Influence of several factors on the heterogeneous photocatalytic degradation of phenol

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Abstract - Photocatalytic degradation of phenol in aqueous solutions was investigated using heterogeneous photocatalysis with titanium dioxide (TiO_2) particles immobilized on the inner wall of an annular upflow reactor. The influence of the concentration of phenol (measured as Dissolved Organic Carbon, DOC) at 15, 50, and 100 mgC L^{-1}, the presence of hydrogen peroxide (H_2O_2), two different irradiation sources (germicidal and black light lamps), and two different reactor geometries (reactor 1 with 3,3 cm and reactor 2 with 7,0 cm outer diameters) were evaluated. To further investigate the effect of these parameters, the rate of phenol degradation, the quantum yield, and the energy consumption were calculated. According to the results obtained, the solution with an initial DOC concentration of 100 mgC L^{-1}, in the presence of hydrogen peroxide (242 mmol L^{-1}), using reactor 2 with the germicidal lamp as the photon source, gave the best performance, with degradation rates reaching 36,8 mgC h^{-1} and with one of the lowest energy consumptions (65 kWh m^{-3} order^{-1}).

Key words: TiO_2, heterogeneous photocatalysis, reactor geometry, H_2O_2

Introduction

Contamination of the environment has been pointed out as one of the major problems of modern society. The present stage of environmental degradation can be attributed to population growth together with the adopted economic model, which is based mainly upon the exploitation of natural resources followed by their transformation into consumer goods[1,2.]

The intensification of agricultural activities has also contributed, due to the input of pesticides and fertilizers. As a consequence, a series of new products were obtained while a higher amount of residues have become waste. It has been evaluated that 2,8 x 10^8 ton of hazardous residues are generated annually, associated with more than 200000 industrial processes. However, only 3% of this amount is destroyed, while the remaining quantity reaches the ecosystems, where they may accumulate[3].

New regulations for air, water and solid residues, resulting from the increasing awareness of the urgent need to protect our environment, have stimulated the search for improvements of existing processes for water treatment as well as for more efficient processes that either destroy or immobilize these toxic residues[4]. Currently used methods for groundwater detoxification show technological and economic limitations. For example, the removal of volatile contaminants by air-stripping transfers liquid contamination into an air pollution problem, while carbon adsorption produces a hazardous solid which in turn must be disposed of. On the other hand, some destructive technologies, such as chlorination and ozonization, use strong oxidizing agents, which can yield toxic intermediates[5,6].

Advanced Oxidation Processes (AOP) are destructive technologies, normally leading to the total mineralization of organic contaminants into carbon dioxide, water and inorganic anions[7]. They have attracted great interest because of their high efficiencies in the degradation of numerous organic compounds associated with low operational costs. These processes are based on the formation of hydroxyl radical ($\cdot OH$), a powerful oxidizing agent[8].
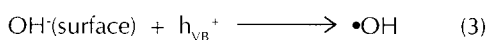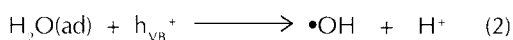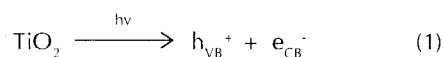
One of these processes involves the use of semiconductors as the photocatalyst, and has recently gained attention in the field of treatment of hazardous wastes. There are many semiconductors that can be used as photocatalysts, including TiO_2, ZnO, Fe_2O_3, kaolin, SiO_2, Al_2O_3[9], ZnS, CdS and V_2O_5[10]. However, heterogeneous photocatalysis using TiO_2 is one of
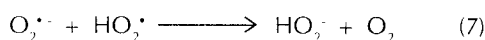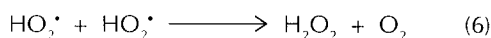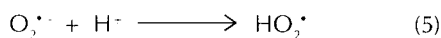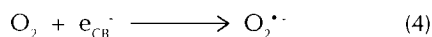
the most promising AOP processes because it is efficient in the degradation of numerous organic pollutants, like alkanes, haloalkanes, aliphatic alcohols, aliphatic carboxylic acids, alkenes, haloalkenes, aromatics, haloaromatics, phenols, aromatic carboxylic acids, polymers, surfactants, herbicides, pesticides and dyes, with low operational costs[6].

