

THE DEGRADATION OF PHENOL IN WATER SOLUTION BY TiO₂ PHOTOCATALYSIS IN A HELICAL REACTOR

N.A. LAOUFI*
D. TASSALIT
F. BENTAHAR

*Université des Sciences et de la Technologie
Houari Boumediène
Faculté de Génie Mécanique et de Génie des Procédés
Département de Cryogénie et de Génie Chimique. Laboratoire
des Phénomènes de Transfert
Bp 32, El Alia, 16111 Bab Ezzouar, Algeria*

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*to whom all correspondence should be addressed:
Fax: 0021321672897; e-mail: nadialaoufi@yahoo.fr

ABSTRACT

Heterogeneous photocatalysis is an advanced oxidation process (AOP) which has been widely studied by numerous researchers in the world and is used to degrade or remove a wide range of pollutants in water and air.

The photocatalytic oxidation and mineralization of phenol in aqueous catalyst suspensions of titanium dioxide (TiO₂) Degussa P25 (80% anatase, 20% rutile) has been carried out in a helical reactor. The photodegradation was investigated using two kinds of high pressure mercury irradiation lamps one emitting at 254 nm (15 Watts) and the other emitting at 365 nm (400 Watts). The effects of the recirculation flow, source of withdrawal, initial phenol concentration, amount of catalyst, suspension pH and light intensity on photodegradation of phenol were investigated. These parameters were studied to find the optimal conditions for a complete and fast oxidation of this organic compound.

Kinetic experiments were performed at 32 °C over a range of phenol concentrations from 2.5 to 25 mg l⁻¹, a range of TiO₂ concentrations from 0.1 to 1 g l⁻¹, a range of suspensions pH from 3 to 9. The helical reactor was operated under a continuous flow-mode.

Results showed that photodegradation is an effective method for the removal of phenol from wastewaters. The efficiency of the process depends strongly on the experimental conditions. The amount of catalyst, UV irradiation time, pH and light intensity were important parameters in the degradation process. The rate constants for the different parameters (TiO₂, phenol concentration) were evaluated. Kinetic studies showed that titanium dioxide photocatalyst P25 was very active in phenol degradation; we observed that 99% of pollutant was degraded after 6 hours of UV irradiation; furthermore, we observed that phenol degradation was more effective under acidic conditions than alkaline. The kinetics were described by the Langmuir-Hinshelwood (L-H) kinetic model. An overall pseudo-first order kinetic constant has been calculated for phenol conversion and values obtained in acidic pH are higher than those calculated for basic pH media.

KEYWORDS: Degradation, AOP, Photocatalysis, Phenol, Catalyst, Kinetic equations, TiO₂/UV.

1. INTRODUCTION

Phenol and its derivatives are widely used in many petrochemical industries and petroleum refineries as well as chemical and pharmaceutical industries. As the toxicity of phenolic compounds is an important problem, their concentration unfortunately inhibits or even eliminates micro-organisms in biological wastewater treatment plant. Therefore, the presence of phenols strongly reduces the biological biodegradation of the other components. Several processes have been used to eliminate phenolic compounds, conventional destructive technologies including biological treatment and adsorption over activated carbon treatment processes are effective in water treatment but they only transfer the contaminants from one

medium to another. Furthermore, they are slow processes and at higher concentrations of the organic contaminants, they present some difficulties during the operation (Pelizzetti *et al.*, 1990). During the past decade, great interest has been focused on a promising technology based on the oxidation of the hazardous and refractory organic compounds, by the use of advanced oxidation processes (AOPs) (Tennakone *et al.*, 1997; Azbar *et al.*, 2004 and Mokrini *et al.*, 1997). The AOPs are based on the generation of hydroxyl radicals (HO[•]) which are the principal agents responsible for the oxidation of numerous aqueous organic contaminants (Legrini *et al.*, 1993; Huang *et al.*, 1993). This species is a powerful oxidant; however due to its high reactivity, it is unstable and must be continuously produced in situ by means of chemical or photochemical reactions. Among the different ways to generate the hydroxyl radicals are: ozone with ultraviolet light (Glaze *et al.*, 1982; Mirat *et al.*, 1997; Espugas *et al.*, 1994), hydrogen peroxide with ultraviolet light, and photocatalysis, which uses a semi-conductor in combination with UV radiation and molecular oxygen (Weir *et al.*, 1993; and Brezova *et al.*, 1991). Some of these processes like ozonation are more expensive than the use of a catalyst with UV irradiation.

As one of the AOPs, photocatalytic oxidation of a wide variety of organic contaminants by semi conductors has been investigated in more detail during the past decade (Ollis *et al.*, 1985). The use of titanium dioxide (Matthews, 1990) as a photocatalyst has been of great interest due to its efficiency nontoxicity, high activity, photochemical inertness and low cost. Degussa P25, which has both anatase and rutile forms, with the ratio of anatase to rutile equal to 4:1, is one of the best TiO₂ photocatalysts and used frequently as a reference in photocatalysis (Hoffman *et al.*, 1995; Hagfeldt *et al.*, 1995; Fox *et al.*, 1993). This photocatalyst is the most studied and is activated by ultraviolet (UV) light (wavelength < 400nm) due to its band gap of 3.2eV (Tang *et al.*, 1994; Kayan *et al.*, 1996).

Numerous methods have been used to effectively degrade phenol (Salinaro *et al.*, 1999). These methods are based on Advanced Oxidation Processes including processes that use hydrogen peroxide and ferrous ions (Al-Hayek *et al.*, 1990; Guélou *et al.*, 2003 and Bremner *et al.*, 2006) or use semi-conductors like titanium dioxide. The advantage of these processes is that they lead to the total mineralization of organic contaminants, whether they are simple or complex molecules. Nowadays, the most efficient procedure for the treatment of contaminated water is the heterogeneous photocatalysis; it consists of UV light irradiation of TiO₂ catalyst suspensions in solutions containing the organic substrate to be degraded.

The purpose of this work was to study the effectiveness of a helical reactor, conceived in our laboratory, on the photodegradation of phenol. The experiments were conducted in aqueous suspensions of TiO₂, varying different parameters such as the amount of catalyst, UV irradiation time, pH and light intensity. The model proposed by Langmuir-Hinshelwood (L-H) was employed to describe the kinetics of the photodecomposition reactions of phenol, and the optimal conditions have been determined.

