

Mathematical modelling of phenol photooxidation: Kinetics of the process toxicity

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Abstract

This work reports the kinetic analysis of the photochemical degradation of phenol making use of the evolution of parameters such as the total organic carbon (TOC), toxicity of the treated water (TU), and oxidant concentration H_2O_2 . The experimental study was carried out working with an initial concentration of phenol of 1000 mg L^{-1} , with a constant flux of radiation of $8.8 \times 10^{-5} \text{ einstein s}^{-1}$ and a variable initial concentration of the oxidant in the range between $17\,000 \text{ mg L}^{-1}$ and $51\,000 \text{ mg L}^{-1}$. The obtained results of TOC fitted to a first order kinetic law whereas zero order kinetics was found to describe H_2O_2 evolution. The decrease of the toxicity followed a constant trend related to TOC, being the ratio TU/TOC dependant on the initial H_2O_2 concentration.

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1. Introduction

Chemical remediation of wastewaters is one of the main objectives in modern environmental chemistry. Because of their toxicity and the frequency of their presence in industrial wastewaters, phenol and substituted phenol compounds have gained increased attention in the last two decades. Moreover, phenol is considered to be an intermediate in the oxidation route of higher molecular weight aromatics, so it is usually taken as a model compound in research studies dealing with advanced wastewater treatments [1].

In order to reduce the environmental impact of harmful phenolic compounds, attention has to be focused on reducing the toxicity of wastewater by eliminating the discharge of these toxic substances or making them less harmful. In this sense, bioassays can complete the chemical characterization of some effluents. The results can be an index of their potential ecological impact [2]. Furthermore, the introduction of the integrated pollution prevention and control (IPPC) regulations requires to control the toxicity of industrial liquid effluents, making toxicity an additional parameter in the wastewater treatment.

Generally, adsorption on activated carbon, air stripping or precipitation were the conventional treatments applied to such

effluents. Nevertheless, these methods transfer the pollutant from water to another phase and, hence, produce secondary wastes. Biological treatment using microorganisms to metabolize the pollutants is a technique broadly applied to the treatment of wastewater. However, a large number of compounds cannot be destroyed by this treatment [3]. Research on alternative methods of wastewater treatment is a matter of current interest.

Advanced oxidation processes (AOPs) are attractive technologies to destroy organic contaminants. AOPs are studied in several combinations but they are all based mainly on the generation of hydroxyl radicals (OH^\bullet), an unstable and very reactive species, resulting in the destruction of the contaminant organic compound due to their high oxidant power [4–6].

The combination of ultraviolet light and H_2O_2 has great potential and could be applicable for the conversion of many types of organic contaminants into mainly CO_2 and H_2O [7]. Moreover, it may occur in nature itself considering the potential applicability of solar radiation as a substitute of artificial UV lamps which increases the interest in this type of process due to the use of a natural resource and the development of a sustainable process.

Degradation of phenol by different AOPs, including UV-based processes, has been reported in the literature [8–14]. It is well known that phenol oxidation treatments lead to the generation of highly toxic intermediate products [1], and there is scarcity of toxicity and environmental impact studies. Besides,

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if there is H₂O₂ in the final effluent, it also contributes considerably to its toxicity [15]. Therefore, additional studies of the intermediate products and their toxicities are essential to describe the UV/H₂O₂ oxidation of phenol.

In this work, the degradation process of phenol in polluted water by UV/H₂O₂ has been studied. An experimental design was carried out to investigate the influence of operation variables. Finally, a generalized kinetic model is developed in order to determine the kinetic behaviour of the main operation variables.

2. Experimental

2.1. Reagents

Phenol (99%, Panreac) and H₂O₂ (35% (w/w), Solvay Interlox) were used as reagents. Deionized water supplied by a Milli-Q water purification unit (Millipore Waters) was used.

