The styrene photocatalytic degradation reaction
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The styrene photocatalytic degradation reaction

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Abstract

In this study the aqueous styrene photocatalytic degradation reaction was evaluated using TiO_2 P-25 (Degussa) as catalyst. The experiments were accomplished in a batch reactor, with temperature control and catalyst in suspension. The radiation source was a 28 W UV lamp. Determinations of styrene concentrations were done by gas chromatography with a flame ionization detector (FID). Preliminary tests were made to determine the necessary contact time to reach the adsorption equilibrium. Besides, seeking to separate the photolysis of the photocatalysis, experiments were made in which the solution was irradiated with and without TiO_2 and also in the presence of TiO_2 but without irradiation. Then the effects of the styrene initial concentration were evaluated, as well as, the catalyst concentration, the hydrogen peroxide addition and the initial pH of the solution. The experimental results showed that styrene can be degraded by photocatalysis and, in 90 min, 95 % of degradation was achieved. It was verified that the styrene degradation rate can be approached by a pseudo-first-order kinetics for styrene initial concentrations from 15.27 to 57.25 ppm, at 30°C. Besides, the addition of H_2O_2 accelerates the degradation reaction until it reaches a certain optimum peroxide concentration in the reactor. Further H_2O_2 additions resulted in reaction rate reduction.

Keywords: Photocatalysis, Styrene, Batch Reactor

1. Introduction

The water sources contamination is one of the great problems of modern society and the wastewaters contaminated by organic molecules worsen the situation due to its toxicity.

The traditional techniques of wastewater treatment which are based on physical-chemical processes promote the pollutants phase transfer. Their product is a phase in

which the pollutant is concentrate and whose total volume is significantly smaller than the volume of the polluted current. However, there is no destruction of pollutant and the most concentrated phase should be disposed somehow in the human environment. Alternatives that take the complete degradation of the pollutants are needed to solve the problem definitively.

Then the "Advanced Oxidation Processes" (AOPs) are of great interest because they are more sustainable. AOPs are based on formation of the radical, highly oxidizer agent. Among AOPs, photocatalysis is a promising process that is being studied a lot lately (Gogate, Prandit, 2004; Pera-Titus *et al.,* 2004; Pirkanniemi, Sillanpää, 2002; Dijkstra *et al.,* 2001; Zhang *et al.,* 1998).

Styrene is found among the organic pollutants. It is produced starting from the dehydrogenization of ethylbenzene and its main use is in the polystyrene production and in the production of plastic, rubber, resins, and insulators. It is classified as a mutagen and potentially carcinogenic. This toxicant also has a detrimental effect on wildlife and marine organisms (Gibbs, Mulligan, 1997).

In this study, the photocatalytic degradation of styrene has been investigated using TiO_2 as catalyst. The goals were: (i) to evaluate the kinetics of styrene disappearance, (ii) to examine the effect of several parameters such as catalyst mass, styrene initial concentration, the oxidants addition and pH change.
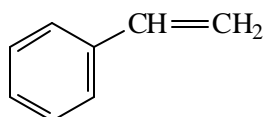

Figure 1: Styrene chemistry structure.

It was not found in the open literature work that is specifically about styrene photocatalytic degradation. Many studies, however, were found about the photocatalytic degradation of aromatic compounds, such as benzene (Hsien *et al.,* 2001; Park, Choi, 2005), phenol (Machado, Santana, 2005; Barakat, Tseng, Huang, 2005; Kanki *et al.,* 2005) and ethylbenzene (Vidal *et al.,* 1994).

2. Experimental

2.1. Material

Titanium dioxide P-25 (Degussa) was used as catalyst. It contains mainly anatase, specific surface area of 50 $m^2\,g^{-1}$ and particle size of 30 nm. The reactant styrene was kindly given for the Innova Petroquímica Company. HCl and NaOH were used to adjust the pH. The water used to solutions and to glaze wash was previously distilled.

2.2. Apparatus

The bath photocatalytic reactor used in the experiments was made of glass, in a cylindrical shape, with a 13 cm height and a 10 cm inner diameter, resulting in a 1.000 mL of useful volume. It was provided with a shirt for water circulation.

There is a lamp support in this reactor and the lamp position was fixed so that the distance between the lamp and the solution surface were 2 cm, without variation from one experiment to another. The photocatalytic reactor can be seen in Figure 2.

