

Utilisation of factorial experiments for the UV/H₂O₂ process in a batch reactor

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Abstract

Factorial experiments provide a comprehensive understanding of the impact of operational variables on process performance. Utilisation of the Hadamard matrix taking into account all interaction effects, appeared to be efficient for giving a mathematical model that conformed to criteria validity. The predictions given by the factorial experiments model were confirmed by the experiments. Phenol oxidative degradation kinetics were not significantly influenced by pH or hardness of the solution to be treated, as is predicted by factorial experiments. On the other hand, initial H₂O₂ concentration, initial phenol concentration and temperature significantly influenced the efficiency of the process. Optimal values were determined: a temperature of about 20°C and a C_{H₂O₂}/C_{phenol} ratio of 120 (mg/mg).

Introduction

Over the last decade several studies have been conducted on the performance of hydrogen peroxide (H₂O₂) and ultraviolet (UV) light in an advanced oxidation process (AOP) which has been successfully utilised for the treatment of various refractory (Doré, 1989; Sundstrom et al., 1990; Legrini et al., 1993; Sapach and Viraghan, 1998; Ho and Bolton, 1998; Von Gunten and Oliveras (1997); Shiraishi et al., 1999; Wenzel et al., 1999; Huston and Pignatello, 1999; Ince, 1999; Wang and Hong, 1999; Andreozzi et al., 2000a; Chiron et al., 2000). These previous studies have given the effect of initial H₂O₂ concentration, initial concentration of the recalcitrant pollutants, and of time and UV light on the performance of the AOP process. Alternatively, various kinetic models for the AOP process using hydrogen peroxide and ultraviolet irradiation have been developed (Turchi and Ollis, 1990; Beltran et al., 1999; Crittenden et al., 1999; Andreozzi et al., 2000b).

The main purpose of this work was to utilise a factorial type experimental design, to determine the effect of each experimental parameter on the performance of the AOP process using H₂O₂ and UV and to establish a mathematical model with a minimum of experiments. This mathematical model may be utilised to explain the phenomenon or to predict the performance of the process without performing the experiment. This last utilisation may be considered to be a simulation (Duea and Girault, 1978). For this purpose, the Hadamard matrix was used. It is an experimental design most frequently used for determining the effect of parameters in an experimental field resulting in a classification with respect to the statistical significance of their influence on the response of the system. This matrix makes it possible to determine the effect of K factors with $K \leq N-1$, where N is the number of the experiments (Perrin and Scharff, 1995).

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A synthetic phenol solution was utilised as a standard solution to test the ability of the factorial type experiments to evaluate the degradation of phenol by the UV/H₂O₂ process. For this purpose a relation between the response parameter function Y representing the remaining phenol concentration, and the operational variables X₁, X₂, X₃, X₄, X₅ and X₆ which represent the peroxide concentration, initial phenol concentration, irradiation time, temperature, pH and hardness of the solution to be treated, was determined.

The first step of the method consisted of the elaboration of the Hadamard matrix, which makes it possible to determine the influent parameter on the response Y. In the second step, a complete Hadamard matrix was applied which provides information about the model and possibilities for its improvement (Goupy, 1988).

The validity of the mathematical model represented by the linear regression was assessed by addressing the following issues: the meaning of the coefficients, analysis of the coefficient of determination (r²), analysis of the residuals, the regression and the confidence interval (Lagrade, 1983). The results obtained with the factorial experiments were then confirmed by an experimental study. Optimum conditions were attained.

Experimental

The experiments were carried out in a cylindrical double-walled reactor with water circulating through the walls to maintain the temperature at the chosen value. The photocatalytic reactor was equipped with a mercury lamp (Kadatyne®, France) with an output of 14 W (Fig. 1), which mainly emits irradiation at 253.7 nm and can be considered to be monochromatic. The solution was stirred by a magnetic stirrer and by a centrifugal pump during the run. The characteristics of the reactor are presented in Table 1.