One of the most promising AOP processes is heterogeneous photocatalysis, where the reaction occurs in the presence of a catalyst in the solid form. When illuminated by photons with energy equal or higher than the band gap energy (3,2 eV or 380 nm), an electronic excitation occurs, and the electron is promoted from the valence band (VB) to the conduction band (CB), generating a hole/electron pair (h_{VB}^+/e_{CB}^-). The electrons and holes can either recombine and produce thermal energy, or interact with other molecules. The positive holes, acting as strong oxidizing agents, can migrate to the semiconductor surface to oxidize organic compounds by direct electron transfer. The holes can also react with electron donors in solution to produce powerful oxidizing free radicals, such as hydroxyl radicals, which can then oxidize the organic compounds adsorbed on the catalyst surface[4,11-16].
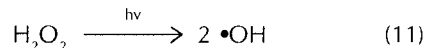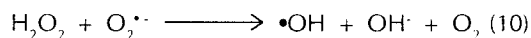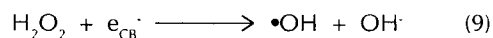
Matthews[15] suggested that oxidation reactions can occur between the hole and adsorbed water or with hydroxyl ions at the catalyst surface, producing hydroxyl radicals, according to the reactions:

$$TiO_2 \xrightarrow{h\nu} h_{VB}^+ + e_{CB}^- \qquad (1)$$

$$H_2O(ad) + h_{VB}^+ \longrightarrow \bullet OH + H^+ \qquad (2)$$

$$OH^-(surface) + h_{VB}^+ \longrightarrow \bullet OH \qquad (3)$$

Okamoto et al.[16] pointed out that reduction processes can be observed between the electron of the CB and any scavenger available, usually adsorbed oxygen, producing $O_2^{\bullet-}$, a precursor of hydrogen peroxide, according to:

$$O_2 + e_{CB}^- \longrightarrow O_2^{\bullet-} \qquad (4)$$

$$O_2^{\bullet-} + H^- \longrightarrow HO_2^\bullet \qquad (5)$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \qquad (6)$$

$$O_2^{\bullet-} + HO_2^\bullet \longrightarrow HO_2^- + O_2 \qquad (7)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad (8)$$
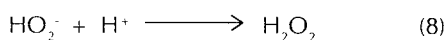
The generation of $\bullet OH$ by way of H_2O_2 may also occur:

$$H_2O_2 + e_{CB}^- \longrightarrow \bullet OH + OH^- \qquad (9)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow \bullet OH + OH^- + O_2 \quad (10)$$

$$H_2O_2 \xrightarrow{h\nu} 2\ \bullet OH \qquad (11)$$

There are many different types of photochemical reactors, such as one having a spiral form around the irradiation source, a packed cylinder, a fixed bed, etc. The light source can be artificial or solar[17], and the catalyst can be used in suspension (slurry) or supported. The light source can be installed around a tubular reactor or in the axis of an annular reactor. The geometry used in the first case is called positive irradiation geometry, and the second one is called negative irradiation geometry, where the photons are absorbed by the reactional system contained in the annular reactor. This later geometry is the most used in photochemical reactors because it tends to be the most efficient form for light absorption.

In the scientific literature, there are many works that involve AOP, with different objectives: degradation of organic compounds in the liquid, solid and gas phases, using different irradiation sources (artificial or solar)[17]; different catalysts, like ZnO and MnO; supported on different matrices, like polymers or sand, etc, and doped with metals[18]; study of the mechanisms of the reactions involved; the evaluation of the toxicity of the intermediates formed during the degradation[19], and modeling of the reactors.

In this work, the oxidation of phenol in dilute aqueous solutions was investigated using TiO_2 as a photocatalyst, in conjunction with H_2O_2, which acts as an auxiliary source of ·OH, with two different irradiation sources (germicidal and black light), and two different upflow annular reactor geometries (reactor 1, with 3,3 cm o.d., and reactor 2, with 7,0 cm o.d.). The best performance was selected after calculating the maximum rate of phenol (carbon) removal using the minimum amount of electricity.

Experimental

1 - Reagents

Titanium dioxide (Degussa P-25, 30 m^2g^{-1}, mainly anatase) was used as a photocatalyst. Phenol (Merck) was used without

purification. Phenol solutions were used at concentrations of 15, 50, and 100 mgC L^{-1} (measured by DOC), by dissolving the equivalent amount of solid in distilled water. Hydrogen peroxide (Merck, 30% w/w) was used as an auxiliary oxidant in the photodegradation experiments.