An aluminum leaf cone was fixed in the support. The purpose of covering was isolating the reactor from external light as well as avoiding the UV radiation emission from the exterior. The lateral side and the bottom of the reactor were also covered with aluminum leaf. In order to avoid the styrene mass transfer to the vapor phase, the reactor was covered with a PVC film.
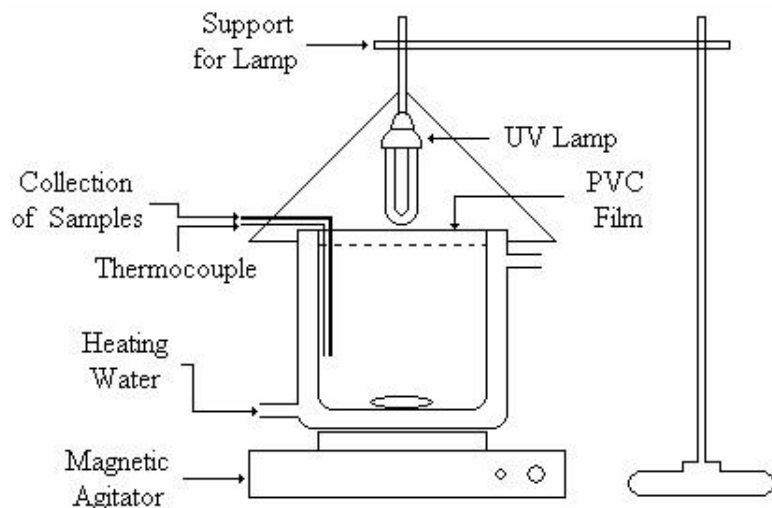

Figure 2: Photocatalytic reactor used in experiments.

To evaluate the possible PVC film influence in the incident radiation on the reactor surface, the used film to forbid the reactor was analyzed being measured its transmittance. It was observed that for the wave length of 365 nm the film reduces the transmittance in 12.9% approximately.

A 28 W UV lamp (Trilux G-Light) was the radiation source used, it emits between 320 and 400 nm, with a maximum of 365 nm, optimum for TiO_2 (Zhao *et al.,* 1998).

2.3. Procedure

The solutions samples were prepared and maintained under agitation for 8 h. The reactor was carried, isolated with the PVC film and maintained in dark operation (without the UV irradiation) during 40 min so that, the equilibrium regarding the

adsorption of organic molecules by catalyst was reached. The experiments were accomplished under agitation and constant temperature. Before each experiment, the lamp was preheated for 30 min to obtain a constant light intensity during the tests. The samples collections were made by syringe and the same ones were centrifuged for catalyst removal. A 2 ml aliquot was collected with 0, 15, 30, 60, 90 min of reaction. The solution initial volume, considered approximately constant, was 900 ml.

2.4. Analysis

The styrene concentration was monitored using a gas chromatograph (Auto System XL, Perkin-Elmer) equipped with a flame ionization detector (FID) and a PE1 capillary column (30 m x 0.53 mm) and 1.5 µm film thickness (dimethylpolysiloxane) (Perkin-Elmer elite series). It operated in the following conditions: injector temperature: 150°C; detector temperature: 180°C; column temperature: 120°C; helium as a carrier gas at a flow rate of 4 ml min^{-1} and a retention time of 6 min. The injection volume was 1 µL (splitless injection). The styrene quantification was made using calibration curves.

The intermediates were analyzed by a gas chromatograph (6890 Model, Agilent) coupled to a mass selective detector (5973 Model, Agilent). The GC column was a HP-5MS (30 m x 0.25 mm) and 0.25 µm film thickness. Total organic carbon (TOC) was analyzed by a StarTOC Benchtop TOC analyzer (Star Instruments Inc.). The influence of the PVC film in the incident radiation on the reactor surface was analyzed by a UV-vis spectrophotometer (VARIAN Cary 300®).

The radiant flux of the UV source was determined by a digital radiometer model EW-09811-50 Cole-Parmer Instruments Co. (half bandwidth of 12 nm ± 2 and accuracy 5%).

2.5. Adsorption test

Adsorption experiments were made with styrene solutions at different pH values. A 900 ml aqueous styrene solution was mixed with 0.55g L^{-1} of TiO_2 for 90 min at 30°C, using a bath reactor with magnetic agitation. To avoid the TiO_2 photoreaction, the solutions were kept in the dark during the experiments. The samples were centrifuged to separate the catalyst after collected. Gaseous chromatography was used in order to determine the styrene concentration in liquid samples. The amount of styrene adsorbed on the catalyst surface was calculated by mass balance.

3. Results and Discussion

Several preliminary experiments were accomplishing before initiating styrene photocatalytic degradation tests and they will be explained in first place.

3.1. Calibration curves

The calibration curves were prepared for a concentration range of (0 - 50) mg L^{-1}. This curve points corresponds to the four areas average obtained for the same

standard solution. The obtained equation was a straight line $(A = 51.181C + 2.7333)$ with correlation coefficient 0.9999, in agreement with the EPA specifications (EPA, 1996). "A" represents the measured area for the chromatograph in arbitrary units and "C " the styrene concentration $(mg\ L^{-1})$ in this equation.