TABLE 1
Characteristics of the photocatalytic reactor

Parameter	Value
Volume (mℓ)	150
Flow rate (mℓ/s)	14
Reactor space time (s)	10.71

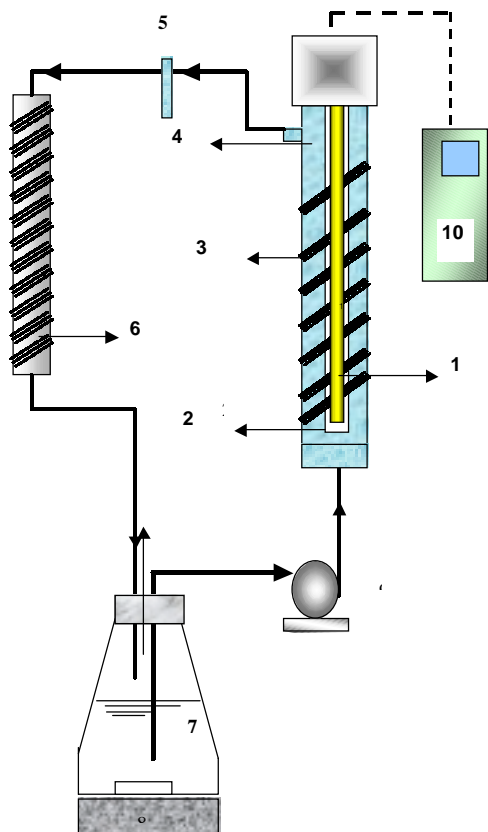


Figure 1
Reactor set-up for UV and UV/H₂O₂ process

- 1) UV Lamp
- 2) Quartz sleeve
- 3) Stainless steel cylindrical reactor
- 4) Cooling water system
- 5) Sample point
- 6) Cooling water system
- 7) Phenolic solution
- 8) Magnetic stirrer
- 9) Centrifugal pump
- 10) Power supply

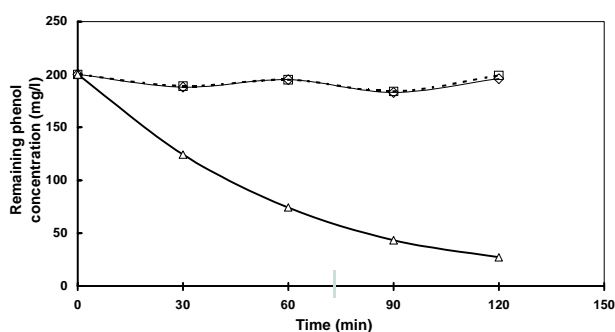


Figure 2
Changes of remaining phenol concentrations for various treatments
 $C_0 = 200 \text{ mg/l}$, $T = 25^\circ\text{C}$ and $C_{\text{H}_2\text{O}_2} = 100 \text{ mmol/l}$
(△) UV/H₂O₂ treatment, (□) UV treatment and (◇) H₂O₂ treatment

Parameter (X_i)		(-1)	(+1)
X_1	H ₂ O ₂ (mmol)	50	300
X_2	Phenol (mmol)	2.12	4.25
X_3	Irradiation time (min.)	30	120
X_4	Temperature (°C)	20	50
X_5	pH	1.8	10.2
X_6	Solution hardness (mgCaCO ₃ /l)	100	800

Analysis

Samples were taken at regular intervals and analysed. The phenol concentration was measured by variable wavelength UV spectrophotometer (MILTON ROY Spectronics 1201) at 270 nm. The excess of hydrogen peroxide was determined by neutralisation with KMnO₄.