2. PRINCIPLE OF THE HETEROGENEOUS PHOTOCATALYSIS

The heterogeneous photocatalysis, one of the Advanced Oxidation Processes, permits the total degradation (mineralization) of the most toxic organic molecules in aqueous solution in the presence of a catalyst. These processes are based on the generation of hydroxyl radicals HO[•] (Okamoto *et al.*, 1985; Serpone, 1996). This species is a powerful oxidant due to its high reactivity. It is unstable and must be continuously produced in situ by means of chemical or photochemical reactions (Andreozzi *et al.*, 1999; Chiron *et al.*, 2000; Galze *et al.*, 1992; Safarzadeh –Amiri *et al.*, 1996).

The heterogeneous photocatalysis is based on a semiconductor used as catalyst which is activated by UV light. The anatase form of Titanium dioxide is mainly used as the catalyst, because of its high activity. The photocatalytic process consists of the excitation of the titanium dioxide by a UV light wavelength of $\lambda \leq 400$ nm, electron-hole pairs (e_{cb}^-, h_{vb}^+) are generated (Figure 1), the hydroxyl radicals are generated by the hole which can degrade organic pollutants present in the wastewater. Oxygen, provided from the air (when the system

is stirred), dissolved in the solution scavenges the electron generated, preventing the recombination of electrons and holes.

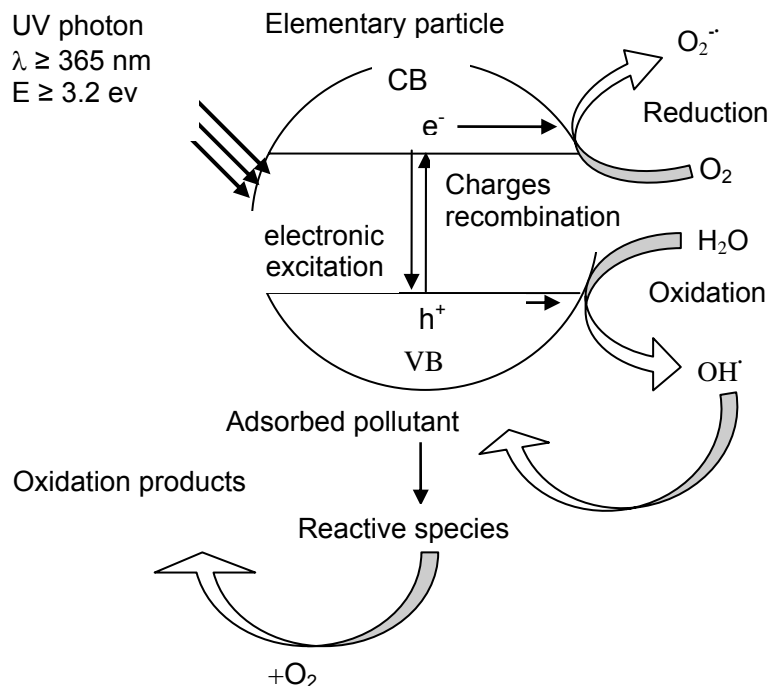


Figure 1. Mechanism diagram of photocatalytic degradation

UV illumination of TiO₂ yields conduction band electrons and valence band holes (eq.i), which interact with surface adsorbed molecular oxygen to yield superoxide radical anions, O₂^{•-} (eq.ii), and with water to produce the highly reactive HO[•] radicals ((eq.iii), respectively. The latter radical species are well known to oxidize a large number of organic substrates (eq.iv), (Horikoshi *et al.*, 2001; Emeline *et al.*, 2001).



3. MATERIALS AND METHODS

3.1. Reagents

The chosen catalyst of titanium dioxide, mainly anatase (80% anatase and 20 % rutile, Degussa P 25) (Datye *et al.*, 1995) with a particle size of 30 nm and a surface area of 50 m² g⁻¹ obtained by BET analysis was used without any pre-treatment; this catalyst is the best one which gives an optimal efficiency of catalysis, furthermore, good interparticle contacts are formed between anatase and rutile particles in water (Ohno *et al.*, 2001). Phenol was obtained with purity > 99.9%. All the chemicals that were used in the experiments were of laboratory reagent grad and used as received without further purification. The solutions were prepared with distilled water. The solution pH was adjusted by nitric acid (HNO₃) or potassium hydroxide (KOH).

3.2. Photoreactor

All experiments were performed in the experimental installation shown in Figure 2. The helical photoreactor of 500 ml capacity was constructed in Pyrex. It is comprised of 23 spires with a 7 mm interior diameter and a length of 400 mm. The source of irradiation is placed in the center of the reactor to assure the maximum energy exchange between the source of irradiation and reaction mixture that flows out continuously. The tubular compartment surrounding the lamp has an interior and outer diameter equal to 60 and 80 mm, respectively, a length of 50 cm are used as a cooling system. A pump recirculates the mixture between the reactor and the reservoir as shown in Figure 1. The reservoir is conceived according to the norms of Holland and Chapman, (1966) it is a cylindrical container made of Pyrex, with a diameter of 23.6 cm. It is equipped with four baffles made of Plexiglas fixed perpendicularly to the partition of the vat. The UV radiation sources are 15W and 400W low-pressure mercury vapor quartz lamps (Philips TL 05 and HPA, respectively). The lamps emissive lengths are 254 nm and 365 nm respectively.

3.3. Photodegradation procedures- Analysis

The reservoir is filled with 3 liters of a distilled water solution containing phenol and TiO₂ catalyst. The experiments were investigated by varying the power of irradiation, TiO₂ concentration mixture, pH and phenol initial concentration.

The experiments of adsorption onto TiO₂ were conducted in a helical Pyrex reactor, having a capacity of 0.5 l. The suspensions were set in circulation during 2 hours in the absence of light in order to reach equilibrium adsorption before irradiation with UV light during 6 hours in presence of oxygen obtained from the air. The samples of reaction suspension (2 ml) were taken with a syringe at pre-determined time intervals and filtered using 0.45 µm Millipore membranes. The sample solutions were analyzed with a UV/Vis spectrophotometer (Perkin Elmer Lambda 25 UV/VIS), the phenol concentration was measured by the absorbance at 270 nm. All the experiments were performed by continuously bubbling air through the liquid phase in order to cover the catalyst surface with oxygen and keep it constant during the oxidation process.