2 - Reactor details

The upflow photoreactors were constructed with the dimensions shown in Table 1:

Table 1. Dimensions of the photoreactors

. .	Outer diameter (cm)	Inner diameter (cm)	Height (cm)	Working volume (mL)
Reactor 1	3,3	2,4	35	145
Reactor 2	7,0	2,4	35	1190

The illumination was provided using either a high-pressure 15 W germicidal lamp or a black light lamp, which were fixed with two supports at the center of the reactor, both measuring 35 cm long and 2,4 cm o.d. The photocatalyst was supported on the inner walls of the glass reactor and the phenol solution is pumped between the light source and the wall (anular space) in a continuous operation. The reactor was fed concomitantly with both the phenol solution and a stream of filtered air used as a source of oxygen, as shown in Figure 1
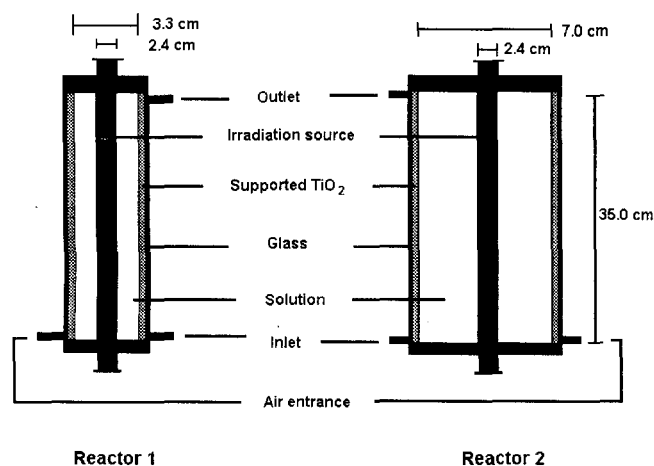

Figure 1. Reactor details.

3 - TiO$_2$ immobilization

The photocatalyst was supported on the walls of the reactor according to the following steps: (a) the inner wall of the glass

(Pyrex) photoreactor cylinder (Figure 1) was sand-blasted for better adherence of the catalyst; (b) the rough surface received a coating of a solution containing titanium isopropoxide and 2-propanol, (c) the reactor was fired at 450°C for 30 minutes and, after cooling, it was rinsed with distilled water to remove the excess TiO$_2$, (d) this process was repeated at least 4 times. A white, firmly fixed TiO$_2$ surface was obtained.

4 - Photodegradation procedures

Phenol solutions were pumped at fixed flow rates of 1,22 mL min^{-1} to reactor 1 or 10 mL min^{-1} to reactor 2, respectively. These flow rates correspond to a retention time of 119 min. All the experiments were performed in a continuous operation mode, using a Ismatec peristaltic pump to circulate the phenol solution, according to the experimental set up shown in Figure 2.

The reactor was fed concomitantly with both the phenol solution and a stream of filtered air (300 mL min^{-1}) used as a source of oxygen, according to equations (4-8). In the experiments carried out in the presence of H$_2$O$_2$, concentrations of 35, 121, and 242 mmol L^{-1} of this oxidant were used in conjunction with phenol solutions of 15, 50, and 100 mgC L^{-1}, respectively. Aliquots of 5 mL were taken at regular time intervals for Dissolved Organic Carbon (DOC) analysis using a Shimadzu TOC 5000 equipment.
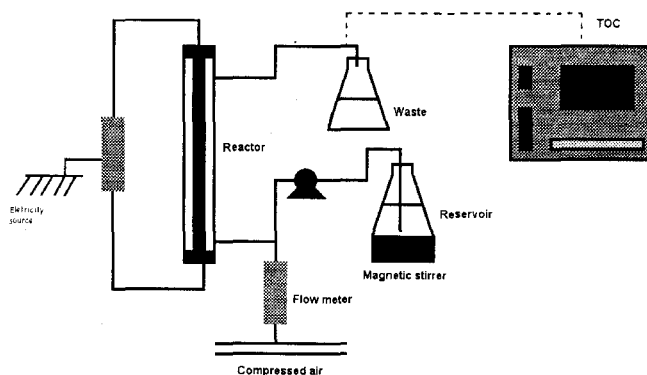

Figure 2. The experimental setup used in the photocatalytic destruction of phenol

5 - Black light lamp and germicidal lamp light intensity measurements

Light intensity from the two different sources of photons was measured using a Cole Parmer Radiometer (model 9811-

50) at 254 or 365 nm, and the quantum yield was obtained with the help of ferrioxalate actinometry[20,21]. The light intensities of the black light lamp and the germicidal lamp were $9,0 \times 10^{-7}$ and $4,8 \times 10^{-6}$ E s^{-1}, respectively.