Methods

A synthetic phenolic solution was prepared with deionised water and phenol. The phenol concentration of the solutions studied was in the range of 50 to 400 mg/l. The peroxide solution utilised was 50% in mass. The advantage of working with this high concentration is that it adds very little volume (on the order of a microlitre) to the reactor containing the phenolic solution. The peroxide concentration utilised varied between 50 to 200 mM. The temperature, which was maintained constant during each run, ranged between 15 and 50°C. The effect of pH as a parameter on the process performance was studied at various pHs (ranging from 1.8 to 10.2) obtained by the addition of 1 M NaOH solution or 1 M HCl acid solution. The effect of hardness was studied by dissolving various amounts of CaCO₃ dissolved in the reactor vessel. Hardness in the range of 100 to 800 mg/l was studied.

In the establishment of the factorial design using a Hadamard matrix, extreme levels (+1: high level and -1: low level) must be chosen for each experimental parameter used in this study (Table 2).

Results and discussion

Test of the effect of UV and H₂O₂ alone on the treatment of the phenolic solution

In Fig. 2 the results obtained by treating the phenolic solution with ultraviolet light (UV alone), peroxide (H₂O₂ alone) and in combination (UV/H₂O₂) are reported. The results indicate that phenol concentrations remained constant after a UV irradiation reaction time of about 120 min. This result may be explained by the fact that the UV irradiation, when applied in short exposure, is not efficient in degrading pollutants. On the other hand, H₂O₂ utilised alone yielded similar results to those with UV alone, although the H₂O₂ concentration was about 100 mmol. In combination, however, UV and H₂O₂ brought about a drastic reduction in the phenol concentration of the solution treated.

These results may be explained by the fact that the hydroxyl radical HO·, which is a powerful oxidant, is generated by photolysis

of H₂O₂ by UV, making possible the degradation of the phenol molecules present in the solution (Chiron et al., 2000).

It is clear that the process is efficient when the physical treatment (UV irradiation) and chemical treatment (H₂O₂ oxidation) are combined.

Mathematical model

The Hadamard matrix was constructed (Table 3a) and the results were obtained by the application of the least squares method. The results obtained, presented in Table 3b, show that coefficients b₁, b₂, b₃ and b₄ were not negligible. Indeed these values are greater than their standard deviation values and need to be taken into account. These coefficients indicate that the experimental parameters such as H₂O₂ concentration, initial phenol concentration, irradiation time and temperature were significant on the degradation rate of the phenol by the UV/H₂O₂ process. On the other hand, the b₅ and b₆ coefficients, which are linked to the pH and the hardness of the solution to be treated, were practically negligible. Indeed these b₅ and b₆ coefficients standard deviation values indicate that these parameters had little influence on the AOP process performance.

The second step consisted of constructing a mathematical model, which takes into account only the statistically significant parameters. For this purpose a 2⁴ factorial design matrix was used (Table 4). The advantage of using this design is to observe the degradation of the phenol with a minimum number of runs. The mathematical model was refined step-by-step. First, a linear model was used without taking into account parameter interactions. The results obtained were assessed using a coefficient of determination (r²), residuals, regression and confidence interval analyses. This was done to estimate the validity of the model without the interactions (Lagrade, 1983), thus in linearity.

The coefficient of determination (r²= 0.72) obtained showed a poor value compared to unity. This indicates that the linear model did not fit the experimental results without taking into account the interaction effects.

When taking into account 2-way interactions, it is possible to obtain a high coefficient of determination r² of about 0.96. It is clear in this case that the 2nd order model fits the experimental results better than the first approach. However, analysis of the residuals indicated that the distribution in reference to the abscissa was not uniform. Consequently, the model was extended to consider all interactions which may exist between parameters. In the latter case, a correlation coefficient close to unity (R² = 0.99) was obtained, and the resulting mathematical model was in agreement with the validation criteria model (Table 5). The mathematical equation obtained by the least squares method was as follows:

Run	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆
1	1	1	1	-1	1	-1
2	-1	1	1	1	-1	1
3	-1	-1	1	1	1	-1
4	1	-1	-1	1	1	1
5	-1	1	-1	-1	1	1
6	1	-1	1	-1	-1	1
7	1	1	-1	1	-1	-1
8	-1	-1	-1	-1	-1	-1