2.2. Apparatus

The experiments were performed in a batch cylindrical glass photoreactor of 0.8 L. It included a medium-pressure Hg lamp TQ 150 (150 W) with a wavelength emission at 200–450 nm (Heraeus Nobelight) immersed in a quartz sleeve placed in the middle of the reactor, which was surrounded by a cooling jacket to maintain a constant temperature thanks to a bath with digital controller (PolyScience). The photon flux entering the reactor was 8.8×10^{-5} einstein s⁻¹ estimated from hydrogen peroxide actinometry [16]. A magnetic stirrer (Selecta Agimatic-S) was used to provide proper mixing.

2.3. Procedure

For a standard run, 0.75 L of aqueous solution were used. The initial phenol concentration was 1000 mg L⁻¹. The H₂O₂ concentration varied in the range of 0–1.5 M. The initial pH value was in a range of 3.5–4. The reaction was carried out at no buffered pH and constant temperature (293 K).

2.4. Analytical determinations

Phenol and identified reaction intermediates (catechol, hydroquinone and *p*-benzoquinone) were measured by a Waters high-pressure liquid chromatograph (HPLC) using a Supelco reversed-phase column LC-8 and a photo diode array (PDA) detector. A Dionex 120 ion chromatograph (IC) equipped with a column IonPac AS9-HC and a conductivity detector was used for organic acids analyses.

The toxicity of the samples was determined by means of a bioassay following the standard ISO 11348-3 (1998) [17] based on the decrease of light emission by photobacterium phosphoreum with a Microtox M500 analyzer (Azur Environmental).

Total organic carbon (TOC) analyses were performed using an analyzer Euroglas model TOC 1200. H₂O₂ concentration was analyzed by iodometric titration. pH was recorded using a pHmeter (Hanna Instruments).

3. Results and discussion

3.1. Kinetic model for phenol degradation

Experiments using only H₂O₂ as oxidant agent were carried out. It was verified experimentally that degradation of phenol was negligible.

3.1.1. Degradation by UV photolysis

Some runs were performed using ultraviolet radiation alone. In this case, a low rate of degradation was observed and only 26% of phenol removal was achieved after 600 min for an initial phenol concentration of 1000 mg L⁻¹ (1.06×10^{-2} M).

The reaction quantum yield is defined for monochromatic radiation and assumes monophotonic absorption. When polychromatic light sources are used for pollutant treatment quantum efficiency can be defined as the ratio of the number of molecules of product formed to the number of photons absorbed in the spectral region [18].

The rate of direct photolysis of an organic compound *i* is usually described by equation (1) which is a combination of Stark–Einstein law and Lambert–Beer law [18–20]:

$$-\frac{dC_i}{dt} = I_0 \Phi_i f_i \left[1 - \exp \left(-2.3L \sum_{j=1}^N \varepsilon_j C_j \right) \right] \quad (1)$$

where Φ_i is the quantum yield of the *i* compound, I_0 the incident flux of radiation, f_i the ratio of light absorbed by *i* to that absorbed by all components of the solution, L the effective path length of the photoreactor, and ε_j is the molar extinction coefficient of the *i* species.

When the only compound absorbing UV radiation is the substrate *i* ($f_i = 1$) and the optical density ($L\varepsilon_i C_i$) is lower than 0.1 (i.e., substrate concentration is relatively low), Eq. (1) can be simplified to a first-order expression [19]:

$$-\frac{dC_i}{dt} = 2.3L I_0 \Phi_i \varepsilon_i C_i \quad (2)$$

This equation is often used for the determination of quantum yield. I_0 is known by actinometry experiments. $\varepsilon_{\text{phenol}}$ was 516 M⁻¹ cm⁻¹ at 254 nm according to published literature [8,21] and the reactor light path was 2 cm. The Φ_{phenol} was calculated from the slope of a plot $-\ln(C/C_0)$ versus t ($r^2 = 0.97$). A value of 0.0014 mol einstein⁻¹ was obtained.

