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# Study and modeling of the organophosphorus compound degradation by photolysis of hydrogen peroxide in aqueous media by using experimental response surface design



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## ABSTRACT

This work was designed to study the effectiveness of hydrogen peroxide photolysis on the degradation of malathion pesticide in an aqueous medium. Experiments were performed in a static reactor with a low-pressure mercury vapor lamp at initial organophosphorus concentrations of 10<sup>-3</sup>. The first result obtained showed that the system H<sub>2</sub>O<sub>2</sub>/UV can completely oxidize the organophosphorus compound. The oxidation yields obtained using the static reactor depended on the reaction time, the initial concentration of H<sub>2</sub>O<sub>2</sub>, and the initial pH solution. However, the oxidation efficiency may be reduced by the presence of radical traps in the reaction medium. Moreover, a model of the hydrogen peroxide photocatalysis is also presented in this paper. The use of experimental design and in particular the response surface methodology (RSM) in addition to the full factorial design allowed the determination of the influence of the simultaneous effects and interaction of the operating parameters on the performance of the photo degradation Demim et al. Ecol. Eng. 57 (2013) 302; Ecol. Eng. 61 (2013) 426; Boudjema et al. Desalin. Water Treat. 1065. 10.1080/19443994.2015.449. Indeed, the operating parameters studied in this research work were the initial concentration of malathion, H<sub>2</sub>O<sub>2</sub> catalyst volume and the pH of the solution. The results found showed that the application of the RSM allowed describing correctly the effect of these three operating parameters on the treatment efficacy. The optimal parameter values giving a maximum yield (100%) were determined.

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## Introduction

The organophosphorus compounds present certain risks to human health [5, 6]. Therefore, they are subject in recent years, for regulations on maximum allowable concentrations in water distribution [7,8]. Among the organophosphorus compounds, we can distinguish the compounds present in natural water because of agricultural contamination (pesticides, fungicides, herbicides, etc.) or industrial contamination (phosphorus solvent, etc.).

The chemical oxidation processes using ozone, chlorine, chlorine dioxide are ineffective. One means of obtaining chemically degradation of these compounds is to generate in the medium very reactive species of radical type, by applying more complex oxidizing systems.

Among the systems capable of forming such entities and applicable in the field of water treatment, we quote:

- The photolysis of ozone by UV: O<sub>3</sub>/UV [9];
- The system oxidant ozone–hydrogen peroxide: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> [10,11];
- Water photolysis, which comprises direct photolysis comprises irradiating the effluent by UV or visible radiation of appropriate wavelength direct and Indirect photolysis comprises irradiating water to be treated in presence of hydrogen peroxide; Fenton process H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> [12];

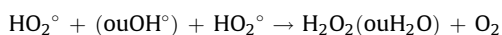
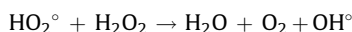
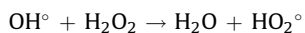
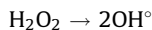
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- Photocatalysis which includes the homogeneous photolysis even called photo-Fenton process, based on the Fenton reaction photochemically assisted, and heterogeneous photo catalytic wastewater based on UV irradiation of semiconductor powder materials, such as  $\text{TiO}_2$ ,  $\text{FeO}_3$ , dispersed in water [13].

In view of these different methods for producing OH radical<sup>o</sup>, advanced oxidation processes are divided into early chemical, electrochemical and photochemical oxidation process. This research work was done based on the third system cited above.

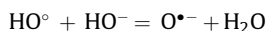
The photolysis of hydrogen peroxide to wavelengths below 365 nm causes cleavage of the O–O bond [14] giving rise to hydroxyl radicals ( $\text{OH}^\circ$ ) which then initiate a succession of chain reactions [15]



Compared to other oxidants used in the field of water treatment, hydroxyl radicals have a higher oxidizing power ( $E_0 = 2.80 \text{ V}$ ) and lead to less selective attacks on organic compounds. The reactivity of  $\text{H}_2\text{O}_2/\text{UV}$  system depends on the nature of the organic product to be oxidized and can be very significantly reduced in the presence of radical traps such as carbonate and bicarbonate ions [16].

Hydroxyl radical is one of the most powerful known oxidants with a redox potential of 2.73 V/NHE in an acid solution. In a strong alkaline medium,  $\text{HO}^\circ$  radicals exist in their basic form together: the oxygen anion radical  $\text{O}^{\bullet-}$  ( $\text{p}K_a = 11.9$ ) reacts slowly by nucleophilic attack [17].

At more acidic pH, the acid form is predominant, which reacts with the organic matter by electrophilic attack.



The half-life of  $\text{HO}^\circ$  radicals is estimated to be less than 70 ns in water [18]. Reaction rates between radicals  $\text{HO}^\circ$  and organic compounds are very fast, in the order of  $10^6$ – $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  [19].

From the values reported in literature [22], the reaction constant ( $k$ ) is on average  $10^2$  times lower for saturated compounds derived from methane than aromatic compounds for which the  $\text{HO}^\circ$  radicals have more affinity.  $\text{HO}^\circ$  radicals react faster on the aromatic carriers of the activating groups ( $-\text{OH}$ ,  $\text{CH}_3$ ) than those substituted with deactivating groups ( $-\text{NO}_2$ ,  $-\text{COOH}$ ).

It should be noted that many parameters other than the electron density of the molecules are to be taken into account for the reactivity study: The strength of the C–H bonds, the stability of the nascent radical, statistical factors (number of attack positions possible) and steric effects. For example, in the case of alkanes, the reactivity is directly related to the stability of the formed radical: tertiary > secondary > primary.

Atkinson [23] showed that depending on its position, the substituent had an antagonistic effect: in  $\alpha$  position, by its high electronegativity, the halogen impoverishes the electron density of the compound while in  $\beta$  position; its stabilizing effect on the radical prevails and thus, increases the reactivity [23].