Coefficients	Values
B ₀	167.7
B ₁	33.3
B ₂	-108.0
B ₃	50.2
B ₄	-25.5
B ₅	0.19
B ₆	0.35

Run	Codified variables				Natural variables				Residual phenol concentration (mg/l)
	X ₁	X ₂	X ₃	X ₄	X ₁	X ₂	X ₃	X ₄	(Y)
1	1	1	1	1	200	400	120	50	70.86
2	1	1	1	-1	200	400	120	20	87.26
3	1	1	-1	1	200	400	30	50	323.00
4	1	1	-1	-1	200	400	30	20	290.00
5	1	-1	1	1	200	200	120	50	50.75
6	1	-1	1	-1	200	200	120	20	43.75
7	1	-1	-1	1	200	200	30	50	100.2
8	1	-1	-1	-1	200	200	30	20	113.34
9	-1	1	1	1	50	400	120	50	329.26
10	-1	1	1	-1	50	400	120	20	275.00
11	-1	1	-1	1	50	400	30	50	385.00
12	-1	1	-1	-1	50	400	30	20	380.00
13	-1	-1	1	1	50	200	120	50	160.00
14	-1	-1	1	-1	50	200	120	20	10.17
15	-1	-1	-1	1	50	200	30	50	20.43
16	-1	-1	-1	-1	50	200	30	20	74.63

TABLE 5
Summary of the results obtained for the establishment of the mathematical model by factorial experiments method

Model	Model without interaction	Model with interactions 2 by 2	Model with multiple interactions
Coefficient of determination (r^2)	0.72	0.96	0.99
Residuals analysis	No uniform distribution	No uniform distribution	Uniform distribution
Regression analysis	This model gave an acceptable simulation of the experiments	This model gave a good simulation of the experiments	This model gave a very good simulation of the experiments

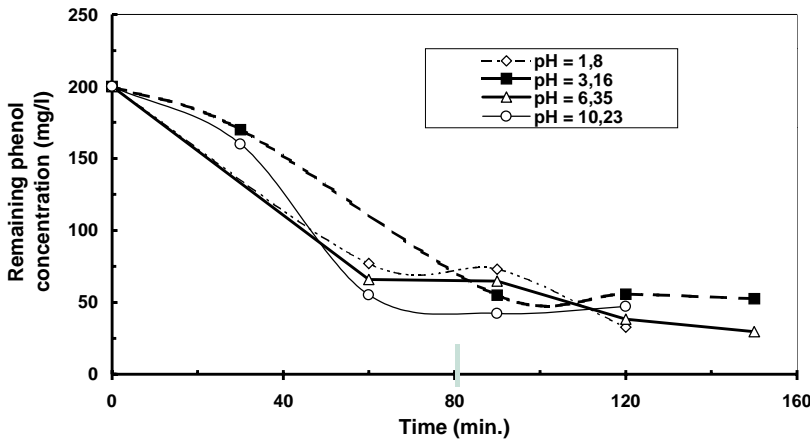


Figure 3a
 Effect of the pH of the kinetic degradation of the phenol by the UV/H₂O₂ process.
 C_O = 200 mg/l, T = 25°C and
 C_{H₂O₂} = 100 mmol/l