3.1.2. Degradation by UV/H₂O₂ process

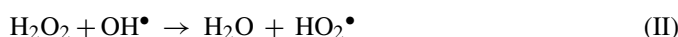
UV/H₂O₂ experiments were conducted working with this same initial phenol concentration and hydrogen peroxide doses were varied between 0.5 M and 1.5 M to determine the effects of the H₂O₂/phenol ratio. The addition of H₂O₂ to the system greatly enhanced phenol degradation compared to direct photolysis even at low initial H₂O₂ concentration due to the generation of OH• radicals (reaction (I)) [4,22].

However, H₂O₂ concentration had two opposing effects on the reaction rate. Increasing the initial hydrogen peroxide concentration enhanced the oxidation process up to a certain concentration, when hydrogen peroxide started to react with

Table 1
Rate constants experimentally obtained for phenol, TOC and H₂O₂ degradation for several initial H₂O₂ concentrations

[H ₂ O ₂] ₀ (M)	<i>k</i> _{ph} (×10 ⁻² min ⁻¹)	<i>r</i> ²	<i>k</i> _{TOC} (×10 ⁻³ min ⁻¹)	<i>r</i> ²	<i>k</i> _{H₂O₂} (×10 ⁻³ M min ⁻¹)	<i>r</i> ²
0.5	3.7	0.99	3.2	0.96	1.1	0.98
0.75	4.6	0.91	4.1	0.98	1.7	0.98
1.0	6.7	0.99	4.8	0.97	2.1	0.97
1.5	5.1	0.99	3.4	0.99	2.1	0.99

hydroxyl radicals. At higher hydrogen peroxide concentrations, reaction (II) became important and hydrogen peroxide acted as a free-radical scavenger itself decreasing the hydroxyl radicals concentration so, there was an optimum H₂O₂ concentration [7,8]:



For all the experiments more than 88% of phenol removal was achieved after 60 min of irradiation and total degradation was achieved after 120 min. An optimum H₂O₂ concentration of 1.0 M (initial H₂O₂/phenol molar ratio = 100) was found [8].

The reaction rate constants *k*_{ph} were calculated based on the pseudo-first-order kinetics assumption (Eq. (3)) by linear regression of the experimental data:

$$-\frac{dC_{\text{ph}}}{dt} = k_{\text{ph}}C_{\text{ph}} \quad (3)$$

where *C*_{ph} is the phenol concentration at time *t*. Table 1 confirms the existence of an optimal dose of H₂O₂ at a concentration of 1.0 M.

3.2. Kinetic model for TOC removal

In general, the oxidation rate is calculated following the disappearance of the target compound as a function of time. But due to the possibility of intermediate species formation, the total degradation of the target compound does not always correspond to the total mineralization of the organics to CO₂ and H₂O [23]. So, TOC is a global parameter that is frequently analyzed.

Decrease of TOC was slower than phenol decrease because intermediate organic compounds were formed during the oxidation. Catechol, hydroquinone and several organic acids, i.e., oxalic, acetic, formic, maleic and malonic acids, were identified (Fig. 1).

The pseudo-first-order kinetic constants *k*_{TOC} determined for TOC removal are shown in Table 1. According to the determined parameters, the optimum value of 1.0 M for the initial H₂O₂ concentration was confirmed.

3.3. Kinetic model for H₂O₂

The values of the mass ratio H₂O₂/phenol ranged from 17 to 51, which represents an excess over the stoichiometric ratio between 3 and 10 times approximately [8,24]. If low values of the ratio are used, phenol cannot be fully mineralized and the intermediate compounds would remain in the solution [25].

Besides, it is interesting to obtain the optimum dosage of H₂O₂, so a wide range of concentrations should be studied.