3.2. Adsorption

The adsorption tests were carried out in the dark in order to determine the minimum styrene - catalyst contact time that guarantees the adsorption equilibrium in the catalyst surface, at different pH values. This test was important to ensure that when initiating the reaction, by lamp activating, the disappearance of styrene was due to photocatalytic degradation. The tests results are shown in Figure 3.
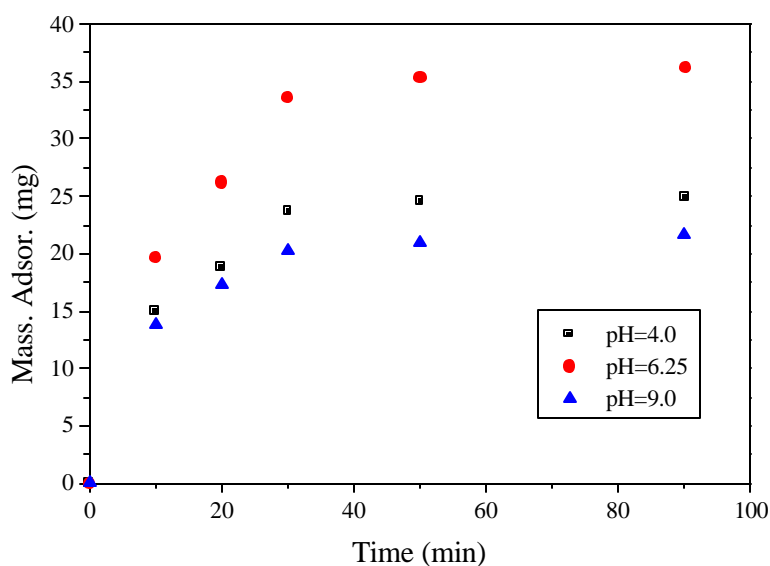

Figure 3: Styrene adsorption on TiO_2 surface.

The styrene is adsorbed on the TiO_2 surface and the adsorption equilibrium is reached in 40 min. The equilibrium concentration of the styrene solution was determined after adsorption, and the initial concentration of styrene for kinetic analysis was taken. The pH effect is discussed latter in this work.

3.3. Styrene loss for the environment

In spite of the reactor have been covered with PVC film in all experiments, it was necessary to evaluate the styrene amount lost to the atmosphere in the tests conditions. So, five tests were carried out without TiO_2 and UV light. The reactor was maintained in operation standard conditions (T, pH, rpm). It was observed that the styrene loss to the environment is a reproductive phenomenon and can be represented by a straight line: $Ln\ (C/Co) = 0.0079\ t + 0.0222$, with correlation coefficient of 0.9919. "Co" is the styrene initial concentration and "t" the time (min), in this equation.

3.4. Styrene degradation

Standard experiments were carried out with and without TiO_2 and with TiO_2 but without irradiation. Figure 4 shows that non-appreciable styrene photodegradation occur in 90 min of irradiation without TiO_2 (photolysis). The same happens with TiO_2 but without irradiation (loss for the environmental). When the styrene solution mixed with TiO_2 was exposed to the UV radiation, a fast decrease in the concentration happened.
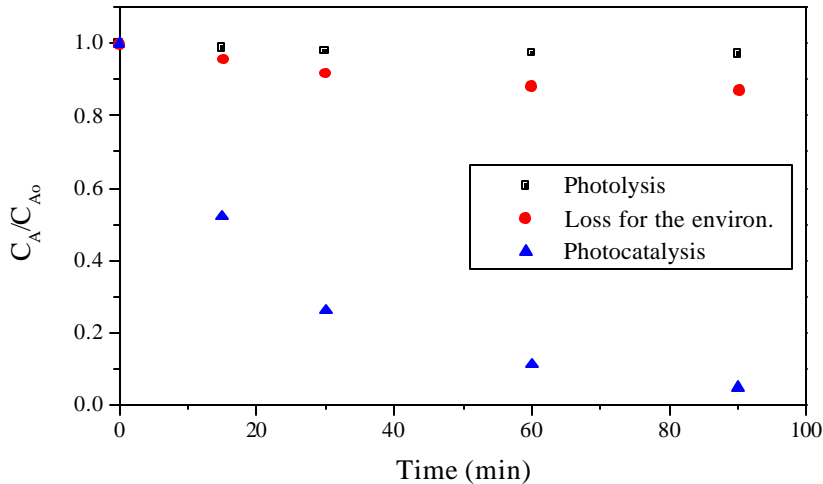

Figure 4: Styrene degradation in the absence of TiO_2 or UV light.

Figure 5 shows the styrene concentration variation due to the photocatalytic reaction. It reaches 22.7 mg L^{-1} in 90 min, which corresponds to 95 % degradation for an initial concentration of 24.2 mg L^{-1}. The styrene concentration reached the GC detection limit in 180 min, corresponding, to approximately 10^{-3} mg L^{-1}.
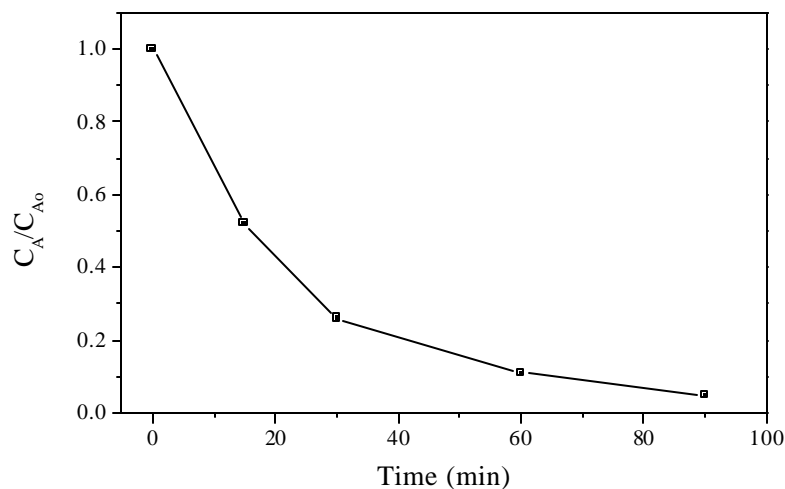

Figure 5: Styrene concentration variation with the irradiation time (T = 30°C, pH = 6.0 and C_{cat} = 0.55 g L^{-1}).