In the case of aromatic compounds, it is more difficult to predict the responsiveness. Indeed,  $\text{HO}^\circ$  can react preferentially with the substituents and the statistical factors are also very important.

The objective of this study is to investigate the photo degradation of Malathion in the presence of  $\text{UV}/\text{H}_2\text{O}_2$ . The influence of the pollutant concentration, the amount of  $\text{H}_2\text{O}_2$  catalyst and the pH of the solution on the performance of the process of Malathion photo degradation will be understood. Using response surface methodology (RSM) and a full factorial design, modeling the effects of these parameters on the efficiency of the process will also be addressed in this paper.

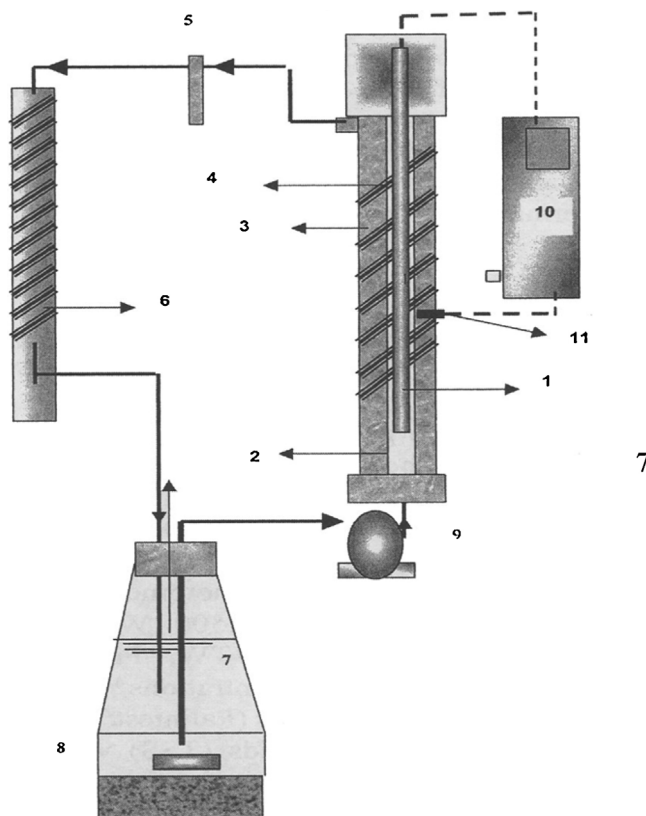
Our approach can be summarized in three main steps; the first step consists in the kinetic study of the effects of the pollutant concentration and the volume of  $\text{H}_2\text{O}_2$  catalyst in addition to the solution pH. The second step is based on the use of full factorial planes with the goal to determine the factor levels to be tested. Graphs of the factors effects, will evaluate the effects of the various parameters tested on the process performance. Finally, in the last step, the use of plans for surface response optimization and identification of interactions between the different parameters tested will be achieved through contour graphs and response surfaces.

## Materials and methods

### Mounting

The experimental disposal (Fig. 1) consists of a cylindrical stainless steel irradiation chamber in which plunges a mercury vapor lamp. This latter is protected by a glass sheath.

The homogenization of the dye solutions was carried out by a liquid recirculation with a constant flow rate. A regulating system comprising a cold source prevents a temperature rise due to the heating of the lamp and maintains the temperature constant.



**Fig. 1.** Experimental setup of dye degradation by UV irradiation. (1) UV Lamp, (2) quartz sleeve, (3) cylindrical steel reactor, (4 and 6) water cooling system, (5) sample point, (7) dye solution, (8) magnetic stirrer, (9) centrifugal pump, (10) electrical power, (11) actinometer.

All experiments were performed starting with an initial volume of the solution equals to one liter (1 L); which corresponds to the working volume of the reactor and the recirculation circuit.

The mercury vapor lamp is inserted in a protective quartz sheath. Stirring of the reaction liquid medium is doubly assured by recirculating the solution through a centrifugal pump with adjustable flow rate and a magnetic stirrer. Hydrogen peroxide  $H_2O_2$  was chosen as the oxidant.

#### Chemical products

The chemical products used in this study (see Table 1) were of analytical grade or better and were purchased from Fluka® (Germany). They were used without prior purification. The solutions were prepared with distilled water.

#### Solutions preparation

The solutions were prepared from demineralized water and malathion. The different concentrations were obtained simply by adding appropriate amounts of malathion.

Hydrogen peroxide retained as the oxidant species was at a concentration of 30% (w:w). The advantage of working at such a concentration returns to use very small volumes of the order of a few micro liters, which injected into the treated solution with used concentrations ranging from 25 to 100 mg L<sup>-1</sup>. In this way the impact on the reaction volume is negligible.

The acidic or basic pHs were achieved by adjusting the solution to the acid solution of sodium hydroxide (NaOH) to 1 N and hydrochloric acid (HCl) to 1 N.

## Results and discussions

In the first part of our work, we studied the photolysis of malathion in the absence of  $H_2O_2$ , and then we studied the use efficiency of  $H_2O_2$ /UV oxidizing system and complemented our results with a study of the effects of the medium (pH) and the volume of  $H_2O_2$  on the malathion degradation kinetic. All experiments done were performed with a radiation corresponding to 100% of the useful area of the lamp surface.

#### Oxidation of malathion

Further study of the decomposition of malathion was performed to show the influence of various parameters namely: Initial concentration, quantity of  $H_2O_2$  and initial pH of the solution on malathion degradation process.

The system  $H_2O_2$ /UV was applied to the malathion solutions. The experiments done were performed at  $T = 25\text{ }^\circ\text{C}$  and initial concentration of 100 mg L<sup>-1</sup>. Taking into account the low rate of degradation of malathion, experiments were performed using the entire useful surface of the irradiation lamp.