A zero-order kinetic expression was found to describe the degradation of H₂O₂ during the oxidation (Eq. (4)) as it had already been reported [25,26]. The values of the kinetic parameters *k*_{H₂O₂} are shown in Table 1:

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 - k_{\text{H}_2\text{O}_2}t \quad (4)$$

Similarly, a maximum value of *k*_{H₂O₂} was observed at an H₂O₂ concentration of 1.0 M. It was also observed that for reaction times higher than 550 min the H₂O₂ had disappeared completely from the reaction medium. That was important because an excess of H₂O₂ concentration at the end of the process would be harmful from the economic and environmental points of view due to its contribution to the toxicity level of the effluent.

The *k*_{H₂O₂} dependence on the initial H₂O₂ concentration could be understood considering that phenol and its degradation intermediates could compete with hydrogen peroxide for the available radiation [26] and the value of the H₂O₂/TOC ratio was different in each experiment. Then, as the value of

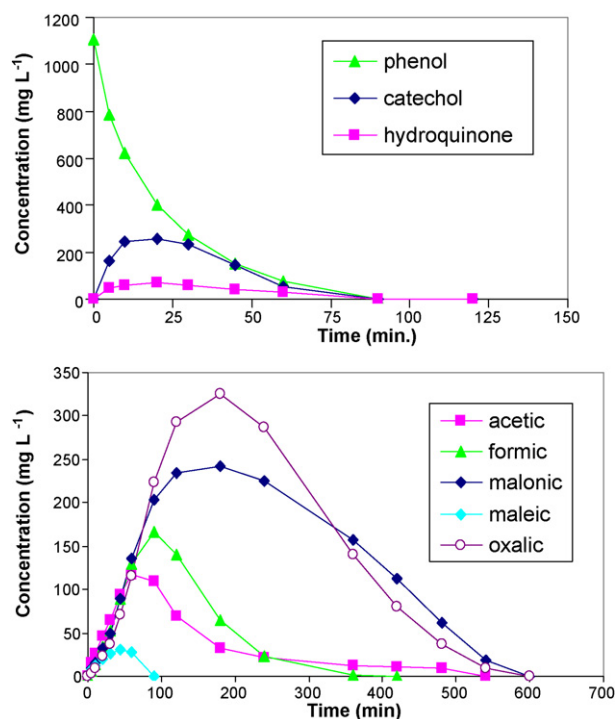


Fig. 1. Phenol and intermediate compounds concentrations during the photooxidation process for initial hydrogen peroxide concentration of 1.0 M (initial phenol concentration = 0.01 M, initial pH 3.5, *T* = 293 K).

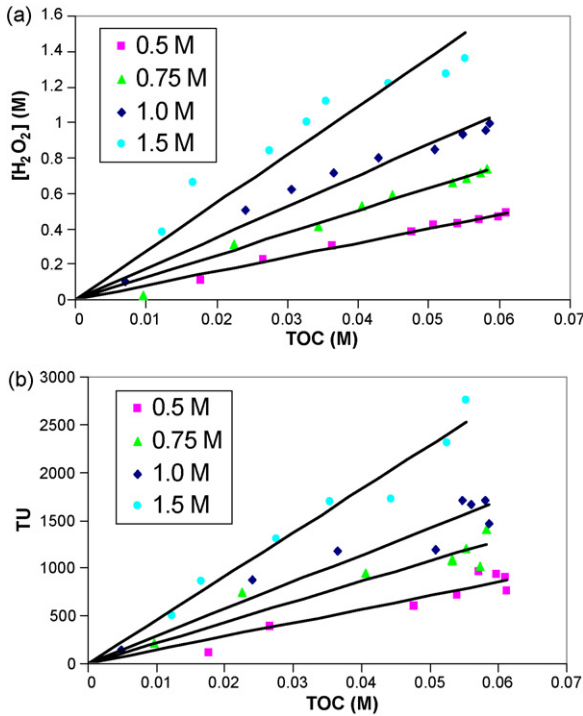


Fig. 2. Empirical relationship between (a) the H_2O_2 concentration and the TOC degradation and (b) toxicity level (TU) and TOC, for several H_2O_2 initial concentrations.

the $\text{H}_2\text{O}_2/\text{TOC}$ ratio increases, the fraction of photons absorbed by H_2O_2 increases leading to an increase in the disappearance rate of H_2O_2 [27].