TiO₂ photocatalyst employed was Degussa P25 with a specific surface area of 50 m² g⁻¹. The experimental studies were carried out by varying concentrations of phenol within a range of 2.5 – 25 mg l⁻¹, concentrations of TiO₂ within a range of 0.1 – 1 g.l⁻¹, suspension flows from 0.07 to 0.23 l min⁻¹ due to some geometric considerations. The 15W and 400W low-pressure mercury vapor quartz lamps were employed as light sources to conduct UV-Visible light experiments.

The reaction temperature was kept at 32.0±0.5°C using a cooling system placed between the light source and the reactor. The pH of the reaction suspension was not adjusted (called pH_{free} = 6.7~7.2), except for the study of the effect of pH. The suspended catalyst in the aqueous system was oxygenated continuously by the ambient air.

3.4. Kinetic studies

The Langmuir-Hinshelwood kinetic model is used to describe the mineralization process kinetics and to assume automatically that reactions take place at the surface of the catalyst particle, without any corroborating independent evidence to support this.

The Langmuir-Hinshelwood (L-H) model was initially developed to quantitatively describe gaseous–solid reactions (Satterfield, 1970). This model was recently employed to describe solid–liquid reactions (Ollis, 1985). In this model, the rate of reaction (*r*) is proportional to the fraction of surface covered by the substrate (θ)

$$r = -dC / dt = k_r \theta \quad (1)$$

Considering Langmuir's equation

$$\theta = KC / (1 + KC) \quad (2)$$

$$r = -dC / dt = k \theta = k_r KC / (1 + KC) \quad (3)$$

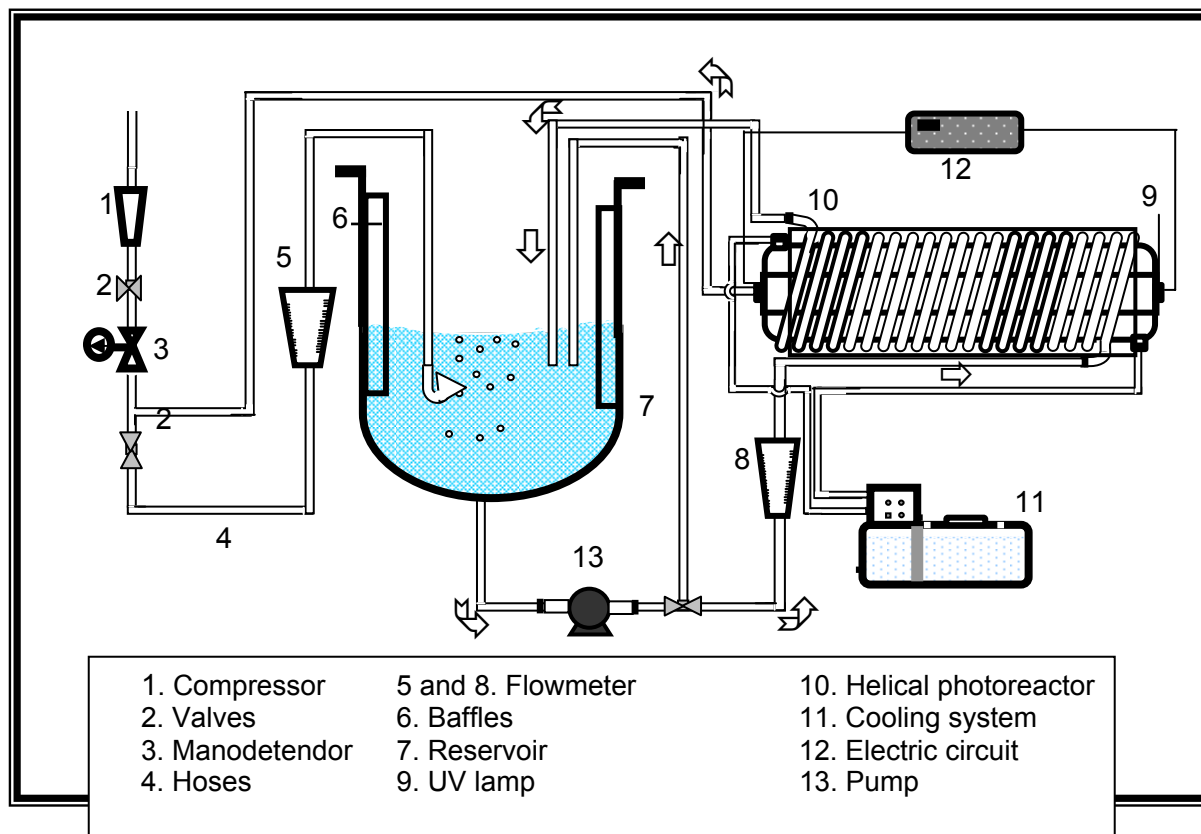


Figure 2. Experimental setup of the helical photocatalytic reactor

Since k_r is the true rate constant, which takes into account several parameters (Fernández *et al.*, 1995) such as the catalyst's mass, efficient photon flow, O_2 layer, etc., K is the constant of adsorption equilibrium of L-H or the Langmuir constant. In photocatalytic studies, the value of K is obtained empirically through a kinetic study in the presence of light, and is better than that obtained in the darkness (Pedro *et al.*, 2006), starting from Langmuir's isotherm. C is the concentration of the organic substrate at any time t . This equation can be integrated, becoming:

$$\ln(C_0 / C) + K(C_0 - C) = k_r K t \quad (4)$$

where C_0 is the initial concentration of the organic substrate and t is the irradiation time. eq. (3) will be of zero order when the concentration C (mol/l) is relatively high, $>5 \times 10^{-3}$ (Herrmann, 1999), $KC \gg 1$, in which case the reaction rate will be maximal. When the solution is highly diluted, C (mol/l) $<10^{-3}$ (Herrmann, 1999), the term KC becomes $\ll 1$, when the denominator of eq.3 is neglected and the reaction is essentially an apparent first order reaction:

$$r = -dC / dt = k_r k C = k_{app} C \quad (5)$$

where k_{app} is the apparent rate constant of a pseudo first order reaction. Thus, eq.4 can be simplified to a first order reaction when C_0 is very small, in which case one has:

$$\ln(C_0 / C) = k_{app} \times t \quad (6)$$

By plotting $\ln(C_0/C)$ versus t , the apparent rate constant (k_{app}) can be determined from the slope of the curve obtained.