Figure 6 shows the linear fit between $\ln(Co/C)$ and the irradiation time. In this Figure, "Co" represents the initial concentration of styrene and "C" its instantaneous concentration. In this graph a 0.9858 correlation coefficient can be observed and thus the photodegradation reaction can be approximated by a pseudo first-order kinetics, when the styrene initial concentration is 25 mg L^{-1}.
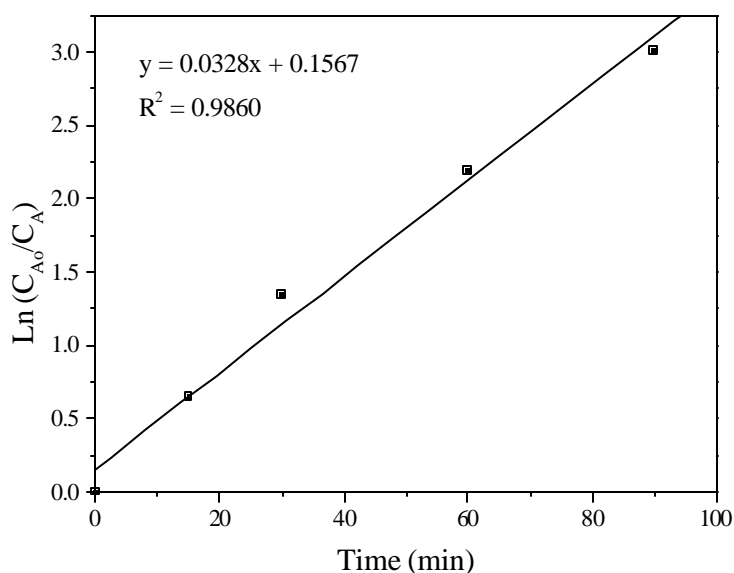

$$y = 0.0328x + 0.1567$$
$$R^2 = 0.9860$$

Figure 6: Relationship between $\ln(Co/C)$ and the irradiation time.

A detailed analysis of Figure 6 reveals, however, that it is possible to trace two straight lines with different inclinations using these same points: the first between 0 and 30 min and the second between 30 and 90 min, each one of them with superior correlation coefficient to the straight line that passes by all these points. Similar behavior was observed in all experiments. The considered most representative rate of styrene photodegradation reactions was that obtained for the first 30 min because after this there could be interference of the intermediary(ies) product(s) formed. This procedure allows us to determine a pseudo-first-order apparent constant of 0.0445 min^{-1}.

3.5. Effect of initial styrene concentration

The styrene initial concentration effect (15.3 - 57.3 mgL^{-1}) was evaluated. The results are presented in Figure 7, which shows the normalized concentration against irradiation time for several styrene initial concentration.

It may be seen that increasing styrene concentration decreases the degradation rate. Similar results have been presented for the photocatalytic oxidation of other organic compounds (Dijkstra *et al.,* 2001; Peiró *et al.,* 2001; Gautam *et al.,* 2005). According to Ishiki *et al.* (2005) it may be duo to the fixed active site number in the TiO$_2$/H$_2$O interface. Thus, at low styrene concentrations, a larger number of water molecules

will be adsorbed on the available TiO_2 particles producing hydroxyl radicals and leading to a rapid oxidation process. On the other hand, at higher styrene concentrations there is a lesser proportion between water molecules and free active sites because the number of active sites remains the same. Consequently, competitive adsorption between the styrene and water molecules increases and leads to a decrease of the degradation rate.
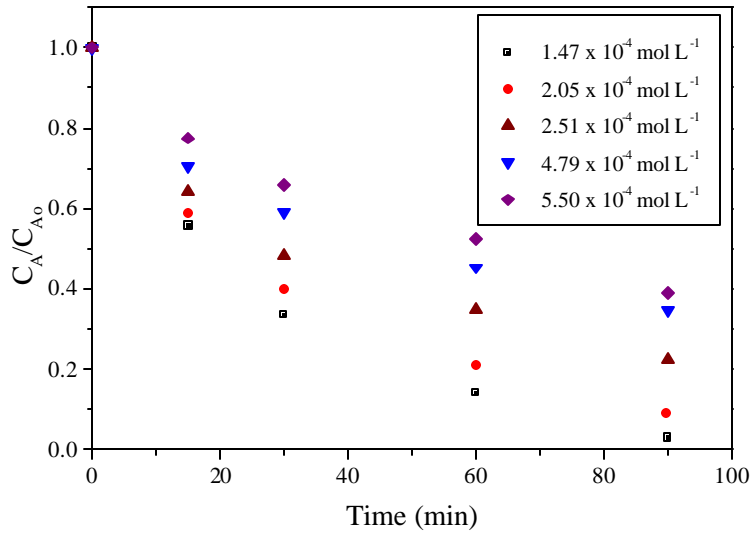

Figure 7: The effect of styrene initial concentration on the photodegradation rate (T = 30°C, pH = 6.0 and C_{cat} = 0.55 g L^{-1}).