Moreover, an empirical relationship between H_2O_2 and TOC was found (Eq. (5)). The value of the $\text{H}_2\text{O}_2/\text{TOC}$ ratio (R_1) was dependent on the initial H_2O_2 concentration (Eq. (6)) in the range of operation variables studied (Fig. 2a):

$$\text{H}_2\text{O}_2 = R_1 \times \text{TOC} \quad (5)$$

$$R_1 = 17.68[\text{H}_2\text{O}_2] \quad (r^2 = 0.99) \quad (6)$$

Eq. (5) shows that TOC removal is proportional to the amount of H_2O_2 available in the solution as it could be expected. Furthermore, this relationship allows the determination of the TOC content from the analysis of the amount of H_2O_2 in the sample, thus simplifying the analytical characterization of the effluent.

3.4. Generalized modelling of the photodegradation process

The kinetic equation describing a substrate degradation with a concentration C_i by the UV/ H_2O_2 process takes into account both its direct photolysis by UV and its degradation by OH^\bullet radicals formed through hydrogen peroxide photolysis (Eq. (7)) [18,19,28]:

$$-\frac{dC_i}{dt} = kC_iC_{\text{OH}^\bullet} + 2.3LI_0\Phi_i\varepsilon_i f_i C_i \quad (7)$$

where Φ_i is the quantum yield of the i compound, I_0 the incident flux of radiation, f_i the ratio of light absorbed by i to that absorbed

by all components of the solution, L the effective path length of the photoreactor, and ε_i is the molar extinction coefficient of the i species. The terms $(kC_iC_{\text{OH}^\bullet})$ and $(2.3LI_0\Phi_i\varepsilon_i f_i C_i)$ represent the specific contributions of OH^\bullet radicals and UV radiation to the overall oxidation reaction, respectively.

At the beginning of the treatment, when the extent of substrate degradation is negligible, the UV contribution is constant as f_i is constant. Integrating Eq. (7) leads to

$$\ln\left(\frac{C_i}{C_{i0}}\right) = -(kC_{\text{OH}^\bullet} + 2.3LI_0\Phi_i\varepsilon_i f_i)t \quad (8)$$

Thus, a pseudo-first-order rate constant can be used as the concentration of OH^\bullet radicals can be assumed constant over the range of reaction variables and function of the initial H_2O_2 concentration, and thus it can be included as part of the rate constant [19]. Therefore, Eq. (8) leads to

$$-\ln\left(\frac{C_i}{C_{i0}}\right) = (k_{\text{OH}^\bullet}[\text{H}_2\text{O}_2]_0 + k_{\text{UV}})t = k't \quad (9)$$

where k_{OH^\bullet} ($k_{\text{OH}^\bullet} = kC_{\text{OH}^\bullet}$) and k_{UV} ($k_{\text{UV}} = 2.3LI_0\Phi_i\varepsilon_i f_i$) represent the kinetic constants of the radical and photolysis oxidation pathway respectively and k' ($k' = k_{\text{OH}^\bullet}[\text{H}_2\text{O}_2]_0 + k_{\text{UV}}$) is the pseudo-first-order constant.