Due to the nature of the products studied, we followed the evolution of the concentration of organic products in the reactor as a function of time for solutions subjected to UV irradiation (no

$H_2O_2$ ) or to an oxidation by  $H_2O_2$  system/UV, the recirculation flow rates being identical.

#### Photolysis of malathion by UV radiation only and UV/ $H_2O_2$

The reaction is considered this time with a solution of malathion at 100 mg L<sup>-1</sup>, in which 5 mL of hydrogen peroxide is injected. The whole solution is irradiated in the field of UV. The results obtained are reported in Fig. 2.

As seen in Fig. 2, in the absence of  $H_2O_2$  the malathion molecule presents low degradation kinetics. For example after 90 min of exposure to UV radiation the malathion molecule records a reduction of 28%. It is clear that in this case the UV radiation applied only is little effective.

Fig. 2 clearly shows that the combined action of ultraviolet radiation and hydrogen peroxide directly affect the kinetics of malathion degradation. Indeed in this case, we reached a total degradation of malathion after 90 min of treatment.

Ultraviolet radiations fragment hydrogen peroxide molecules giving birth to  $OH^\bullet$  radicals, which due to their high oxidizing power initiate a whole chain of radical reactions until partial or complete mineralization of the target molecule, i.e. malathion. Thus, it appears that the combined UV/ $H_2O_2$  treatment is more effective than UV alone.

#### Effects of hydrogen peroxide content

Malathion solutions at  $C = 100\text{ mg L}^{-1}$  have been subjected to different oxidation rates. The variation of the oxidation rate was obtained by varying the initial volume of  $H_2O_2$  from 1 mL to 10 mL. The results reported in Figs. 3 and 4 show a more rapid photolysis at a volume of  $H_2O_2$  equal to 3 mL.

The results obtained show that the rate of decomposition of malathion is function of the initial concentration of  $H_2O_2$ . Calculates showed that the decomposition rate of malathion follows a kinetic law of order 1 in our experimental conditions. Constant  $K$  values obtained are shown in Fig. 4. Indeed, increasing the kinetic constant  $K$  indicates a larger decomposition rate of malathion for a volume of  $H_2O_2$  equals to 3 mL and decreases when the initial volume of  $H_2O_2$  increases.

In contrast, the molar absorption coefficient of  $H_2O_2$  is quite low in the UV region ( $18.6\text{ L mol}^{-1}\text{ cm}^{-1}$ ). It is then necessary to use a high concentration of hydrogen peroxide causing effective oxidation of organic pollutants. Thus, increased the initial concentration of  $H_2O_2$  and the intensity of the UV light resulted in an increase in the rate of oxidation, because a higher

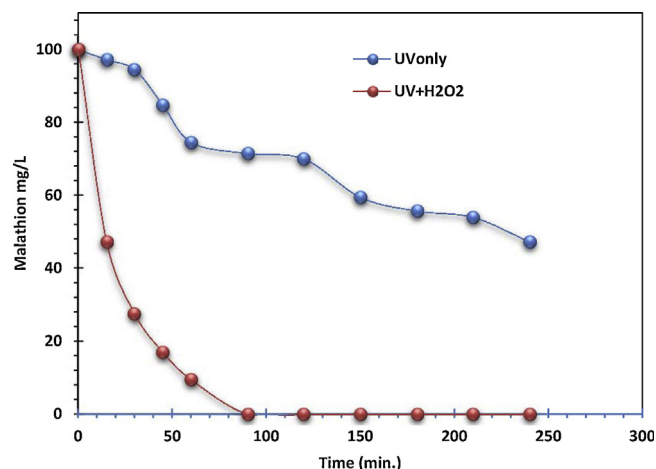


Fig. 2. Degradation of malathion by coupling UV/ $H_2O_2$ .

Table 1

Chemicals used in this investigation.

Products	Purity (%)
Hydrogen peroxide( $H_2O_2$ )	30
Ethanol ( $C_2H_5OH$ )	95
$CCl_4$	99
Sodium hydroxide (NaOH)	98
Hydrochloric acid (HCl)	99
Ammonium molybdate ( $(NH_4)_2MoO_4 \cdot 4H_2O$ )	99

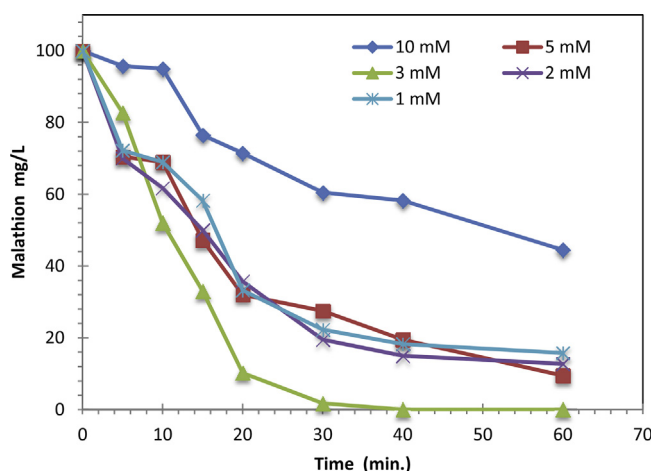
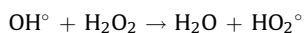


Fig. 3. Influence of hydrogen peroxide content on the degradation of the malathion using UV/H<sub>2</sub>O<sub>2</sub> system.

concentration of OH<sup>°</sup> will be generated in solution. However, at excessively high concentrations of hydrogen peroxide, there is consumption of hydroxyl radicals by the excess hydrogen peroxide according to the following reaction:



#### Influence of the initial concentration of malathion

The system H<sub>2</sub>O<sub>2</sub>/UV was applied to different concentrations. The experiments were performed at pH = 7.5 and a volume of H<sub>2</sub>O<sub>2</sub> equals to 3 mL. Due to the low malathion degradation rate, experiments were performed using the entire useful surface of the irradiation lamp.