Results and discussion

Photocatalytic degradation of phenol using TiO_2 depends on many parameters, e.g. the concentrations of the organic contaminant, oxygen and other auxiliary oxidants, the form of the TiO_2 present in the system (suspension, supported), light characteristics, temperature, pH, etc. Despite the fact that the number of parameters affecting photocatalysis is large, this study focused on those considered to be the most important in terms of cost and performance. They include the concentration of phenol, ([DOC] = 15, 50 or 100 mgC L^{-1}), the presence of hydrogen peroxide acting as an auxiliary generator of ·OH radicals, the irradiation source (germicidal or black light lamps), and the reactor geometry. The value of pH in the experiments was fixed at 7.

Preliminary experiments (not discussed here) were conducted to evaluate the optimized conditions of flow rate of phenol solution, flow rate of air and relative concentration of H_2O_2 (for both reactors).

Possible losses of phenol to the atmosphere caused by air bubbling during the irradiation were also investigated, while the photolysis of phenol, the degradation rates obtained in the absence of catalyst and the adsorption of the target compound onto the supported catalyst were also evaluated.

It was observed that the photolysis of phenol in an aqueous solution, exposed to the germicidal lamp, accounts for approximately 10 % degradation, which is higher than that observed with black light (about 2 %). This is expected since the germicidal lamp has emission in the 254 nm region, which is strongly absorbed by phenol. Black light has a strong emission at 365 nm, which is not energetic enough to promote irreversible chemical changes in the phenol molecule.

Influence of the photon sourceand the presence of H_2O_2

To carry out this study, reactor 2, with 7,0 cm outer diameter, and an active (illuminated) area of 770 cm^2 were used, and the

illumination was provided using either a high-pressure 15 W germicidal lamp or a black light lamp. The experiments were performed using phenol solutions with [DOC] = 15, 50 e 100 mgC L^{-1}, in the presence and in the absence of hydrogen peroxide.

Figures 3 and 4 show the influence of the photon source as well as the presence of hydrogen peroxide on the photocatalytic conversion of dissolved organic carbon obtained at different phenol concentrations as a function of the irradiation time, using the reactor 2.

(a)
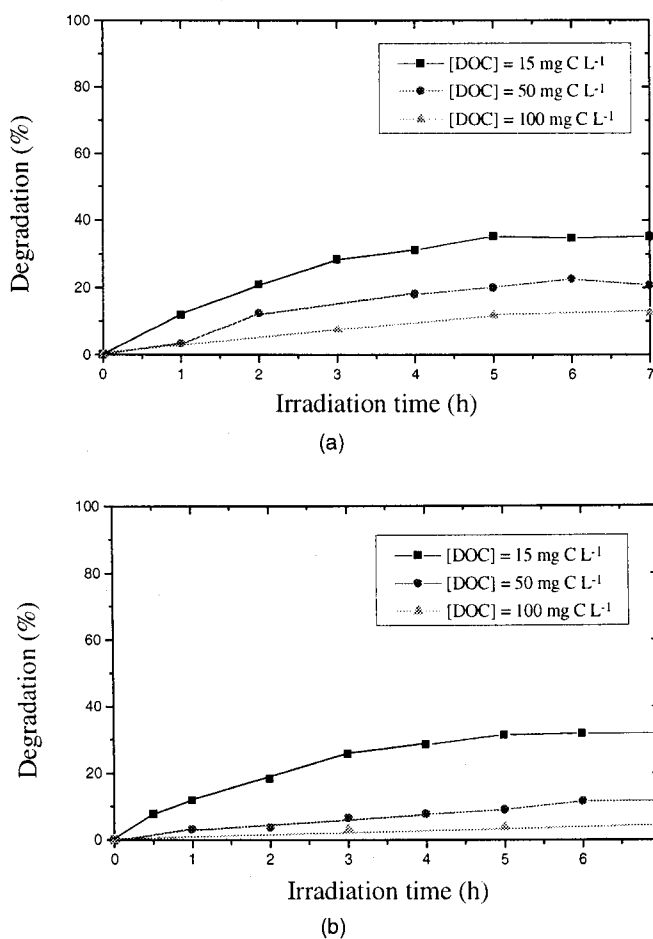

(b)