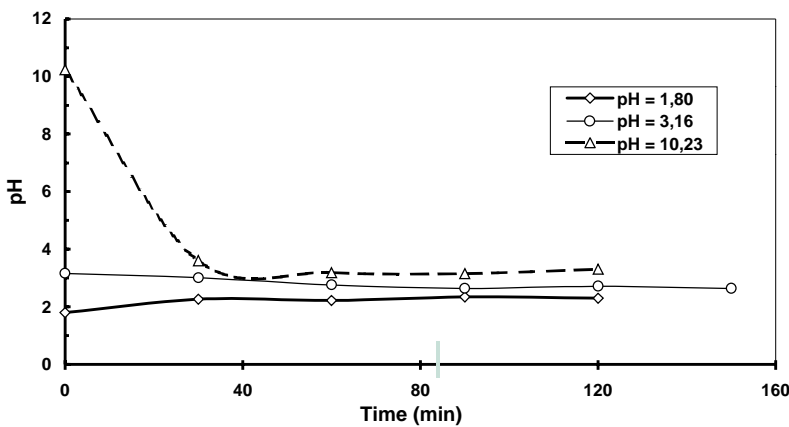


Figure 3b
 Change of the pH of the phenolic solution during treatment with the UV/H₂O₂ process at various initial pHs.
 C_O = 200 mg/l, T = 25°C and
 C_{H₂O₂} = 100 mmol/l

$$\begin{aligned}
 Y = & -193.345466 + 1.17684339 X_1 + 1.54367308 X_2 \\
 & - 1.005026 X_3 - 6.17063443 X_4 - 0.00395244 X_{12} \\
 & - 0.00348682 X_{13} + 0.00640827 X_{14} - 0.00116229 X_{23} \\
 & + 0.01500932 X_{24} + 0.08305249 X_{34} - 0.00014844 X_{124}
 \end{aligned}$$

Before optimisation of the phenol degradation rate was realised, the results obtained from the factorial experiments, i.e. the effects of the pH and the hardness of the phenolic solution on the performance of the process, were tested.

Influence of initial pH and solution hardness on phenol degradation kinetics

The effect of the pH on the phenol degradation kinetic by UV/H₂O₂, presented in Fig. 3a, shows that the remaining phenol concentration

rapidly reached a threshold value of about 50 mg/l, regardless of the initial pH value. These observations confirm the results from the factorial experiments predictions.

pH was monitored during the various experiments. The results, presented in Fig. 3b indicate that the pH of the solution rapidly reached a pH value of about 3. These results may explain the similar performance of the UV/H₂O₂ process with various initial pHs. On the other hand, the pH value obtained was similar to a pH solution saturated by CO₂ gas: pH = 3.9 (Stumm and Morgan, 1972). This indicates that carbon atoms within the phenyl group of the phenol molecules were converted by the oxidation process to CO₂ gas, which by saturation of the solution tends to the equilibrium pH. A similar explanation was proposed by Crittenden et al., 1999 who constructed a kinetic model for a H₂O₂/UV process by considering the change of the pH during the experiment while mineral acids and

Figure 4
Influence of the hardness (TAC)
of the phenolic solution on the
performance of the UV/H₂O₂
process

$C_o = 200 \text{ mg/l}$, $T = 25^\circ\text{C}$ and
 $C_{\text{H}_2\text{O}_2} = 100 \text{ mmol/l}$
(◇) TAC = 100 mg CaCO₃/l
(○) TAC = 400 mg CaCO₃/l
(△) TAC = 600 mg CaCO₃/l
(□) TAC = 800 mg CaCO₃/l
(x) TAC = 0 mg CaCO₃/l