The same assumptions made to develop Eq. (9) were used to describe the evolution of the global TOC parameter (Eq. (10)) when C_i is substituted by TOC in Eq. (7). The kinetics can be described by the following generalized equations:

$$-\frac{d\text{TOC}}{dt} = (k_{\text{OH}^\bullet}[\text{H}_2\text{O}_2]_0 + k_{\text{UV}})\text{TOC} = k'\text{TOC} \quad (10)$$

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{\text{H}_2\text{O}_2} = k'_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]_0 \quad (11)$$

The system of ordinary differential equations was solved using gPROMS software (PSE Ltd., UK). Therefore, the simultaneous resolution of the model equations and the experimental data with the minimum standard deviation (Eq. (12)), led to values of the parameters $k'_{\text{H}_2\text{O}_2}$, k_{OH^\bullet} and k_{UV} of $2.02 \times 10^{-3} \text{ min}^{-1}$, $4.50 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$ and $4.61 \times 10^{-4} \text{ min}^{-1}$, respectively with deviations between 7.12% and 10.31%:

$$S = \sqrt{\frac{\sum_{i=0}^n [(C_{\text{exp}} - C_{\text{model}})/C_{\text{exp}}]^2}{n-1}} \quad (12)$$

where C_{exp} and C_{model} were experimental and predicted concentrations respectively and n was the total number of available data.

Fig. 3 shows the comparison between experimental and predicted data corresponding to H_2O_2 and TOC concentrations for several initial H_2O_2 concentrations up to its optimum value. The model predictions describe reasonably well the evolution of both concentrations. Therefore, the reported model and parameters could be useful to predict the concentration of H_2O_2 and TOC for initial H_2O_2 in the range of work.

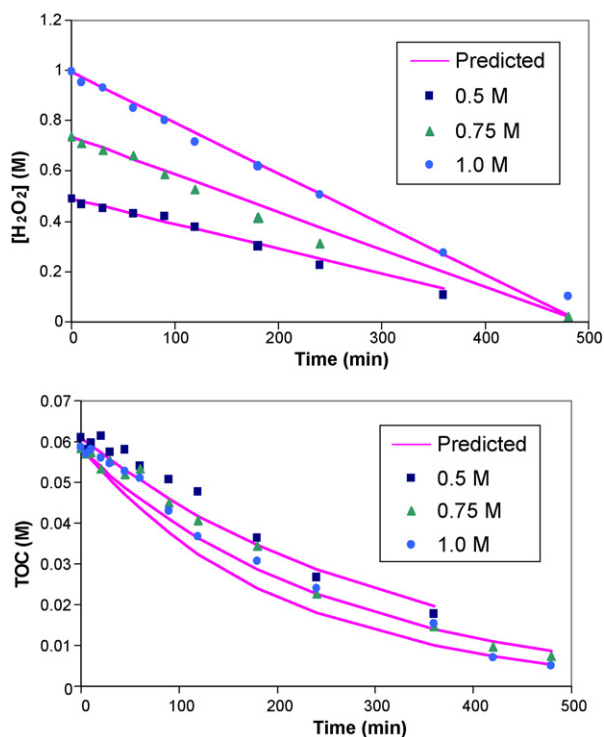


Fig. 3. Comparison between experimental and predicted concentrations of H_2O_2 and TOC for several H_2O_2 initial concentrations.

3.5. Toxicity study in the photooxidation process

The European Directive 2000/60/EC stresses the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants. Several Spanish regions have established a legal limit of toxicity of 25 TU for discharge of wastewater to sewage collectors. Toxicity units (TU) of the wastewaters were calculated as

$$\text{TU} = \frac{100}{\text{IC}_{50}} \quad (13)$$

where IC_{50} must be expressed as the ratio of the initial sample volume to the one yielding, after the required dilution, a 50% reduction of light emitted by the microorganisms.

In AOPs, some intermediate compounds in the oxidation route can present higher toxicity than the initial compound [1,23]. Therefore, from an environmental point of view, it is not sufficient to describe the decrease of phenol concentration. Besides, the existence of hydrogen peroxide must be also considered due to its contribution to the toxicity level. It could be very useful to predict the toxicity of the treated effluent based on common analyses such as H_2O_2 determination or a global parameter as TOC concentration.

The individual toxicity of the main intermediate compounds and hydrogen peroxide was determined, finding values similar to the literature [1,2,29].