We noticed that at higher concentrations greater than 100 mg L<sup>-1</sup>, degradation of malathion is slowed (see Fig. 5), it could mean that there is a close relationship between the rate of hydroxyl radicals generated by the photolysis reaction and instantaneous concentration of malathion in reaction medium.

Indeed, many molecules of Malathion increasingly come into competition with the molecules of hydrogen peroxide against the hydroxyl radicals, thus the constant reaction rate of Malathion degradation is slowed. Stefan and Bolton [27] suggest that

intermediate species created during the chain reaction which takes place in this type of treatment become in their turn's pitfalls to hydroxyl radicals.

The results obtained show that Malathion is photodegradable by a first order kinetics, and in a similar manner to the lower concentration of 100 mg L<sup>-1</sup> (see Table 2). It is noted that for these concentrations the difference between degradation constants obtained is not significant, what drives us to conclude that for concentrations less than 100 mg L<sup>-1</sup>, malathion concentration has no influence on the direct photolysis of malathion in the field of concentrations less than 100 mg L<sup>-1</sup>, as soon as we exceed this concentration, it is noted that the degradation of malathion has slowed.

These results can be explained as follows:

- The first and the second one may be due to the dilution of the photolysis medium,
- The third to the equality between the material to degrade and the amount of OH<sup>°</sup> radicals,
- The fourth one, the matter to be degraded is greater than the amount of OH<sup>°</sup> radicals.

This could mean that there is a close relationship between the rate of hydroxyl radicals generated by the photolysis reaction and the concentration of malathion in the reaction medium.

Indeed, many molecules of malathion increasingly come into competition with the molecules of hydrogen peroxide against hydroxyl radicals and the constant rate of malathion degradation reaction is slowed and half-life time is increased.

#### Influence of the solution pH

Solutions Malathion (C<sub>0</sub> = 100 mg L<sup>-1</sup>) were irradiated at pH ranging from 3 to 10. The results reported in Fig. 6a shows a more rapid photolysis in basic medium.

Fig. 6b shows the evolution of the rate constant of the malathion photodegradation as a function of pH. From this figure, the degradation constants increase with pH up to a pH value of 10. This can probably be explained by the fact that the molar absorption coefficients of the molecule are slightly higher at higher pH compared to acidic pH. The *K* constants values obtained are equal to 0.16 s<sup>-1</sup> for all pH ≤ 10. In contrast, in a basic medium, the increase of the kinetic rate constant *K* (see Fig. 8) indicates an optimal decomposition rate, but the Malathion is completely destroyed in a pH range from 2 to 8.

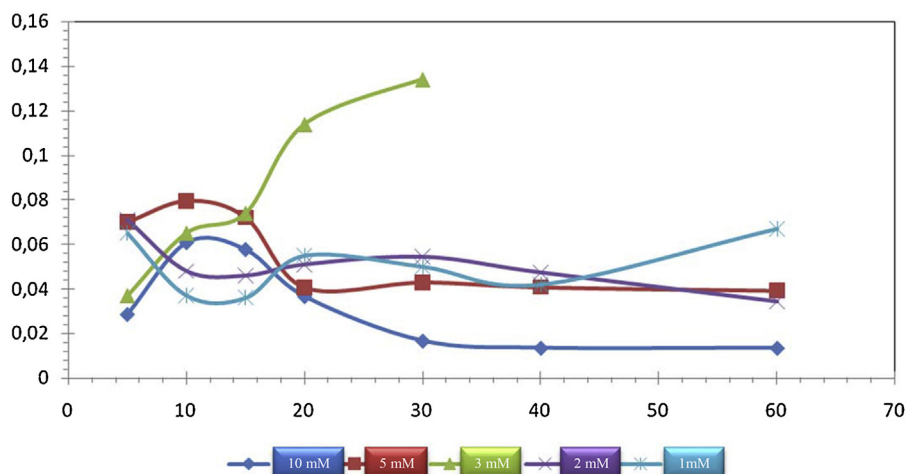


Fig. 4. Kinetic constant of malathion decomposition as a function of H<sub>2</sub>O<sub>2</sub> volume.



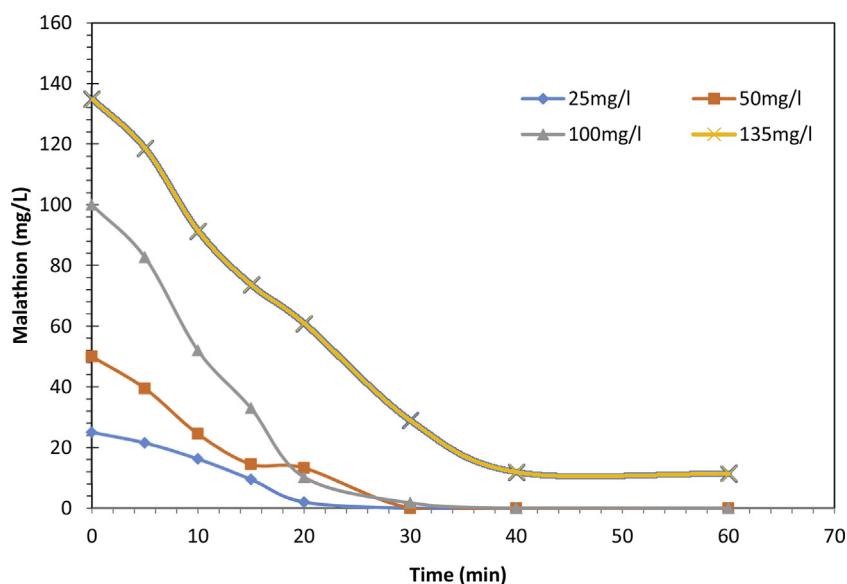


Fig. 5. Effect of pesticide concentration on the advanced degradation of malathion by the UV/H<sub>2</sub>O<sub>2</sub> system.