Figure 3. Degradation of phenol using reactor 2 and the black light lamp (a) in the presence and (b) in the absence of H_2O_2.

A common trend in all 4 graphs is centered on the fact that, independent of the photon source used, the higher the concentration of phenol, the lower the destruction rate observed. This behavior was also observed by Tseng and Huang[11] and Trillas et al[22].
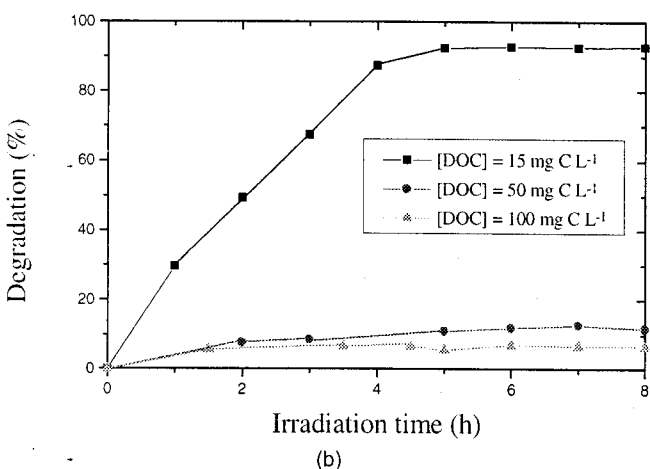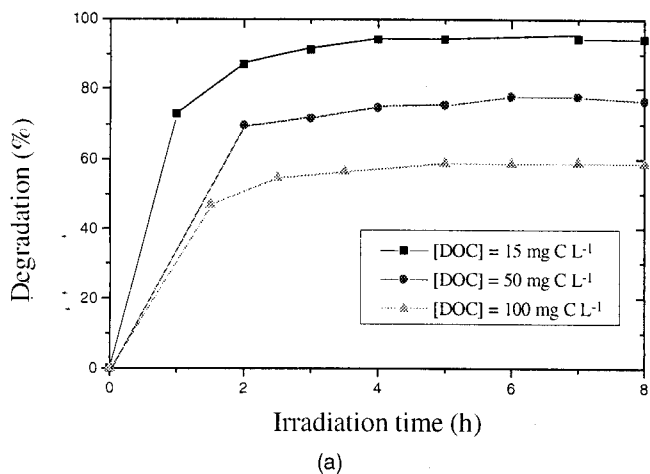
(a)

(b)

Figure 4. Degradation of phenol using reactor 2 and the germicidal lamp (a) in the presence and (b) in the absence of H_2O_2.

The use of H_2O_2 as an auxiliary oxidizing agent also improves the degradation of phenol due to the fact that this molecule contributes as an additional source of ·OH radicals when exposed to UV radiation[23].

However, degradation rates differ markedly as a function of the photon source. For instance, for a 15 mgC L^{-1} solution, the destruction of phenol reaches 92% after 6 h of exposure to the germicidal lamp, but under black light exposure, the destruction reaches only 32% in the same time.

Influence of the reactor geometry and the presence of H_2O_2

Another parameter studied in this document is the reactor geometry, which implies changing the ratio of light intensity

to the illuminated area of the catalyst. To carry out this study, two different reactors were used: (a) reactor 1 with 3,3 cm outer diameter and an active (illuminated) area of 373 cm^2, and (b) reactor 2 with 7,0 cm outer diameter and an active (illuminated) area of 770 cm^2. The illumination was provided using a high-pressure 15 W germicidal lamp ·and the experiments were performed using the same phenol solutions as described in the first part of this work (measured as Dissolved Organic Carbon, [DOC] at 15, 50 and 100 mgC L^{-1}), in the presence and in the absence of hydrogen peroxide.

