number of molecules of phenylalanine initially degraded divided per the number of photons absorbed during the same time. In our experimental conditions, the concentration of TiO_2 used allows to absorb all photons emitted.

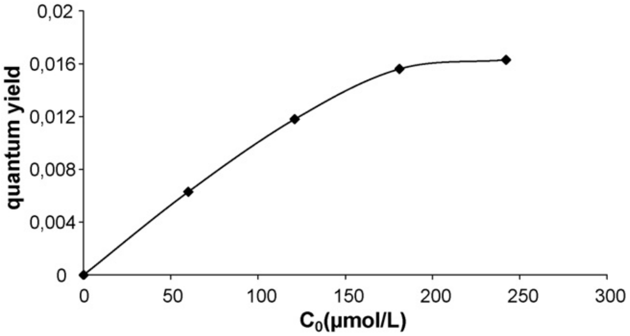


Fig. 9. Quantum yield as a function of initial concentration of phenylalanine.

$$\frac{r}{\Phi} = \frac{S}{N_A E} \times \rho$$

With the radiant flux Φ in W cm^{-2} (J s^{-1} cm^{-2}), the radiant flux energy E in J photons^{-1}, the Avogadro's number (N_A), the surface of optical window (S) and the quantum yield (ρ).

The evolution of the quantum yield as a function of initial concentration at different radiant flux is represented on Fig. 9. The maximal quantum yield obtained is 1.6%, it means that if the reaction is performed under a higher initial concentration or radiant flux, in 1 s, the maximum of molecules degraded by 100 photons emitted will be 1.6. This result is very important to the industrialisation of the process because the percentage of degradation can be estimated. From this figure it can be seen that the quantum yield increases as a function of Phe concentration before reaching a plateau indicating that recombination of (e^-, h^+) pairs is more important.

4. Conclusions

In spite of a multilayer adsorption of phenylalanine in the dark, the effect of initial concentration of phenylalanine on its photocatalytic degradation seems to be modelized by Langmuir–Hinshelwood model. However, the rate constant found by using this model is too important compared to the experimental value. This behaviour shows that this mathematical model must be used with caution and that kinetic of adsorption in the dark has to be considered, although it can be suggested a modification of adsorption site under UV.

The study of mineralization of carbon and heteroatom show that a total mineralization seems to be obtained after 4 h and that ammonium ions are the major inorganic ions formed. Six aromatic products were identified by LC–MS techniques corresponding to mono-, di-hydroxylated compounds and to deamination. Five linear organic acids are also identified by LC–UV analysis.

Whatever the pH, a multilayer adsorption is observed. In the dark, adsorption is more important in acid solution, while basic solution favour the degradation under UV. This result suggests that the degradation mechanism could differ depending on pH. Actually, first the presence of carboxylate group at basic pH should favour the decarboxylation by photo-Kolbe reaction, and secondly the number of OH° should be lower at acid pH due to the presence of hydrogen ions favouring the presence of hole. This last hypothesis is in a good agreement with the effect of pH on the formation of hydroxylated compounds.

The study of the effect of radiant flux allowed us to determine the maximal quantum yield which can be reached, 1.6% for this amino acid. This value is very important for dimensioning the reactor. Our results also underlined that at low coverage of TiO_2 surface, the quantum yield is lower, showing the important part of recombination of active species.

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