Table 2

Rate constants and half-life of malathion at various concentrations.

Concentration (mg L <sup>-1</sup> )	<i>K</i> (min <sup>-1</sup> )	<i>T</i> <sub>1/2</sub> (min)
25	0.065	10.66
50	0.066	10.50
100	0.085	8.15
135	0.047	14.74

This behavior is general for most of the organophosphorus pollutants that are degraded efficiently at pH 10 by the system H<sub>2</sub>O<sub>2</sub>/UV.

Fig. 6c illustrates that the pH increases or decreases depending on the initial pH used, where we see the convergence of the obtained curves at the end of treatment by advanced oxidation.

As expected, the pH increases or decreases during the treatment over time according to its initial value. We find the largest change for an initial pH of 10. Thus, in all cases, the pH tends to converge to a final pH value of about 3.

### Modeling using experimental designs for response surface of malathion mineralization

In this section, we studied the influence of three parameters, namely: the concentration of the solution (*U*<sub>1</sub>), H<sub>2</sub>O<sub>2</sub> volume (*U*<sub>2</sub>) and the hydrogen potential (*U*<sub>3</sub>) on the rate of reduction of malathion during photolysis by advanced oxidation process (H<sub>2</sub>O<sub>2</sub> + UV).

We adopted the methodology of experimental research, according to the approach of experimental designs for response surfaces. Experimental designs are intended to estimate the effects of factors [1–3,20,26]. However, the problem does not only consist in determining and comparing the effects of factors, but the problem is to find a methodology that enables an overall analysis to be used in practice.

This modeling of abatement rates based on factors identified in the previous study will be presented. For this, we retake the different steps of the method of experimental designs for the study of response surface.

#### Definition of objectives and answers

As indicated in the previous study, we aim through this investigation to improve the percentage of malathion reduction.

For this, the referred purpose is setting up of polynomial models expressing the removal percentage.

#### Definition of factors

- *U*<sub>1</sub>: Concentration of malathion,
- *U*<sub>2</sub>: volume of H<sub>2</sub>O<sub>2</sub> added,
- *U*<sub>3</sub>: PH of the solution.

#### Experimental chosen field

The experimental domain is made up of all combinations of factors that are possible to carry (see Table 3).

To translate the variation of the experimental response studied in the experimental chosen field, we use the following mathematical model:

$$R\% = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$

with *R*% is the experimental response; *b*<sub>*i*</sub> is the estimation of the main effect of a factor *i* for the response *R*%; *b*<sub>*ii*</sub> is the estimating of the second order factor *i* effect for the response *R*%; *b*<sub>*ij*</sub> is the estimating of the interaction effect between the factor *i* and the factor *j* for the response *R*%.

Calculation of the model coefficients is made by the method of least squares.

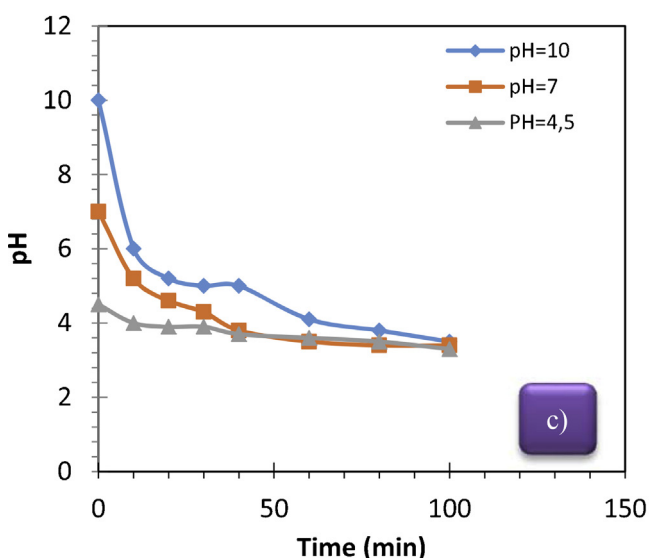
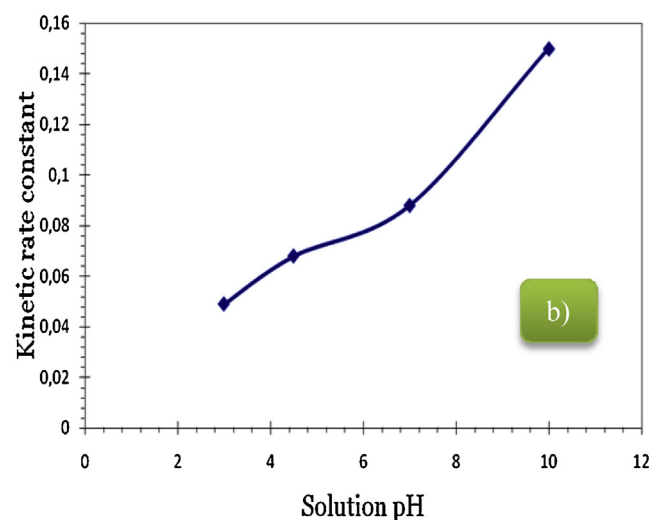
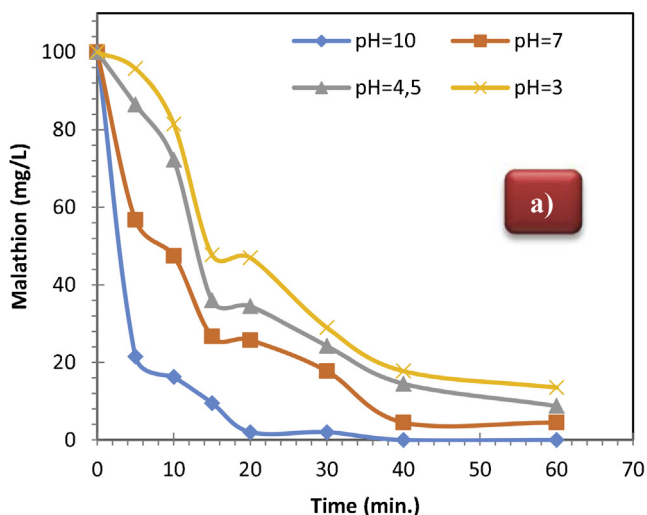
#### Definition of the empirical model