The Langmuir-Hinshelwood rate expression (Equação1) has been successfully used for describe relationship between heterogeneous photocatalyst degradation rate and the initial pollutant concentration (Vidal *et al.,* 1994; Chen, Ray, 1998; Evgenidou, Fytianos, Poulios, 2005).

$$r = \frac{k.K.C_A}{1 + K.C_A} \tag{1}$$

In this equation, "C_A" is the instantaneous pollutant concentration at time "t", "K" is the constant of adsorption at equilibrium and "k" is the reaction constant kinetics. For diluted solutions ($C_A < 10^{-3}$M), KC_A becomes much smaller than 1 and the reaction is apparent first order (Herrmann, 2005). A lineal form of the Langmuir-Hinshelwood (Equation 2) can be represented as showed in Figure 8.

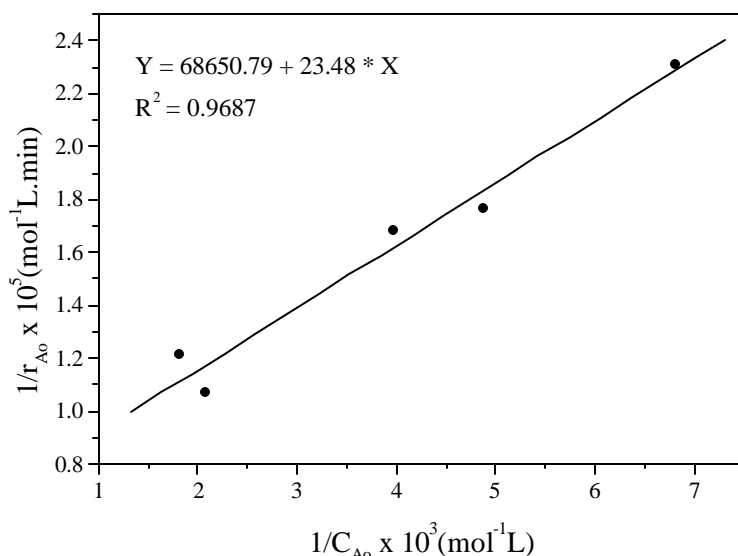$$\frac{1}{r_o} = \frac{1}{k} + \frac{1}{k.K} \cdot \frac{1}{C_A} \tag{2}$$

Figure 8: The reciprocal of degradation rate versus the styrene initial concentration reciprocal (C_{cat} = 0.55 g L^{-1}, pH = 6.0, T = 30°C).

A reasonable adjustment was obtained for experimental results to Equation 2, with values of 1.46 x 10^{-5} mol L^{-1} min^{-1} and 2.92 x 10^3 mol^{-1} L for k and K, respectively. This indicates that the Langmuir-Hinshelwood expression can describe the photodegradation rate of styrene.

In the conditions which the experiments were accomplished, the apparent pseudo-first-order constant (0.0445 min^{-1}) is actually the multiplication between the adsorption constant and the kinetic constant, as Equation 1 shows. If the constants obtained with Figure 8 aid are multiplied, a 0.0425 min^{-1} value is reach. The likeness among these values checks the good quality of experimental results.

3.6. Effect of catalyst concentration

The effect of catalyst concentration in the mixture can be visualized in Figure 9, which presents values of the pseudo-first-order apparent kinetic constant for several initial catalyst concentrations. In Figure 9 it is observed that the reaction constant kinetics increases with the catalyst concentration increment from 0.11 to 0.55g L^{-1}; after that these value decreases.
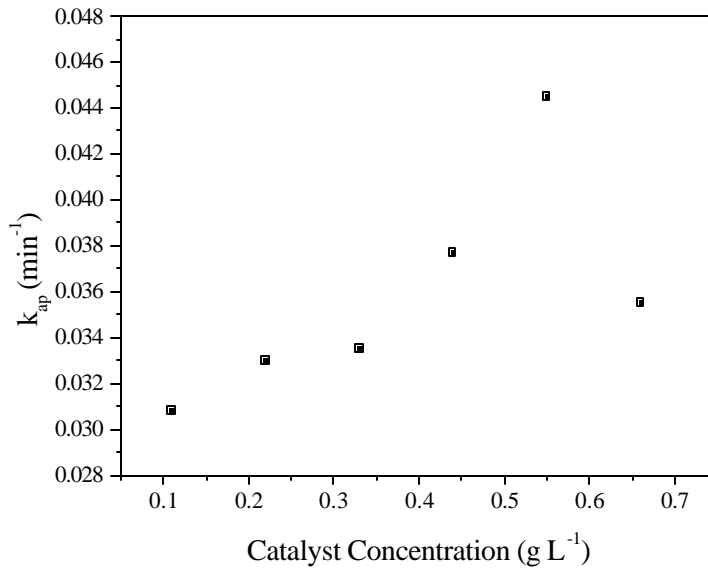
Figure 9: Apparent kinetics constant variation with the catalyst concentration (T = 30°C and pH = 6.0).