4. RESULTS AND DISCUSSION

Several parameters have been studied in order to determine their influence on the degradation of phenol by the photochemical process $O_2/UV/TiO_2$. We will mention the withdrawal point for sample analysis (reservoir and outflow), the irradiation light, the pollutant

and the amount of catalyst, the pH of the solution, and the recirculation flow of the solution. The effect of these parameters on the photocatalytic reaction of phenol elimination has been studied by measuring the phenol concentrations over time and comparing kinetic constants. It has been observed that during the adsorption period (2 hours) the amount of phenol adsorbed was limited. The photodegradation of phenol using TiO₂ as a catalyst could be modeled assuming a pseudo-first-order kinetics.

The photodegradation efficiency for each experiment also called conversion is calculated by the following relation:

$$X(\%) = 100 \times (C_0 - C) / C_0 \quad (7)$$

Where X is the photodegradation efficiency, Co the concentration of phenol before illumination and C the concentration of phenol in suspension after time t (mmol l⁻¹).

4.1. Influence of sample point

In order to study the influence of the sample point on the experiments, we used two different sources: one at the outflow of the reactor and the other from the reservoir. As shown in Figure 3, the photodegradation of phenol was very important and quick for a 400 W light, and for both the reservoir and the outflow of the reactor, the points of the two curves are close together. This means that the choice of sample point doesn't have any effect on the phenol conversion rate. It is due to a good homogenization of the solution by the recirculation pump. Furthermore, the volume exposed to UV light is weak in relation to the total volume of solution in reservoir.

4.2. Effect of flowrate recirculation

Adsorption and photodegradation of phenol was carried out with varying flowrates (0.07 to 0.23 l min⁻¹). According to Figure 4 and 5 which represent the evolution of phenol degradation

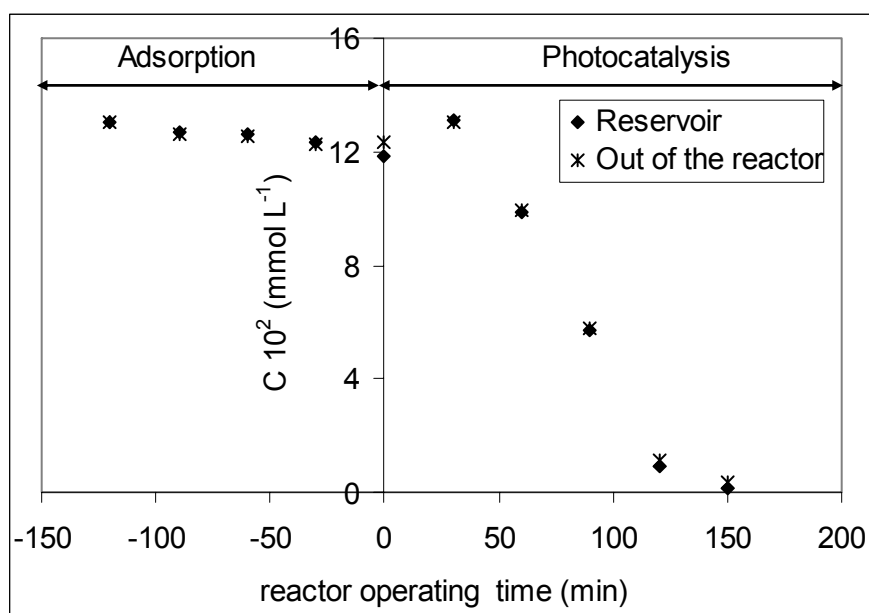


Figure 3. Effect of sample point on phenol degradation
(C₀(phenol)=10 mg l⁻¹, C_{TiO₂}=1 g l⁻¹, Q=0.23 l min⁻¹, T=32°C, P= 400 W)

while using 15 W and 400 W lights respectively, the photocatalytic activity of TiO₂ and the reduction of phenol concentration with reaction time was more effectiveness with a 400 W light and a weaker flow (Okamoto *et al.*, 1985), indeed, it appeared that the conversion of the phenol was very weak (2% for 15 W light), compared with 99.8% for the 400 W light, where phenol nearly disappeared completely (Blake, 1997).

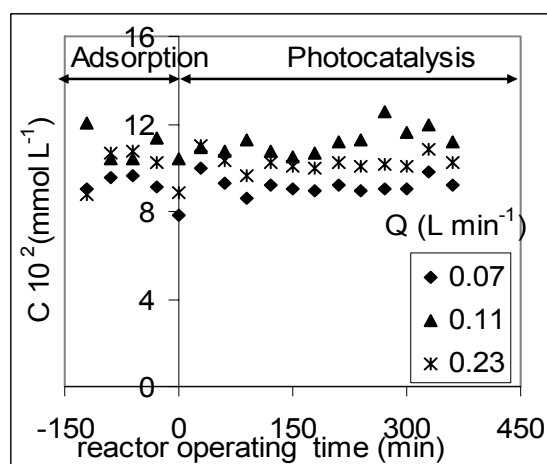


Figure 4. Evolution of phenol concentration with reactor operating time using a 15 W lamp. ($C_{0(\text{phenol})}=10 \text{ mg l}^{-1}$, $C_{\text{TiO}_2}=1 \text{ g l}^{-1}$, $T=32^\circ\text{C}$, pH free)

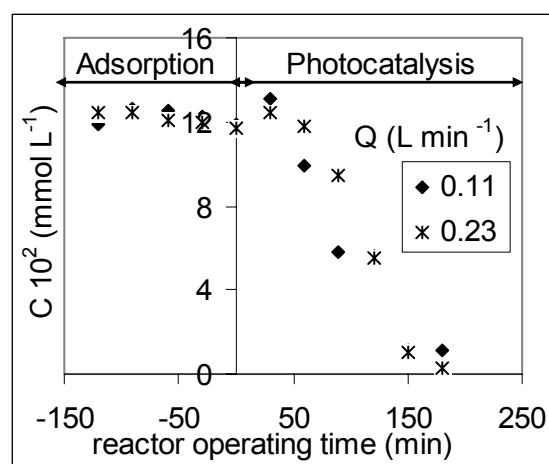


Figure 5. Evolution of phenol concentration with reactor operating time using a 400 W lamp. ($C_{0(\text{phenol})}=10 \text{ mg l}^{-1}$, $C_{\text{TiO}_2}=1 \text{ g l}^{-1}$, $T=32^\circ\text{C}$, pH free)

By plotting $-\ln(-dC/dt)$ versus $-\ln(C)$, which gives a straight line for the studied samples, the apparent rate constants (k_{app}) have been determined from the slope of the curves obtained by the least squares method. Table 1 summarizes the values of Q , X and the pseudo first-order rate constant (k_{app}) for the 400W light source where the degradation of phenol was more effective. As shown in table 1, even if k_{app} is slightly better for a flowrate of 0.11 l min^{-1} , we chose as the limit flowrate $Q= 0.23 \text{ l min}^{-1}$ in order to avoid the deposit of catalyst on the photoreacteur and to get a better output.