The empirical model is shown in Table 4, where *R*% is the reduction rate of malathion, which is defined by the following relation:

$$R\% = \frac{C_{0-c}}{C_0} \times 100$$

#### Overall analysis of test results

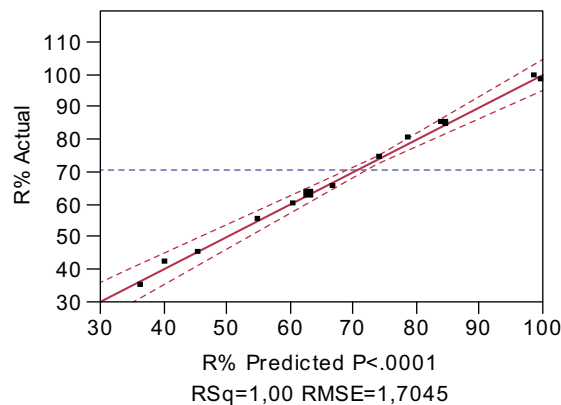
Each test was performed three times. The values recorded during the measurement are specific values of random variables, repeat measures have ensured of not being in the presence of an extreme value during the experiment. The results of 15 tests of the matrix of experiments are shown in Table 4.



**Fig. 6.** Influence of the initial pH. (a) Influence of the initial pH of the solution on the advanced degradation reaction of malathion pesticide by the UV/H<sub>2</sub>O<sub>2</sub> system. (b) Evolution of the rate constant as a function of the solution pH. (c) Solution pH evolution over time.

#### Mathematical analysis of test results

The mathematical analysis is essentially to identify  $p$  model coefficients from the results of  $N$  experiments (see Table 5).



**Fig. 7.** Model adequacy graph of malathion abatement rate without interaction.

**Table 3**

Experimental field for the mineralization of malathion.

Coded experimental variables ( $X_i$ )	Factors ( $U_i$ )	Units	Field	
			Lower level	Higher level
$X_1$	$U_1$ : Concentration	mg L <sup>-1</sup>	100	10
$X_2$	$U_2$ : H <sub>2</sub> O <sub>2</sub> volume	L	1	5
$X_3$	$U_3$ : pH		3	12

**Table 4**

Matrix of experiments and experimental design.

Experimen	Pattern	Experimental matrix			Experimental design			R%
		$X_1$	$X_2$	$X_3$	$U_1$	$U_2$	$U_3$	
1	0--	0	-1	-1	55.55	1	3	63
2	-0-	-1	0	-1	10	3	3	80
3	+0-	1	0	-1	100	3	3	60
4	0+-	0	1	-1	55.55	5	3	35
5	--0	-1	-1	0	10	1	6.5	65
6	+00	1	-1	0	100	1	6.5	55
7	-+0	-1	1	0	10	5	6.5	45
8	++0	1	1	0	100	5	6.5	42
9	0+-	0	-1	1	55.55	1	10	85
10	-0+	-1	0	1	10	3	10	99
11	+0+	1	0	1	100	3	10	98
12	0++	0	1	1	55.55	5	10	74
13	000	0	0	0	55.55	3	6.5	84.7
14	000	0	0	0	55.55	3	6.5	84.5
15	000	0	0	0	55.55	3	6.5	84.5

**Table 5**

Analysis of model coefficients of malathion abatement rate.

Coefficient	Value	Standard deviation	$t$ -Statistic	$T_{crit}$ 2.015
Constant	84.566667	0.984096	85.93	Significant
C	-4.25	0.602633	-7.05	Significant
V	-9	0.602633	-14.93	Significant
pH	14.75	0.602633	24.48	Significant
C × C	-6.408333	0.887052	-7.22	Significant
C × V	1.75	0.852252	2.05	Not significant
V × V	-26.40833	0.887052	-29.77	Significant
C × pH	4.75	0.852252	5.57	Significant
V × pH	4.25	0.852252	4.99	Significant
pH × pH	6.0916667	0.887052	6.87	Significant

Note that in these models, some factors such as the coefficient associated with the interaction  $C \times V$  have a very low value.

To perform the statistical evaluation of the significance of the coefficients, student test is used. If  $t_i > T_c$ , then the coefficient is significant, if not it is rejected from the model.

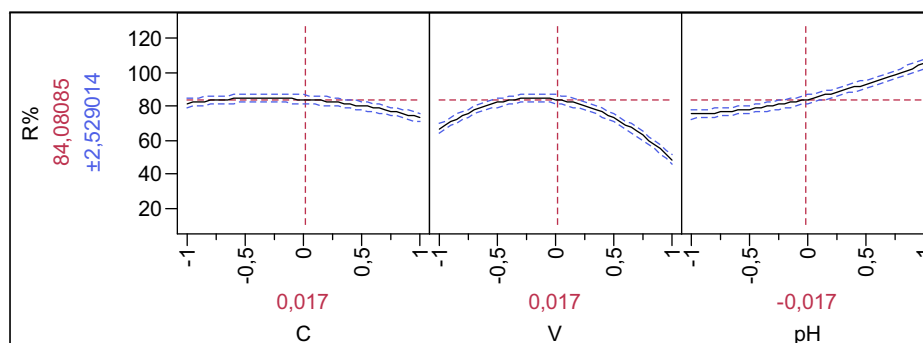


Fig. 8. Graphical analysis of the effects.