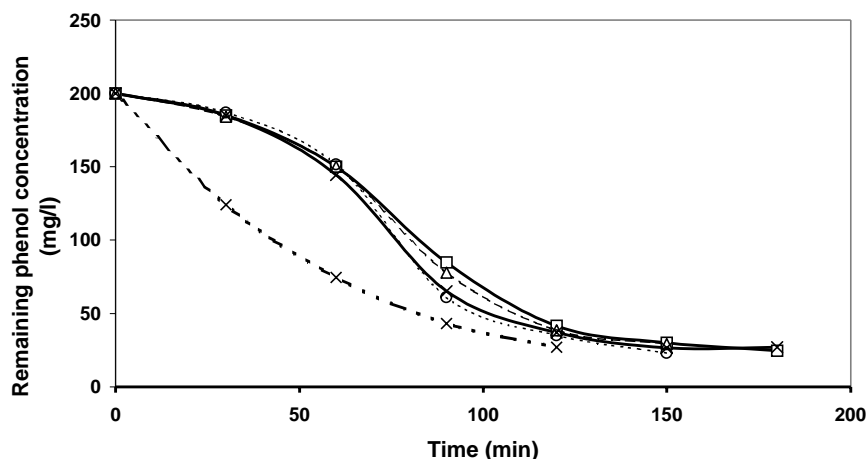
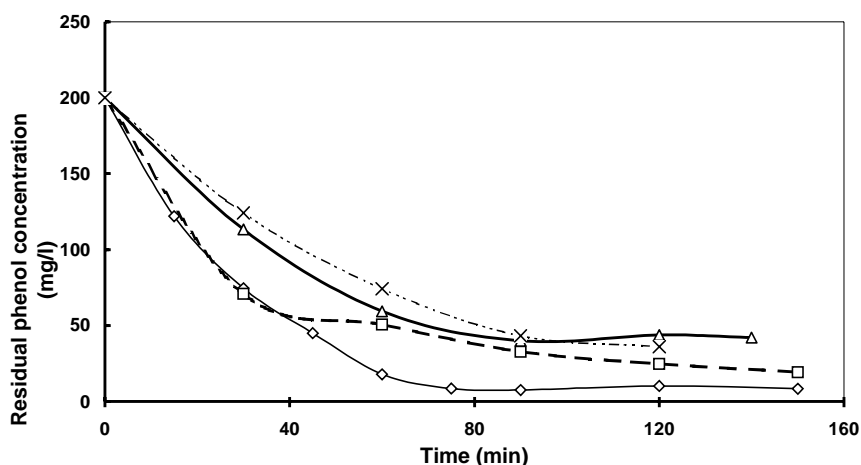


Figure 5
Influence of peroxide
concentration on phenol
degradation kinetics by the
AOP process. $C_o = 200 \text{ mg/l}$
and $T = 25^\circ\text{C}$

(◇) $C_{\text{H}_2\text{O}_2} = 50 \text{ mmol/l}$
(□) $C_{\text{H}_2\text{O}_2} = 100 \text{ mmol/l}$
(△) $C_{\text{H}_2\text{O}_2} = 200 \text{ mmol/l}$
(x) $C_{\text{H}_2\text{O}_2} = 300 \text{ mmol/l}$



carbon dioxide form as final oxidation products.

Figure 4 presents the effect of hardness of the solution, ranging from 100 to 800 mg CaCO₃/l on the degradation rate of the phenol. The CaCO₃ concentration range corresponds to the change of this parameter of the North African waters (surface and underground). The results indicate that the addition of CO₃²⁻ ions had no effect on the performance of the degradation of the phenol by AOP reactor. Indeed, a similar performance was obtained with hardness ranging from 100 to 800 mg CaCO₃/l. These results also confirm those obtained from the Hadamard experimental design.

On the other hand, these results are quite surprising since early investigations have indicated that various inorganic substances and background organic matter contained in natural waters usually reduce the oxidation efficiency of target pollutants by consuming significant amounts of hydroxyl radicals in the H₂O₂/UV system. These substances are called hydroxyl radical scavengers and the carbonate and bicarbonate ions are considered to be the most common inorganic hydroxyl radical scavengers in natural waters (Crittenden et al., 1999). Carbonate and bicarbonate ions react with OH[•] to produce carbonate radicals CO₃^{•-} and HCO₃[•] which are reported to be a weak oxidant (Glaze and Kang, 1988). The performance of the UV/H₂O₂ reactor in this work, using water hardness ranging from 100 to 800 mg CaCO₃/l may be explained by the fact that addition of carbonate may exert an effect until a threshold concentration is reached and beyond this value the effect would be negligible. For this work, the concentration limit is in the order of 100 mg CaCO₃/l. To confirm this explanation comparison of the results obtained at various hardnesses and those with synthetic water without hardness (without addition of CaCO₃) was realised

(Fig. 4). It is clear that the process performance increased with phenolic solution without carbonate ions added. The degradation of the phenol was faster than those obtained with various hardness solutions. These results confirm the validity of the previous assumption and demonstrate that the high values and the variation of the hardness in North African waters negate the effect of this parameter with respect to the performance of the H₂O₂/UV as an AOP.