Table 1. Kinetic constants for different flowrates while using the HPA 400W lamp after 6 hours of irradiation time

Parameter	Units	Values	
Flowrate Q	l min^{-1}	0.11	0.23
Conversion X	%	97.3	99.8
k_{app}	min^{-1}	2.34 ± 0.02	1.70 ± 0.02

4.3. Effect of light intensity

The incident light intensity is expected to be one of the rate-controlling parameters. In order to illustrate this effect, experiments were carried out under two levels of incident light intensity, and the conversion rate at different times is represented in Figure 6. The mineralization processes at 15 and 400 W of light intensity are also displayed in Figure 6.

Based on Figure 6, the conversion depended strongly on the incident light intensity, thus, increasing the light intensity from 15 W to 400 W enhanced phenol degradation in a remarkable way, since at 400 W, conversion reached 100% after less than 4 hours, whereas the conversion at 18 W led to less than 15 % even after a long irradiation time.

These results may be explained based on the relative amounts of photons in the reaction system at low light intensity; on the other hand, at high intensity, photons were present in excessive amounts leading to more reactive species generation and more destruction of phenol; this proved that higher catalyst activity occurred under high light incident intensity.

4.4. Effect of the dose of semiconductor (TiO_2)

The effect of the amount of TiO_2 Degussa P25 on the removal of phenol was also significant as shown in Figure 7, confirming the positive influence of the increased number of TiO_2 active sites on the process kinetics. Figure 7 displays phenol concentrations in the suspension for various catalyst dosages (interval $0.1 - 1.0 \text{ g l}^{-1}$). These results show that the photocatalytic efficiency for phenol degradation increased with the increase of the amount of TiO_2 . This observation can be explained by the photocatalyst optical properties as the main cause for

the differences, indeed, the total active surface area increased with increasing catalyst dosage, because of the penetration of UV light into the suspension which in turn increases the number of hydroxyl, and superoxide radicals.

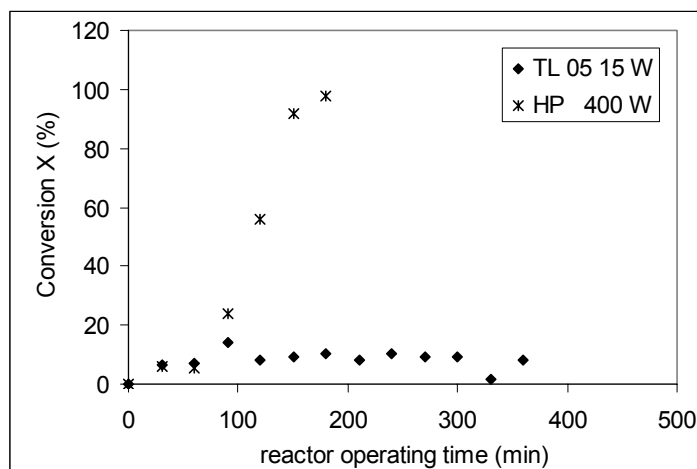


Figure 6. Effect of UV light on conversion with reactor operating time for two different light intensities. ($C_0(\text{phénol})=10 \text{ mg l}^{-1}$, $C_{\text{TiO}_2}=1 \text{ g l}^{-1}$, $Q=0.23 \text{ l min}^{-1}$, $T=32^\circ\text{C}$)

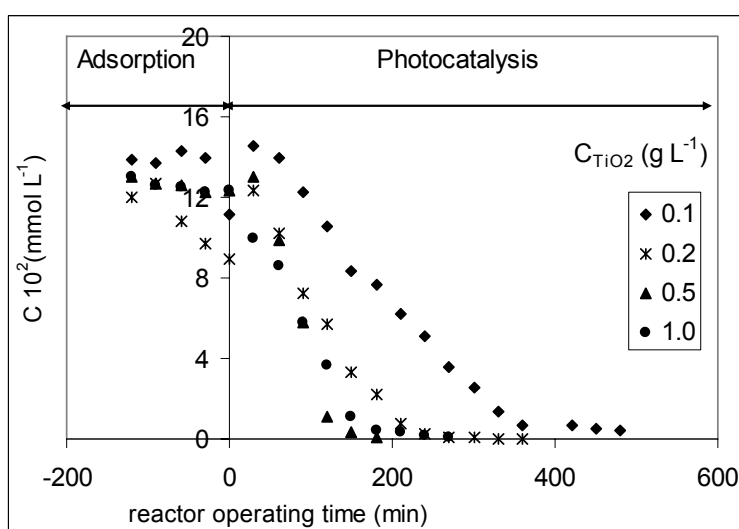


Figure 7. Effect of titanium dioxide concentration on phenol degradation ($C_0(\text{phenol})=10 \text{ mg l}^{-1}$, $Q=0.23 \text{ l min}^{-1}$, $T=32^\circ\text{C}$, pH free, $P=400 \text{ W}$).

As shown in table 2, the phenol degradation was achieved after 4 hours for the major chosen concentration ($X=99\%$). However, as shown in Figure 8, over the whole range of TiO₂ loading values (0.2 to 1.0 g l⁻¹), there were no significant changes, so the other experiments were performed in the TiO₂ concentration of 0.2 g l⁻¹ (Hermann, 1999).

Table 2. Decomposition of phenol solutions at different initial TiO₂ concentrations

Parameter	Units	Values			
Amount of TiO ₂	g l ⁻¹	0.1	0.2	0.5	1.0
Period of reaction	hour	6.0	4.0	4.5	3.0
Conversion X	%	94.00	99.00	97.55	99.15
k_{app}	min ⁻¹	0.37 ± 0.03	0.78 ± 0.01	1.40 ± 0.02	1.77 ± 0.01

In this study, in the dynamic flow photoreactor, apparent first-order reaction rate constants were found to be directly proportional to the concentration of catalyst (Figure 8). This indicates a true heterogeneous catalytic regime.