Figures 4 and 5 show the effect of the reactor geometry and the presence of hydrogen peroxide on the photocatalytic degradation of dissolved organic carbon present in solutions of phenol with different concentrations, as a function of the irradiation time, using the germicidal lamp.
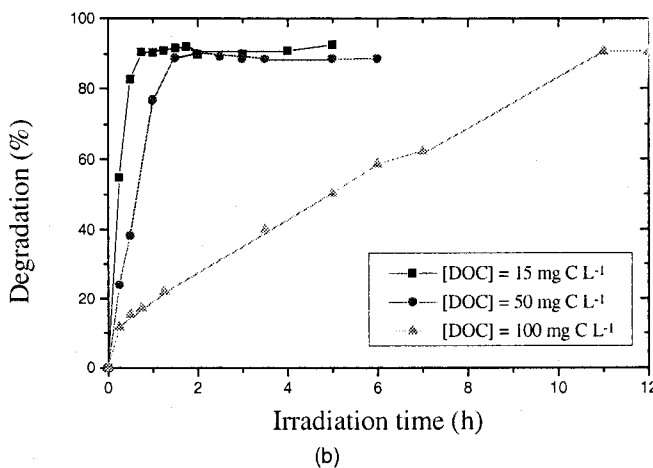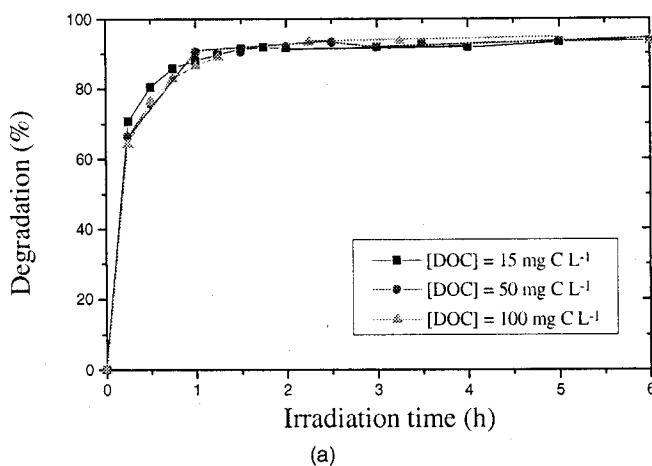

(a)

(b)

Figure 5. Degradation of phenol using reactor 1 and the germicidal lamp in the presence (a) and in the absence (b) of H_2O_2.

The presence of hydrogen peroxide in the reaction system produces an increase in the efficiency of the degradation process, since it acts as an additional source of hydroxyl radicals ($\cdot$OH)[23]. However, in the presence of larger amounts of H_2O_2, degradation is inhibited. This behavior can be explained because hydrogen peroxide can compete with oxygen as an electron acceptor and, consequently, this scavenging action tends to decrease the oxidation rate[13,14].

Figure 5(a) shows that, when in the presence of H_2O_2, reactor 1 performs almost equally for the different phenol solutions, reaching 95% destruction in 90 min.

Figure 5 (b) shows that, in the absence of H_2O_2, the time needed to reach maximum destruction, attained at steady state, decreases as the phenol concentration decreases. It changes from 1 h for a 15 mgC L^{-1} solution, to 2 h for a 50 mgC L^{-1} solution, while finally, the 100 mg L^{-1} solution needs 11 h to reach the same extent of degradation.

Figure 4 shows the results obtained in similar experiments performed with reactor 2. In this case, the performance in the absence of H_2O_2 is very poor when compared to reactor 1 (Figures 4 (b) and 5 (b)). Despite the fact that, at 15 mgC L^{-1}, phenol can be destroyed at rates around 93%, when the concentration increases to 50 and 100 mgC L^{-1}, the destruction rates barely reach 20%. Figure 4 (a) shows that the use of H_2O_2 improves the destruction of more concentrated phenol solutions, but the overall destruction remains below 80%.

Assuming the central annulus as the only source of photons to be delivered to the solution, the intensity of the radiation decreases as one moves towards the bulk solution, according to the absorbing capacity of the aqueous medium. Assuming the molar absorptivity (e) of phenol as 398 L $mol^{-1}cm^{-1}$ (at 254 nm), with 19 for H_2O_2 at this same wavelength, the total absorbance of photons (A) at a given point in the solution is given by:

$$A = e_p.b.c_p + e_h.b.c_h \qquad (12)$$

Where the first term is the absorption contribution due to the phenol and the second term is the contribution due to the hydrogen peroxide. The term e has already been described, b is the optical path (distance from the lamp to a given point at the bulk solution, in cm), and c is the molar concentration of the absorbing species at any given time.