Similar behavior was observed by several authors for different pollutants (Dijkstra *et al.,* 2001; Barakat, Tseng, Huang, 2005; Gogate, Mujumdar, Prandit, 2002; Andreozzi, Caprio, Insola, 2000). With the increased amount of catalyst, the number of photons absorbed and the number of molecules adsorbed also increased due to an increase in the number of TiO_2 particles. The density of particles in the area of illumination also increases and thus the degradation rate also increases. However, a further catalyst concentration increase implies that some photocatalyst particles may not receive enough energy to start the styrene oxidation. Gogate and Prandit (2004) attributed this behavior to the increase in opacity, which leads to a decrease in the passage of irradiation through the reactor.

In catalyst high concentrations particle aggregation may also happen, reducing the interface area between substratum and catalyst, causing a decrease in the number of surface active sites and consequently decreasing the photodegradation efficiency (Chen, Ray, 1998; Muruganandham, Swaminathan, 2006).

3.7. Effect of initial pH

The efficiency of the photocatalytic degradation is affected by the TiO_2 surface properties, the molecules charge and the hydroxyls radical concentration. These properties are dependents of pH.

The effect of the pH on the styrene photocatalytic degradation was evaluated in this study. Figure 10 shows the pseudo-first order apparent constants kinetic values for several initial pH.
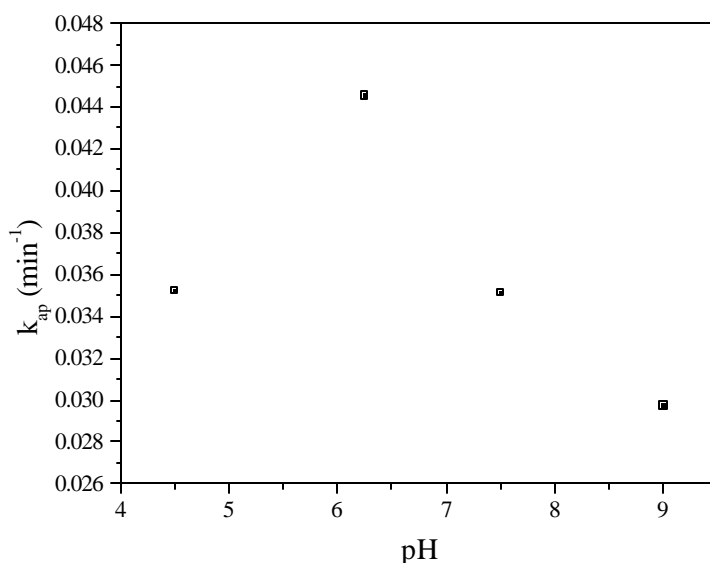
Figure 10: Effect of initial pH on the styrene degradation rate constant (C_{Ao} = 25 mg L^{-1}, Ccat = 0.55 g L^{-1}, T = 30°C.

Electrostatic attraction or repulse between the catalyst's surface and the organic molecule depends on the ionic form of the organic compound (anionic or cationic) and of the surface charge (Evgenidou, Fytianos, Poulios, 2005). The electric charge of a solid surface in an aqueous solution is determinate by the Zero Point Charge (ZPC). At pH values lower than ZPC the catalyst's surface is positively charged and at higher pH values it is negatively charged. The TiO$_2$ catalyst (Degussa P25) ZPC is pH 6.8 (Zhang *et al.,* 1998; Konstantinou, Albanis, 2004; Guillard *et al.,* 2003).

It may be observed in Figure 10 that the reaction presented a maximum degradation rate for pH 6.0 (natural pH). At pH 6.0 the TiO$_2$ surface is with low charge (near ZPC), a situation in which molecules probably reach its surface more easily, being the adsorption of the pollutant, and consequently the degradation rate, in its maximum value (Evgenidou, Fytianos, Poulios, 2005; Subramanian, Pangarkar, Beenackers, 2000).

At acid pH (4.0) the adsorption is relatively low. This is due to (i) at low pH values, the TiO2 particle agglomeration reduces the styrene adsorption as well as photon absorption, (ii) at low pH the TiO$_2$ surface is positively charged (TiOH$_2^+$) and when the pH is adjusted with HCl, as in this study, the Cl$^-$ anions are also adsorbed and there is competition between the anions adsorption and the styrene molecules.

On the other hand, in basic pH, the TiO$_2$ surface is negatively charged (TiO$^-$), and the Na$^+$ ions adsorption competes with organic molecule adsorption. Moreover, in the alkaline solution there is repulsion between the negative charged surface of photocatalyst and the hydroxide anions. This fact could prevent the formation of and thus decrease the photooxidation (Konstantinou, Albanis, 2004).