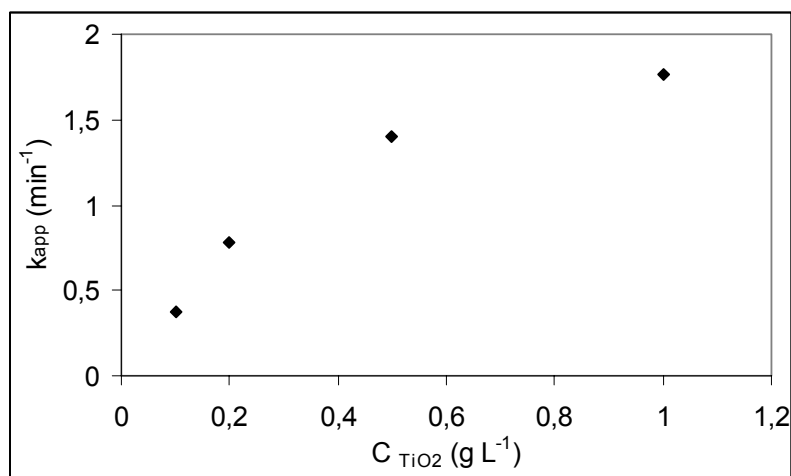


Figure 8. Apparent first-order constant rate vs. initial concentration of TiO_2 ($C_0(\text{phenol})=10 \text{ mg l}^{-1}$, $Q=0.23 \text{ l min}^{-1}$, $T=32^\circ\text{C}$, pH free, $P=400 \text{ W}$)

However, above a certain value of C_{TiO_2} , the reaction rate became constant and independent of C_{TiO_2} . These limits correspond to the maximum amount of TiO_2 in which all the particles and the entire surface exposed were totally illuminated. To be sure that we had total absorption of efficient photons and to avoid excess catalyst in our recirculation plug flow reactor, we have chosen an optimum C_{TiO_2} concentration of 0.2 g l^{-1} , as suggested by Hermann, (1999) and as shown in table 2, where it was indicated that 99 % of phenol has been degraded after 4 hours.

4.5. Effect of pH on the degradation of phenol

The effect of pH on the photocatalytic degradation efficiency of AOPs, according to some literatures (Wang *et al.*, 2000), is one of the major factors influencing the rate of degradation of some organic compounds (Pera-Titus *et al.*, 2004). The degradation of phenol under UV irradiation at different pH is shown in Figure 10; Figure 9 shows that the suspension pH (without any adjustment) changed with time, during the adsorption period, no change was observed, so the influence of adsorption can be neglected. Initially, the solution was colorless, but immediately after the irradiation, the suspension pH decreased, and a pink coloration appeared. After a few minutes the color changed to vivacious red, after a few more minutes, the color began to disappear and the solution finally became colorless.

The increase of the pH from 7.2 to 6.7 was noticed from the beginning and this latter pH remained constant during the whole run, thus acid compounds were produced. The acids seem to be the most difficult compounds to be mineralized (Mantzavinos *et al.*, 1996), likewise, for the formed intermediates reaction products, such as aromatics (hydroquinone, benzoquinone and catechol), which result from reaction of hydroxyl radicals with phenol, at the initial stage of the reaction and undergo further photocatalytic oxidation to yield the very polar products like aldehydes and carboxylic acids which increased rapidly. The aromatic intermediates disappeared some minutes after the disappearance of phenol. After reaching a maximum, acids decreased with increasing reaction time and at the end of the degradation phenol was mineralized to CO_2 and H_2O (Okamoto *et al.*, 1985). As shown in Figure 10 and table 3, Phenol conversions were found to

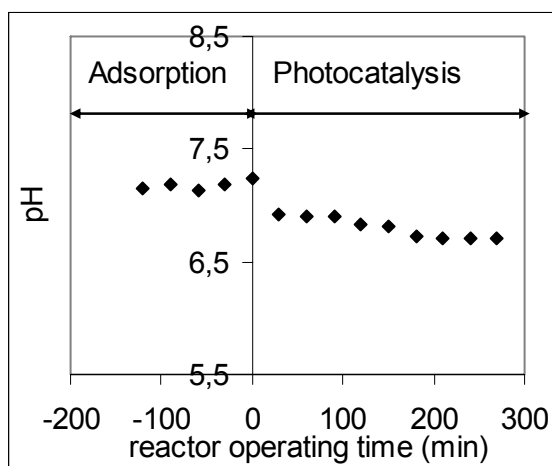


Figure 9. Effect of pH on the photocatalytic degradation of phenol with an irradiation of 400 W. ($C_o(\text{phenol})= 10 \text{ mg l}^{-1}$, $C_{\text{TiO}_2}= 0.2 \text{ g l}^{-1}$, $Q= 0.23 \text{ l min}^{-1}$, $T= 32^\circ\text{C}$)

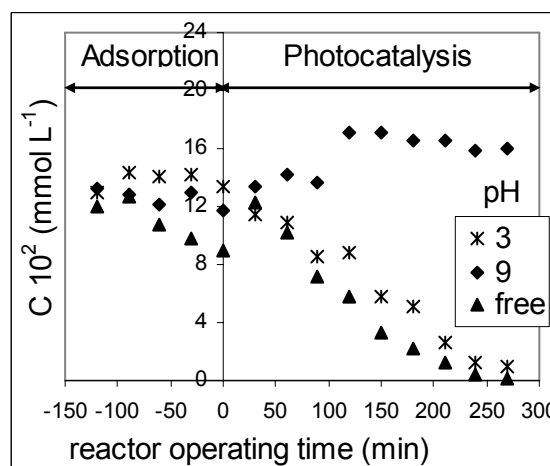


Figure 10. Effect of pH on photocatalytic degradation of phenol with an irradiation of 400 W. ($C_o(\text{phenol})= 10 \text{ mg l}^{-1}$, $C_{\text{TiO}_2}= 0.2 \text{ g l}^{-1}$, $Q= 0.23 \text{ l min}^{-1}$, $T= 32^\circ\text{C}$.)

be more important for acid than for basic media, Okamoto *et al.*, (1985) and Serpone *et al.*, (1996) have reported that pH 3 was the optimum for the photocatalytic decomposition of phenol. The photodegradation of phenol was complete after 5 hours. On the other hand, the pH value obtained at the end of the experiment was similar to the initial pH solution; this indicated that mineral acids and carbon dioxide would be considered as the final oxidation products. Whereas in pH 9, conversion reached a threshold value of about 46%, indeed, higher pH retarded the formation of HO[•] radicals and decreased the photocatalytic reaction rate. Besides, TiO₂ coagulates at pH 9 and the samples of the reaction slurry could not be filtrated and analyzed (Leyva *et al.*, 1998) the residual phenol indicates a moderate degradation, Table 3 shows that the order of reaction rates was $\text{pH}_{\text{free}} (6.7-7.2) > \text{pH}3 > \text{pH}9$. This means that it was more effective for phenol to be degraded under natural conditions.