It was observed that initially, the main contribution to toxicity was due to H_2O_2 , however, as the photooxidation proceeded, some intermediates such as hydroquinone or *p*-benzoquinone which are more toxic than H_2O_2 appeared in the solution. The

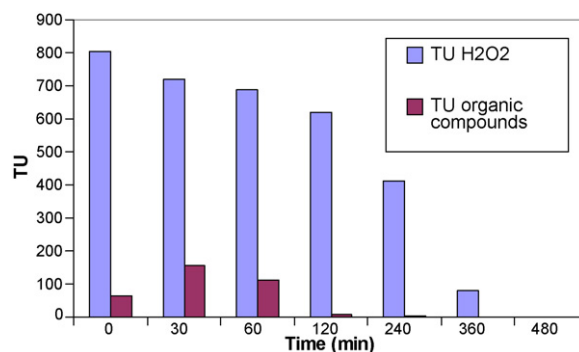


Fig. 4. Contribution of hydrogen peroxide and organic compound concentrations to toxicity level of the solution during the photooxidation process for phenol and H_2O_2 initial concentrations of 0.01 M and 0.5 M, respectively.

toxicity of the initial samples after adding H_2O_2 was between 903 TU and 2749 TU. With the oxidation process there was an important decrease both in the concentration of H_2O_2 as well as in the concentration of the organic substrate expressed as TOC and values of toxicity lower than 25 TU (legal standard) were achieved. Fig. 4 shows the contribution to toxicity of H_2O_2 and the organic compounds during the phenol degradation. Although the toxicity level of the effluent was mainly due to hydrogen peroxide concentration, high dosages had to be used to reduce the TOC concentration to a desired level.

During the experiments a linear relationship between the values of TU and TOC was found (Eq. (14)), as it is shown in Fig. 2b. The TU/TOC ratio (R_2) (M^{-1}) depends on the initial H_2O_2 concentration in the range of operation variables (H_2O_2 concentration between 0.5 M and 1.5 M) (Eq. (15)):

$$\text{TU} = R_2 \times \text{TOC} \quad (14)$$

$$R_2 = 2.99 \times 10^4 [\text{H}_2\text{O}_2] \quad (r^2 = 0.99) \quad (15)$$

Thus, a simple predictive model can be proposed to determine the time needed for the oxidation of the organic compounds to a desired level (toxicity ≤ 25 TU).

4. Conclusions

The present work reports the analysis of the kinetic behaviour of phenol degradation by UV/ H_2O_2 . A simple predictive model based on the description of the kinetics of the main operation variables of the photochemical oxidation process, i.e., TOC, TU and oxidant concentration has been proposed. These are the main conclusions:

- The total organic carbon concentration, TOC, was used as a representative parameter to describe the oxidation kinetic process, finding that it fitted to a first order expression, while zero order kinetics were found for the decrease of H_2O_2 concentration.
- Best results were obtained for an optimum value of H_2O_2 concentration of 1.0 M ($34\,000\text{ mg L}^{-1}$) obtaining a complete mineralization of the organic compounds.
- An empirical relationship between H_2O_2 and TOC was found. $\text{H}_2\text{O}_2/\text{TOC}$ ratio (R_1) was dependent on the initial H_2O_2

concentration in the range of operation variables (H_2O_2 concentration between 0.5 M and 1.5 M).

- The toxicity of the treated water was measured and a linear relationship between the values of TU and TOC was found. The TU/TOC ratio (R_2) (M^{-1}) depends on the initial H_2O_2 concentration in the range of operation variables.

The reported method is a simple way to analyze the kinetic behaviour of the oxidation of organic compounds with the UV/ H_2O_2 process and enables to predict the evolution of environmental parameters namely total organic carbon (TOC), toxicity units (TU), and the remaining concentration of the oxidant H_2O_2 needed in the development of environmental technologies.

Acknowledgments

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