3.8. Effect of H_2O_2 addition

The major energy wasting step in the photocatalytic reaction is the electron-hole recombination. The prevention of this recombination is achieved by adding a proper electron donor or an acceptor to the system. Usually molecular oxygen and hydrogen peroxide are used as electrons acceptors in heterogeneous photocatalysed reactions.

 In order to investigate the effect of H_2O_2 addition in styrene photodegradation, experiments with several H_2O_2 concentrations (1.93; 3.86; 5.79; 7.72; 9.65 mmol L^{-1}) were made. The results are presented in Figure 11. It may be observed that the degradation rate pass by a maximum and optimum peroxide concentration is 5.8 mmol L^{-1}.
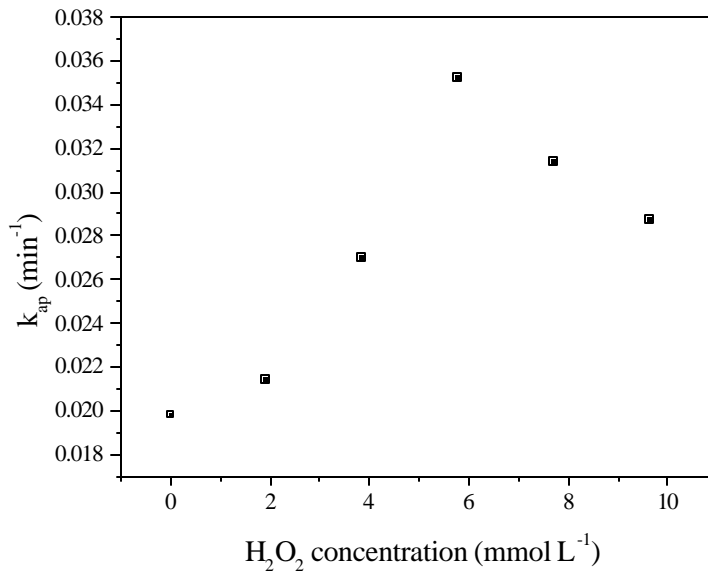

Figure 11: Effect of H_2O_2 on the styrene degradation rate (C_{cat} = 0.55 g L^{-1}, T = 30°C).

The addition of hydrogen peroxide increases the radicals concentration by the direct H_2O_2 photolysis, as showed in Equation (3). Besides, (Ollis, Serpone, Pelizzetti, 1991), proposed another mechanism, where the H_2O_2 is considered a better electron acceptor than oxygen, as showed in Equation (4).

$$H_2O_2 + hv \rightarrow 2HO^\bullet \tag{3}$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + HO^\bullet \tag{4}$$

Therefore, the photocatalytic degradation rate is expected be increase with the elevation of the amount of H_2O_2 added to the system. However, H_2O_2 great amount decreases the rate of degradation. This negative effect of a high H_2O_2 concentration may be due to the formation of $HO_2^\bullet$, that is significantly less reactive than the $HO^\bullet$ (Senthilkumaar, Porkodi, 2005). The excess of H_2O_2 molecules on the catalyst surface

also acts as a powerful scavenger of radicals (Evgenidou, Fytianos, Poulios, 2005; Galindo, Jacques, Kalt, 2001), as showed in Equations (5) and (6). The competition for the adsorption between the styrene and hydrogen peroxide as observed by (Hachem *et al.,* 2001; Malato *et al.,* 1998), still happens.

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \tag{5}$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + HO^{\bullet} \tag{6}$$

3.9. Detection of intermediates

Chromatographic analysis of a sample collected during the styrene photocatalytic degradation revealed the benzaldehyde presence as intermediate (Figure 12).
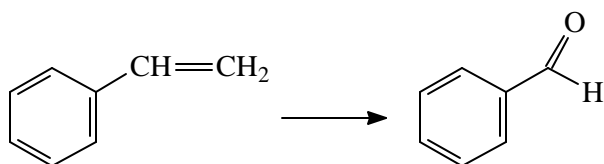

Figure 12: Benzaldehyde formation during the styrene degradation.

Styrene clearly offers two main possibilities to hydroxyl radicals attack: the ring or the double bond in the side chain. Those reactions involve eletrophilic substitution in the aromatic ring or free-radical substitution in the side chain (Morrison, Boyd, 1983). Benzaldehyde formation in relatively great amount evidences the preferential attack by radical in the styrene side chain molecule.