Table 3. K_{app} rate constants and conversions at different pH values with a HPA 400W lamp

Parameter	Units	Values		
pH	--	3	free pH (6.7- 7.2)	9
Conversion X	%	96.51	98.96	46.59
k_{app}	min^{-1}	1.032 ± 0.007	1.34 ± 0.01	0.450 ± 0.008

Table 3 shows that the better removal efficiency of phenol is in low pH values, and the optimal pH for the studied system is the free one, this is due to the process of the photocatalytic degradation of phenol, which involves not only radical oxidation, but also direct electron transfer and surface sorption reactions. Notice also the lower values of the pseudo-first order kinetic constant obtained when runs were carried out at basic pH.

4.6. Effect of the initial concentration of Phenol

The effect of the initial phenol concentration on its kinetic degradation by the UV/TiO₂/O₂ process was investigated. Figure 11 and Table 4 show that between 56 and 99 % of the phenol content was removed by the AOP for initial phenol concentrations ranging from 2.5 to 25 mg l⁻¹, at free pH and illumination light of 400W. As shown in Figure 11, the fact that a negligible adsorption took place indicates that the phenol was not physically adsorbed but chemically reacted on the catalyst surface (Santos *et al.*, 1999).

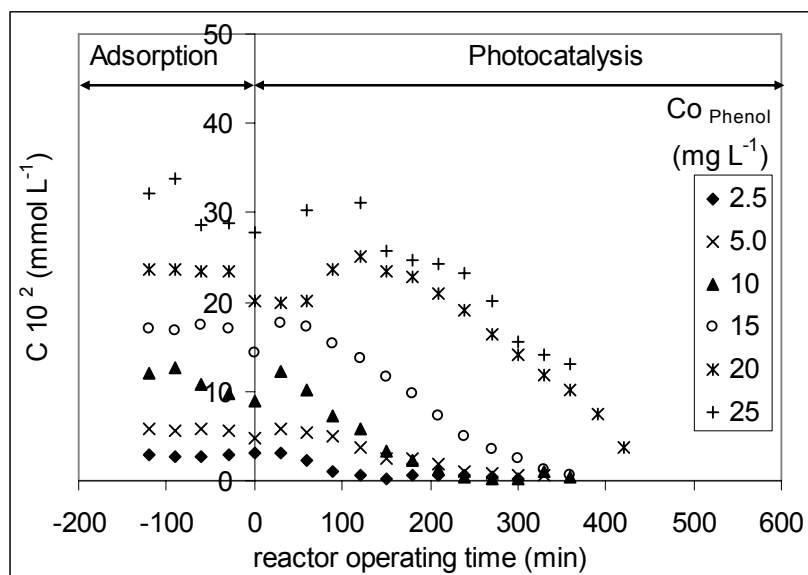


Figure 11. Effect of initial concentration of phenol on the Photocatalytic degradation under UV light illumination ($C_{TiO_2} = 0.2 \text{ g l}^{-1}$, $Q = 0.23 \text{ l min}^{-1}$, $T = 32 \text{ }^\circ\text{C}$, pH free, $P = 400 \text{ W}$).

Afterwards, the time required for complete degradation of phenol solutions increased with increasing initial phenol concentration. On the other hand, an optimal value was obtained for $C_0 = 2.5 \text{ mg l}^{-1}$, where a high degradation efficiency of phenol (about 99%) was attained with an irradiation time less than 2 h. This is not the case for other concentrations where the required time to obtain this performance was much longer. An explanation at this behavior is that as initial concentration increases, a bigger quantity of phenol is adsorbed on the surface of TiO_2 , therefore, the generation of hydroxyl radicals would be reduced since there were fewer active sites for the adsorption of hydroxyl ions and the generation of hydroxyl radicals. Further, as the concentration of phenol in solution increased, the photons would be able to be intercepted before they could reach the catalyst surface, hence the absorption of photons by the catalyst decreased, and consequently the degradation was reduced.

Table 4. Apparent first-order rate constants and conversions for different initial concentrations of phenol. ($C_{TiO_2} = 0.2 \text{ g l}^{-1}$, $Q = 0.23 \text{ l min}^{-1}$, $T = 32 \text{ }^\circ\text{C}$)

Parameter	Units	Values					
C_0 phenol	mg l^{-1}	2.5	5	10	15	20	25
X	%	90.44	89.00	98.62	96.62	83.9	56.2
k_{app}	min^{-1}	7.73 ± 0.02	2.62 ± 0.02	1.78 ± 0.01	0.761 ± 0.009	0.600 ± 0.009	0.2300 ± 0.0005

It has been observed that in photocatalytic processes, formation, migration and reaction of photogenerated radicals with organic compounds were consecutive reactions, therefore, any of these processes could determine the overall degradation rate. As shown in table 4, the apparent first-order rate constants decreased with the increase of initial phenol concentrations (Matthews, 1988). This is the consequence of the Intermediates, which were generated during the photocatalytic process and affect the degradation of phenol by producing higher concentrations of intermediates adsorbed at higher initial concentrations of phenol; this could affect negatively the overall degradation rate. The competitive adsorption on the surface of TiO_2 particles between the HO^\bullet radicals generated by the active site OH^- and phenol molecules adsorbed on the surface catalyst which react with radicals has the similar effect. When the initial concentration is high, the number of these available active sites are decreased by phenol, and since the intensity of irradiation light was constant the HO^\bullet and O_2^\bullet radicals formed on the surface of the catalyst were also constant, the attack of these

radicals on the compound molecules decreased and simultaneously the photodegradation efficiency also decreases.