Taking as an example the photodegradation of 100 mg L^{-1} of carbon (1,39 mmol L^{-1} as phenol) being destroyed in both reactors and in the presence of 242 mmol L^{-1} of H_2O_2, the maximum absorbance (worse case scenario) occurs at the beginning of the experiment, when the concentration of both absorbing species is maximum. According to the Beer-Lambert equation, the absorption of photons by the solution drops in an exponential way as one moves away from the lamp with an attenuation of 90% for every 0,2 cm in the reaction medium. In reactor 1, the amount of photons that reach the wall containing the catalyst is around 2,3 u.a. Considering that the distance of reactor 1 (d1) is 0,45 cm (the inner annulus has a diameter of 2,4 cm) while this distance in reactor 2 is 2,3 (d2), the ratio d2/d1 is 5,1, which means that the intensity of photons reaching the catalyst in reactor 2 is at least 10^9 times lower than the one reaching the inner wall of reactor 1. In the geometry with the longer distance, the catalyst area doubles (770 cm^2 and 373 cm^2), but with a significant cost in terms of the light intensity reaching the active area of the reactor.

Despite this difference in the amount of photons reaching the catalyst coated walls of both reactors, the results obtained showed that reactor 2 presented a better performance than reactor 1, indicating that there is an excess of photons in both cases.

To better provide comparisons of the results obtained, carbon degradation rates (expressed as mgC h^{-1}) were calculated for all experimental setups using the carbon load instead of carbon concentration in the feeding solution. The carbon load is calculated according to eq. 13.

$$\text{Carbon Load} = [DOC]_0 \ (mgC \ L^{-1}) \times Q_{sol} \ (mL \ min^{-1}) \times 10^{-3} \ L \ mL^{-1} \times 60 \ min \ h^{-1} \qquad (13)$$

When the reactor reached the steady state in the upflow continuous (single-pass) mode, the carbon removal rate was then calculated according to the maximum degradation rate observed, and the values are shown in Table 2.

Table 2. Calculated values of carbon removal rates for phenol (mgC h^{-1})

System	[DOC] Initial (mgC L^{-1})	Degradation rate (mgC h^{-1})		
		Germicidal light Reactor 1	Germicidal light Reactor 2	Black light Reactor 2
Single pass without H_2O_2	15	0,92	9,63	2,62
	50	3,41	3,87	3,46
	100	6,45	4,25	2,47
Single pass with H_2O_2	15	1,16	9,46	3,16
	50	3,73	24,6	6,74
	100	6,59	36,8	7,50

The results presented in Table 2 show that destruction rates increase with the increase of the concentration of phenol solution as well as with the addition of hydrogen peroxide. The majority of the results obtained with reactor 2 yield higher rates of degradation and, as expected, experiments with the germicidal lamp also produced higher rates of degradation.

In heterogeneous photocatalysis it is difficult to determine efficiency due to the lack of standard procedures. Recently, to overcome this problem, Bolton et al.[24] proposed the use of two parameters to evaluate photocatalytic processes applied to waste treatment technologies. The authors assumed that the electrical energy consumption is a function of two phenomenological kinetic order regimes: a zero order for high contaminant concentrations (electrical energy per mass, EE/M), not the case in this study, and first order kinetics for low concentrations (electrical energy per order of magnitude per m^3, EE/O).

The EE/O value (in kWh m^{-3} order[1]) can be calculated using the following equation for flow-through operations, the lower the EE/O values, the better the performance of the reactor[24].

$$EE/O = \frac{P}{Q.\log(C_i/C_f)} \quad (14)$$

where:

P is the rated light power (kW) (0,015 kW in this study); Ci e Cf are the initial and final concentrations of C (mol L^{-1}). Q is the water flow rate (m3 h-1)

Energy consumption values were calculated for all the experimental conditions tested, as shown in Table 3. The results show that for the majority of the results, energy consumption increases with increasing concentrations of the phenol solution and decreases in the presence of hydrogen peroxide. Again, experiments using reactor 2 yield lower values of energy consumption and the experiments using the black light lamp produce higher values of energy consumption.