Process optimisation

The effect of the H₂O₂ concentration on the performance of the process was studied. The results, presented in Fig. 5, show a decrease in the phenol concentration during the first hour, after which the remaining phenol concentration reached various concentration limits depending on the initial phenol concentrations. The results obtained also indicate that an excess of peroxide product produced an inhibitory effect. Indeed, at high concentrations (greater than 50 mmol/l), the remaining phenol concentration increased with an increase in the initial H₂O₂ concentration, indicating that the performance was reduced. This phenomenon has been reported in previous studies (Andreozzi et al., 2000 and Crittenden et al., 1999), indicating that it is possible to locate value of H₂O₂ concentration beyond which further additions are not effective for the substrate consumption. On the other hand, kinetic degradation of the phenol was faster with initial H₂O₂ concentrations of about 50 mmol/l than with those obtained with other H₂O₂ concentrations. This phenomenon may be explained by the fact that an excess of H₂O₂ could produce other oxidant products such H₂O^{•+}

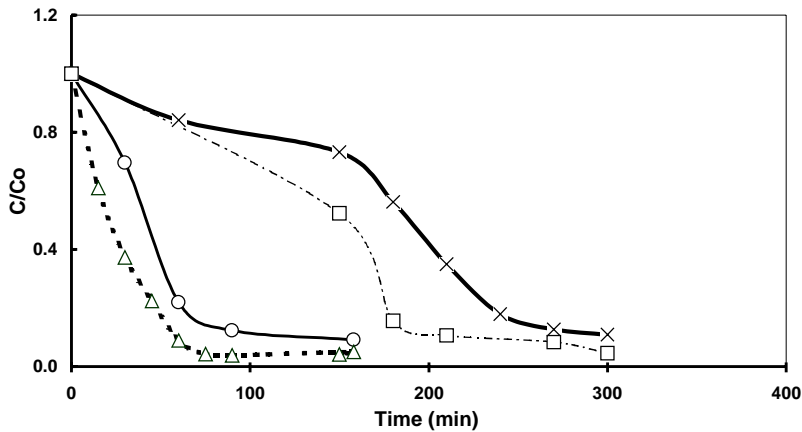


Figure 6
 Influence of the initial phenol concentration (C_0) on phenol kinetic degradation by the UV/ H_2O_2 process.
 $C_{H_2O_2} = 50 \text{ mmol/l}$ and $T = 25^\circ\text{C}$
 (□) $C_0 = 400 \text{ mg/l}$
 (x) $C_0 = 300 \text{ mg/l}$
 (△) $C_0 = 200 \text{ mg/l}$
 (○) $C_0 = 100 \text{ mg/l}$

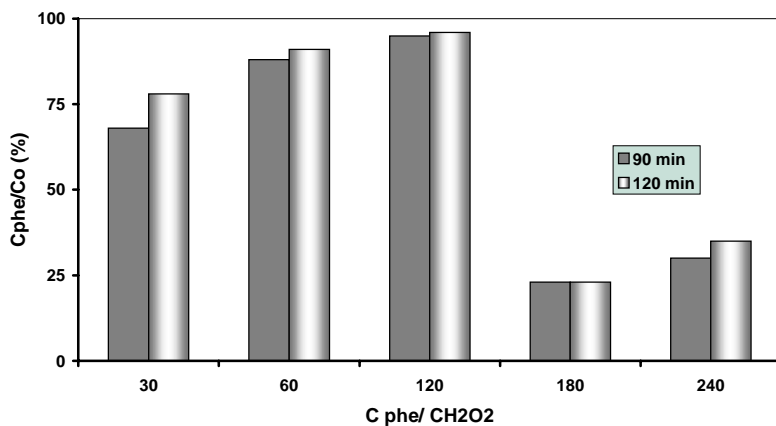


Figure 7
 Influence of the $C_{H_2O_2}/C_0$ ratio on phenol concentration abatement
 $T = 25^\circ\text{C}$