The value of student coefficient restraint from the student table with a degree of freedom  $ddl$  equals to 6 has a confidence level of 95% and a critical value of 2.015. The following Table 6 lists the calculated values of the student coefficient obtained for the model studied.

An analysis of variance (see Table 7) is a means of validating the mathematical model by using *Fischer criterion* which consists mainly of comparing two dispersions; residual and experimental.

The value  $F$  (critical) read from the table of Fisher-Snedecor, with  $(p-1)=10$  and  $(n-p)=7$  degrees of freedom and a confidence level equals to 95% is 4.77.

From the results obtained,  $F_{obs}(\text{chlorophyll}) = 157.06$ . We note that  $F_{obs} \gg F_{critical}$ ; so, the hypothesis is verified, therefore the regression is significant [21,28].

We obtained for our two responses a very low value of  $P$ , which reinforces the hypothesis of the use of quadratic model to model the responses obtained. Descriptive qualities (adjusted  $R^2$  and predictive  $R^2$ ) were calculated for these models (see Table 8).

These values close to 1 testify to the good quality of our models. It is also possible to translate the predictive quality of a model from the predictive correlation coefficient  $Q^2$  [Chin, 98]:  $Q^2 = 0.96$  this value close to 1 reflect again the good quality of our models.

#### Graphic model analysis

The Model adequacy graph of malathion abatement rate without interaction is shown in Fig. 7

The regression curves presented above shows that the values of the estimated responses are very close to that observed, and are aligned with the diagonal. Therefore, the proposed models approach strongly the degradation phenomenon of malathion with a coefficient  $R^2$  that approaches unity.

Based on the results found, the model equation for the rate of malathion reduction is calculated using JMP software [V9].

It takes the following form:

$$R\% = 84.56 - 4.25 \times X_1 - 9 \times X_2 + 14.75 \times X_3 - 6.41 \times X_1^2 - 26.04 \times X_2^2 + 6.09 \times X_3^2 + 4.75 \times X_1 \times X_3 + 4.25 \times X_2 \times X_3$$

Table 6  
Regression analysis.

Source	Degrees of freedom	Sum of squares	Mean square	Report $F$	Critical value
Model	8	5619.5907	700.918	157.06	4.77
Residues	6	26.7767	4.463	Prob. > $F$	
Total	14	5634.1173	-	0.0001	

We note that the cloud point is near the line  $y = x$ , therefore, the model is enough descriptive.

The Graph drawing of the effects is given in Fig. 8.

We note that the use of plans for surface response modeled very well the effect of factors.

We note also from Fig. 8, a negative effect of concentration and a positive effect of hydrogen potential. In contrast, for the volume of  $H_2O_2$  there is an increased rate of malathion reduction to an average value and as soon as it exceeds this value we notice a decrease.

#### Graphical representation of response surfaces

The response surfaces may present changes in responses depending on two factors only at a time, keeping other factors being set to a fixed value [24]. To determine the mineralization optimal conditions, we traced the evolution of malathion reduction rate as a function of malathion concentration,  $H_2O_2$  volume and Hydrogen potential (pH) (see Fig. 9).

Based on the above figure, we see that the increase in pH promotes an increase in the rate of reduction of malathion.

More potential Hydrogen is basic, more mineralization is better. The response is maximum when the concentration is low in the field chosen. And the response is maximum when the volume of  $H_2O_2$  is at the center of the chosen field.

Table 7  
Descriptive qualities (adjusted  $R^2$  and predictive  $R^2$ ).

$R^2$	0.99
$R^2$ adjusted	0.99
Root mean square error	1.70
Average response	70.31
Observations (or weighted sums)	15

Table 8  
Optimizing response after fixing  $X_1$  and  $X_2$  [ $\Delta X_3 = 0.25$ ].

$X_1$	$X_2$	$X_3$	Response of malathion abatement rate
-1	-1	-1	65.34
-1	-1	-0.75	64.1
-1	-1	-0.5	63.64
-1	-1	-0.25	63.94
-1	-1	0	65
-1	-1	0.25	66.81
-1	-1	0.5	69.39
-1	-1	0.75	72.73
-1	-1	+1	76.84



### Optimization

The search for the optimum is done by the method of the greatest slope the partial derivative of each factor is given as follows:

A positive response means that we must increase the value to have a higher response unlike a negative response where it is necessary to reduce the value to increase the response [25]. The equation of the mathematical model of degradation is given as follows:

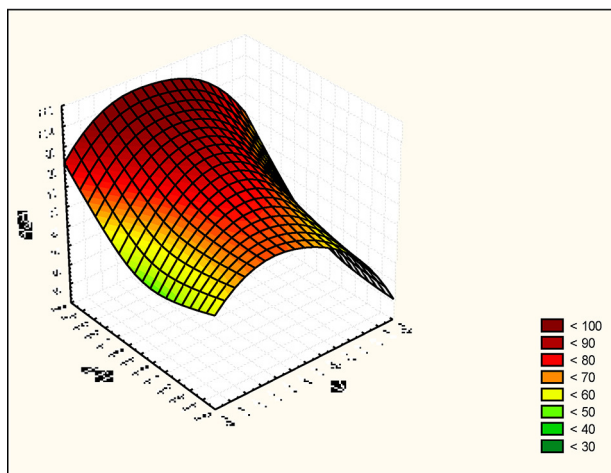
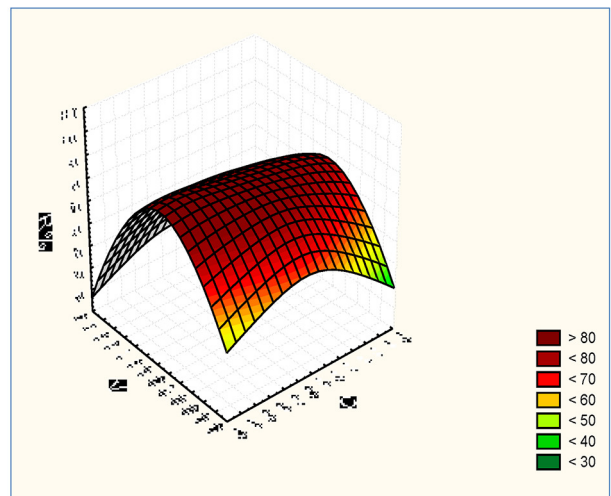
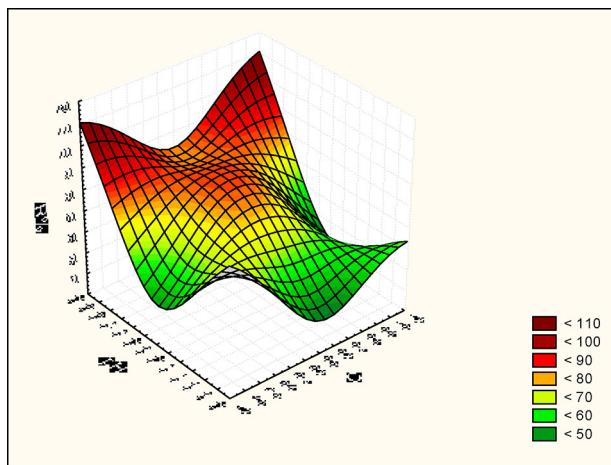


Fig. 9. Response surface in a three dimensional space, as well as iso-response curves which are a projection of the surface in a horizontal plane.

$$R\% = 84.56 - 4.25X_1 - 9X_2 + 14.75X_3 - 6.41X_1^2 - 26.40X_2^2 + 6.09X_3^2 + 4.75X_1X_3 + 4.25X_2X_3.$$

$$\frac{\partial R\%}{\partial X_1} = -4.25 - 12.82X_1 + 4.75X_3 = 0 \quad (1)$$

$$\frac{\partial R\%}{\partial X_2} = -9 - 52.80X_2 + 4.25X_3 = 0 \quad (2)$$

$$\frac{\partial R\%}{\partial X_3} = +14.75 + 12.18X_3 + 4.75X_1 + 4.25X_2 = 0 \quad (3)$$

Solving this system of equations gives an optimal point of coordinates

$$X_1 = -0.65$$

$$X_2 = -0.24$$

$$X_3 = -0.87$$

$$\frac{\partial R\%}{\partial X_1} = -0.0495$$

$$\frac{\partial R\%}{\partial X_2} = -0.0255$$

$$\frac{\partial R\%}{\partial X_3} = -0.0459$$

Must decrease the values of two parameters ( $X_1$  and  $X_2$ ) and increase the value of  $X_3$  to maximize the response. The factor  $X_1$  and  $X_2$  are in low level, so the signs ( $-1$ ) are kept in the columns  $X_1$  and  $X_2$  and the value of  $X_3$  is increased with an advancing step of 0.25. The Table 8) gives the values of the response according to levels  $X_1$  and  $X_2$  and the progression step  $X_3$ .

It appears that the optimum response is found at the low level of the two factors ( $X_1, X_2$ ) and presents a malathion reduction of 76.84%.

The value of the response that corresponds to the optimal point is equal to 80% of the values of  $X_1, X_2, X_3$  equal successively to  $-0.65, -0.24, -0.87$ .

### Conclusion

This study was aimed to study the effectiveness of  $H_2O_2$ /UV oxidation system on malathion degradation.

The oxidation mechanism of these compounds involving radical entities resulting from the photolysis of  $H_2O_2$ . The kinetic study performed in a reactor equipped, a low pressure mercury vapor lamp, has shown that the rate of photolysis is relatively slow in the absence of  $H_2O_2$ .

We have shown that the system  $H_2O_2$ /UV can degrade the malathion in an aqueous medium. Effectiveness of the system depends on a number of parameters such as  $H_2O_2$  initial volume and solution pH as well as temperature.

The results obtained showed that the degradation kinetics of malathion is a first order reaction

Accordingly, this study also showed, first that the photodegradation of malathion was more effective for higher values of pH and temperature.

As with other oxidizing systems involving radical species such as hydroxyl radicals OH. H<sub>2</sub>O<sub>2</sub>/UV system efficiency can be greatly decreased by the presence of radical trap in the reaction medium.

We then used the methodology of experimental designs as an optimization tool. Through this study, three factors have been identified as having a statistically significant influence on the rate of malathion reduction.

The matrix used (plan for response surface) consists of eighteen (18) experiments. Mathematical and statistical analyses of the eighteen measured values for each of the responses enabled the calculation for the first time of the 8 model coefficients and in a second time, refine these models by maximizing their descriptive qualities and especially predictive ones. Finally, models of abatement rates consist of more than 8 elements and are presented by the following equation:

$$R\% = 84.56 - 4.25 \times X_1 - 9 \times X_2 + 14.75 \times X_3 - 6.41 \times X_1 \times X_1 - 26.04 \times X_2 \times X_2 + 6.09 \times X_3 \times X_3 + 4.75 \times X_1 \times X_3 + 4.25 \times X_2 \times X_3.$$

These models, with quality descriptive and predictive indicators greater than 98%, have been validated and therefore reflect correctly the abatement rate of malathion in the experimental field. The value of the response corresponding to the optimum point is 80%.

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