Experiments were carried out in order to analyze, simultaneously, styrene concentration, benzaldehyde concentration and total organic carbon (TOC). The results, which are presented in Figure 13, were used to do a mass balance, and CO_2 formed during reaction was calculated, as can be seeing in Table 1.
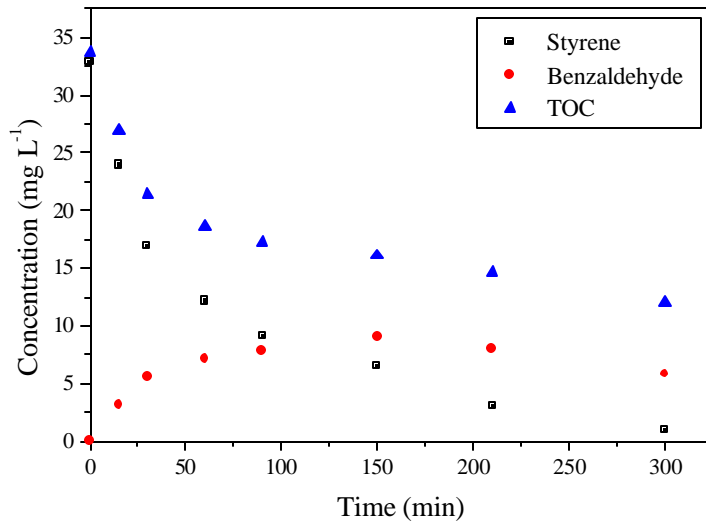
Figure 13: Total organic carbon and benzaldehyde formation during the styrene photocatalytic degradation (C_{Ao} = 32.9 mg L^{-1}, T = 30ºC, pH = 6.25, Ccat = 0.55 g L^{-1} e radiant flux = 3.8 mW cm^{-2}).

Column V in Table 1 presents the carbon balance {$TOC_{(t)} - [C_{(t) \text{ in styrene}} + C_{(t) \text{ in benzaldehyde}}]$}. Its non null results reveal the formation of not identified molecules, which are present in significant amount starting from 90 min reaction. It is possible to infer that these molecules are products of benzaldehyde photodegradetion, because they only appears when a significant amount of benzaldeyde exists. The column VII presents the difference [$TOC_{(t=0)} - TOC_{(t)}$], indicating the formed CO_2 amount.

Table 1: Carbon mass balance results.

I	II	III	IV	V	VI	VII
Time (min)	Carbon in styrene (gmol L^{-1})	Carbon in benzaldehyde (gmol L^{-1})	TOC (gmol L^{-1})	Carbon in molecules not identified (gmol L^{-1})	Carbon % in molecules not identified	CO_2 concentration (gmol L^{-1})
0	2.53×10^{-3}	0	2.53×10^{-3}	≈0	≈0	0
15	1.84×10^{-3}	2.03×10^{-4}	2.03×10^{-3}	≈0	≈0	5.02×10^{-4}
30	1.30×10^{-3}	3.64×10^{-4}	1.61×10^{-3}	≈0	≈0	9.21×10^{-4}
60	9.38×10^{-4}	4.71×10^{-4}	1.40×10^{-3}	≈0	≈0	1.13×10^{-3}
90	6.99×10^{-4}	5.14×10^{-4}	1.29×10^{-3}	8.20×10^{-5}	6.339	1.23×10^{-3}
150	5.03×10^{-4}	5.95×10^{-4}	1.21×10^{-3}	1.11×10^{-4}	9.208	1.32×10^{-3}
210	2.32×10^{-4}	5.24×10^{-4}	1.10×10^{-3}	3.42×10^{-4}	31.169	1.43×10^{-3}
300	7.21×10^{-5}	3.86×10^{-4}	9.08×10^{-4}	4.50×10^{-4}	49.549	1.62×10^{-3}

4. Conclusions

The styrene photocatalytic degradation in an aqueous solution was studied in a bath slurry reactor irradiated with a UV light source, using titanium dioxide (TiO_2) catalyst. It can be concluded that:

- in this study conditions the styrene degradation is a photocatalysed process, because styrene concentration reduction was not observed without catalyst or radiation;

- the adsorption equilibrium is reached in 40 min for three tested pH values (4.0, 6.25, 9.0). Besides, the amount of adsorbed styrene depends on the solution pH. In this case, the adsorption maximum happened in pH 6.25;

 - the styrene degradation kinetics can be approached by a pseudo-first order model. When T = 30°C, pH = 6.25, C_{cat} = 0.55 g L^{-1} and C_{Ao} ~ 25 mg L^{-1}, the pseudo-first order kinetic constant is 0.0445 min^{-1};

- the reaction rate is dependent of styrene initial concentration, TiO_2 concentration , pH, and H_2O_2 concentration. The styrene degradation rate decreases with the increase of its initial concentration and it increases with the increment of catalyst concentration until reach a maximum of 0.55 g L^{-1}. Besides, the degradation rate is maximum when pH is about 6.25 and H_2O_2 concentration is 5.8 mmol L^{-1};

- styrene photocatalytic reaction rate is pseudo-first-order according to Langmuir-Hinshelwood kinetic model. The kinetic constant (k) and adsorption constant (K) are 1.46 x 10-5 mol L^{-1} min-1 and 2.92 x 10^3 L mol^{-1}, respectively;

- CG-MS results revealed the benzaldehyde formation during the styrene photocatalytic degradation;

- the carbon balance indicated that, at least, one unknown organic molecule is formed, being detected after 90 min reaction time.

Nomenclature

C_A instantaneous pollutant concentration
C_{Ao} instantaneous pollutant concentration at t = 0
C_{cat} catalyst concentration
$C_{(t)}$ carbon moles at t
K   constant of adsorption at equilibrium
k   reaction constant kinetics
t   time
T   temperature
$TOC_{(t)}$ total organic carbon at t

5. Acknowledgment

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