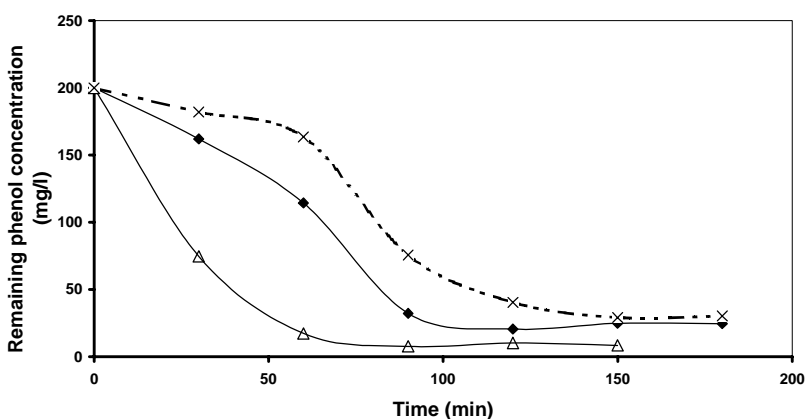


Figure 8
 Influence of temperature on phenol kinetic degradation by the UV- H_2O_2 process
 $C_{H_2O_2}/C_0$ ratio = 120, $C_{H_2O_2} = 50 \text{ mmol/l}$ and (x) $T = 15^\circ\text{C}$
 (△) $T = 20^\circ\text{C}$
 (◆) $T = 50^\circ\text{C}$

which has a low oxidant power compared to OH^\cdot and then reduces considerably the performance of the AOP process (Kharoune, 2000).

The effect of the initial phenol concentration on kinetic phenol degradation kinetics by the UV/ H_2O_2 process was investigated. The results (Fig. 6) show that between 90 and 95% of the phenol content was removed by the AOP process for initial phenol concentrations ranging from 100 to 400 mg/l and an optimal initial peroxide concentration of 50 mmol/l. It is important to note that the time required to obtain this performance depended considerably on the initial phenol concentration.

On the other hand, an optimal value was obtained for $C_0 = 200 \text{ mg/l}$. Here a high degradation efficiency of phenol (about 95%) was attained with an irradiation time less than 1 h. This is not the case for other concentrations where the required time to obtain this performance was much longer.

These results imply that there is an optimal H_2O_2 concentration - phenol concentration ratio ($C_{H_2O_2}/C_0$) for the treatment of phenolic solutions by the UV/ H_2O_2 process. By plotting the phenol concentration abatement against $C_{H_2O_2}/C_0$ (both concentrations expressed in mg/l, it is demonstrated that an optimal ratio would be about 120 (Fig. 7).

The effect of temperature on the performance of the UV/ H_2O_2 process was investigated at the previously determined optimal $C_{H_2O_2}/C_0$ ratio of about 120. The results obtained, presented in Fig. 8, indicate the existence of an optimal temperature of about $T = 20^\circ\text{C}$. Indeed, at this temperature a greater phenol concentration abatement and lower required irradiation time were obtained than for other temperatures.

Conclusions

The factorial experiments used in this study enable the determination of the significant experimental parameters for the treatment of phenol in water by the UV/ H_2O_2 oxidation process. Using a Hadamard design matrix taking into account all interaction effects, appeared to be an efficient means of obtaining a mathematical model in conformity with criteria validity. The predictions given by the factorial design experiments were confirmed by actual experiments. The phenol degradation kinetics were not influenced by the pH or the hardness of the solution to be treated. On the other hand, initial H_2O_2 concentration, initial phenol concentration and temperature influenced the oxidation efficiency of the process considerably and optimal values were obtained for temperature (of about 20°C) and $C_{H_2O_2}/C_0$ ratio (of 120 mg/mg).

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