Table 3. Calculated values of energy consumption (EE/O, kWh m^{-3} order[1]) for the degradation of phenol

System	[DOC] Initial (mgC L^{-1})	Energy consumption EE/O (kWh m^{-3} order[1])		
		Germicidal light Reactor 1	Germicidal light Reactor 2	Black light Reactor 2
Single pass without H_2O_2	15	183	22	150
	50	205	424	455
	100	-	803	1370
Single pass with H_2O_2	15	175	20	132
	50	171	38	224
	100	171	65	429

The quantum yield represents the content of destroyed organic compound for each absorbed photon[4]. The f value (in %) can be calculated using equation 15:

$$\phi = \frac{\text{Amount of organic compound destroyed}}{\text{absorbed photons}} \quad (15)$$

In heterogeneous photocatalytic processes, the quantum yield must be calculated with the photons that reach the system by using an actinometer[25]. Table 4 shows the quantum yield values for all the experiments. The results show that the quantum yield, in the majority of the results, increases with the increase of the concentration of the phenol solution and with the addition of hydrogen peroxide.

Table 4. Calculated values of quantum yield for the degradation experiments of phenol

System	[DOC] Initial (mgC L^{-1})	Quantum yield (%)		
		Germicidal light Reactor 1	Germicidal light Reactor 2	Black light Reactor 2
Single pass without H_2O_2	15	0,4	4,6	6,7
	50	1,6	1,9	8,9
	100	3,1	2,0	6,3
Single pass with H_2O_2	15	0,6	4,6	8,1
	50	1,8	11,9	17,3
	100	3,2	17,8	19,3

Conclusions

The photocatalytic destruction of phenol with TiO_2 in an upflow reactor is feasible. The results show that the degradation experiments using the germicidal lamp yield better performances than the ones using the black light lamp. This behavior can be partially explained by the fact that the germicidal lamp has a emission band in the UV region, 254 nm, that not only causes the photolysis of phenol, but also splits the H_2O_2 molecule into two ·OH. The black light lamp, with an emission in the range of 365 nm, does not cause a similar effect due to the low energy of its photon. Besides, the emission intensity of the germicidal lamp (4,8 x 10^{-6} Es[-1]) is higher than that of the black light lamp (9,0 x 10^{-7} Es[-1]). Experimental results also show that the production of hydroxyl radicals by TiO_2 alone limits the process. Thus, the addition of an additional source of ·OH, such as H_2O_2, improves the performance of the TiO_2/UV process

According to the results presented, it was concluded that the experiment with the better performance used a phenol solution with [DOC] = 100 mgC L-1, in the presence of

hydrogen peroxide in photoreactor 2, where the highest degradation rate and quantum yield, coupled to the lowest energy consumption, were achieved.

Despite the fact that, in photoreactor 2, the optical pathway measured from the photon source to the wall of the annulus where the photocatalyst was fixed is about 5 times the one found in photoreactor 1, the overall performance obtained in the destruction of phenol in the presence of H_2O_2 was higher. This means that, even when the radius increases from 0,45 to 2,3 cm, the hydrodynamics allow the constant renewal of the catalyst with respect to the substrate and that, in both cases, there is an excess of photons being generated by the germicidal lamp.

The results also show that the photocatalytic degradation of phenol using UV/TiO_2 and H_2O_2 as an auxiliary oxidant is feasible and is a promising process to destroy this target compound to complete mineralization to CO_2 and H_2O.

SYMBOLS USED

AOP	Advanced Oxidation Process
DOC	Dissolved Organic Carbon
EE/M	Electrical energy per mass
EE/O	Electrical energy per order of magnitude per m3
CB	Conduction Band
VB	Valence Band
UV	Ultraviolet
h_{VB}^+	Hole in the valence band
e_{CB}^-	Electron in the conduction band
•OH	Hydroxyl radical
o.d.	Outer diameter
i.d.	Inner diameter
ε	Molar absortivity
A	Total absorbance
b	Optical path
c	Concentration (mole L -1)
d	Distance between the catalyst and the light source
Q	Effluent flow rate
P	Rated Power
C_i and C_f	Initial and final concentrations of the compound
ϕ	Quantum yield

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