4.7. Kinetic studies

The photocatalytic oxidation kinetics of many organic compounds has often been modeled with the Langmuir–Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model, developed by Turchi *et al.* (1990) and Emeline *et al.* (2000), is expressed as eq.3, where r is the reaction rate ($\text{mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$), k_r the reaction rate constant ($\text{mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$), K the adsorption equilibrium constant of phenol ($\text{l} \cdot \text{mmol}^{-1}$), and C the concentration of phenol ($\text{mmol} \cdot \text{l}^{-1}$). The initial degradation rate of phenol was studied as a function of the initial phenol concentration in the range 2.5 to 25 $\text{mg} \cdot \text{l}^{-1}$, for a fixed loading of TiO₂ ($0.2 \text{ g} \cdot \text{l}^{-1}$). The results were reported in Figure 11. The initial phenol degradation rate versus initial phenol concentration under photocatalytic conditions showed at high initial concentration a plateau, the approximate value was $[\text{phenol}]_0 = 30 \times 10^{-2} \text{ mmol} \cdot \text{l}^{-1}$. Eq.8 shows a pseudo-first order reaction with respect to the phenol concentration.

The relationship between the initial degradation rate (r) and the initial concentration of organic substrate for a heterogeneous photocatalytic degradation process has been described by Langmuir–Hinshelwood model and can be written as follows:

if we consider that the kinetic of phenol degradation is of pseudo-order, at $t=0$ and $C=C_0$, eq.3 becomes:

$$r_0 = k_r K C_0 / (1 + K C_0) \quad (8)$$

This equation can be rearranged into linear form:

$$1/r_0 = (1/k_r K) \cdot 1/C_0 + 1/k_r \quad (9)$$

where $1/r_0$ is the dependent variable, $1/C_0$ the independent variable, $1/k_r$ is the linear coefficient and $(1/k_r K)$ the angular coefficient of the straight line (Figure 13). From this model, the L-H adsorption constant and the rate constant were obtained by plotting $1/r_0$ versus $1/C_0$ (Wang *et al.*, 2000).

The values of the adsorption equilibrium constant, K , and the kinetic rate constant of surface reaction, k_r , were calculated. The representation of $1/r_0$ versus $1/C_0$, as shown in eq.9 in the presence of different concentrations of phenol versus initial phenol concentration yields a straight line indicating a pseudo-first order reaction. The reaction rate constants k_r for photocatalytic degradation of phenol were evaluated from experimental data (Figure 13) using a linear regression. The R^2 (correlation coefficient) value was higher than 0.99, which

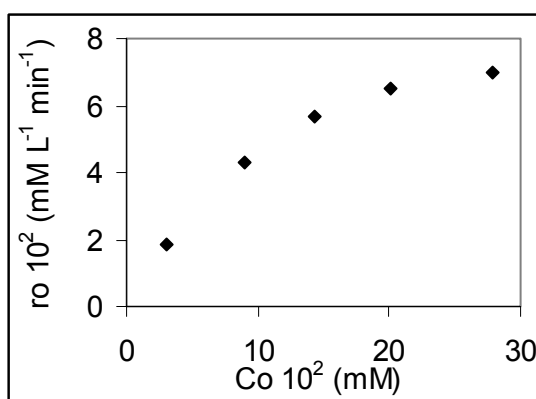


Figure 12. Initial phenol degradation rate vs. initial phenol concentration. ($C_{\text{TiO}_2} = 0.2 \text{ g} \cdot \text{l}^{-1}$, $Q = 0.23 \text{ l} \cdot \text{min}^{-1}$, $T = 32^\circ\text{C}$).

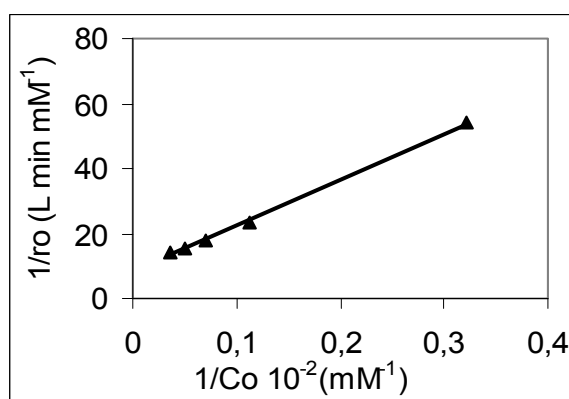


Figure 13. Linearization of Langmuir-Hinshelwood's equation for phenol. ($C_{\text{TiO}_2} = 0.2 \text{ g} \cdot \text{l}^{-1}$, $Q = 0.23 \text{ l} \cdot \text{min}^{-1}$, $T = 32^\circ\text{C}$)

confirms the proposed kinetics for degradation of phenol in this process. The constants k_r and K in Langmuir–Hinshelwood model were obtained as $0.1204 \text{ mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$ for k_r and $0.0604 \text{ l} \cdot \text{mmol}^{-1}$ for K , with correlation coefficient R^2 equal to 0.995.

5. CONCLUSION

The performance of the helical reactor conceived in our laboratory for the heterogeneous photocatalysis of phenol in suspension were studied. This reactor appears to be a promising technology to degrade phenol and many other environmentally persistent compounds. This process proved to be a very efficient method for water pollution remediation as a complete mineralization of phenol. The photodegradation of phenol in presence of TiO₂ suspension was found to be the best method for its degradation. Several parameters have been studied, it appears that the flowrate recirculation, irradiation time, light intensity, catalyst load, pH and concentration of phenol mainly controls the rate of degradation for which optimum conditions for achieving maximum efficiency were established. Taking into account the role of the different parameters should be of great importance for the optimization of the experimental conditions for technological applications.

In this work, it appears that the degree of degradation of phenol was obviously affected by illumination time, recirculation flowrate, light intensity, amount of photocatalyst, suspension pH and initial concentration. A weak recirculation flowrate, high light intensity, moderate catalytic concentration, free pH of the suspension with a value of 6.7-7.2, and a weak initial concentration of phenol promoted the photodegradation of phenol. Indeed, the capacity of TiO₂ towards phenol degradation strongly depended on the suspension pH. At basic pH, degradation was negligible, and at acid or free pH, degradation of phenol was fast indicating that the mechanism involving complete mineralization could be achievable under prolonged exposures. At the optimal conditions, 99 % of phenol was degraded after approximately 4 hours. Under the operational conditions employed, the phenol oxidation reaction could take place by the free radicals mechanism, the catalyst being an initiator of such reactions. However, the total mineralization of the intermediates is affected by the catalyst concentration, especially when the reaction takes place under basic conditions. The kinetics of photocatalytic removal of phenol followed the Langmuir–Hinshelwood model, with apparent first-order kinetic.

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