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Optimisation of transformation kinetic of fenamiphos in aqueous media using experimental design

A. Yadini, L. El Fakir, B. Birich, M. El Azzouzi and S. El Hajjaji*
Laboratoire de Spectroscopie, Modélisation Moléculaire, Matériaux et Environnement (LS3ME), Equipe Physico-chimie des Matériaux et Environnement (EPCME), FSR, University Med V - Agdal, Av Ibn Battouta, BP 1014, Agdal. Rabat, Morocco.

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* Corresponding auteur: E-mail: *selhajjaji@hotmail.com;* Tel: 06 61 30 31 02

Abstract:
The intensive use of pesticides in modern agriculture has led to serious problems in the quality of superficial or underground water, which led to the development of diseases and destruction of fauna and flora. Water pollution by these pesticides is a reality more and more present in Morocco that requires control and elimination of these compounds in the aqueous medium. Therefore, it is important to take interest in their ability to be degraded and the degradation pathway. Pesticides are only partially degraded in the field and transformation products are formed which can also be found in groundwater or rivers. The downside of partial degradation is that transformation products are often more mobile than their parent compound, can be more persistent and even more toxic; inducing the increase of total contamination. In this study, we focused on fenamiphos as pesticide. This product belongs to the chemical family of organophosphates and it is widely used as an insecticide and nematicide on a number of crops. Fenamiphos oxidize on fenamiphos sulfoxide and fenamiphos sulfone that are more toxic and persistent. To determine the main effects and interactions of various parameters (pH, concentration (fenamiphos / Fe^{2+} ions) on the effectiveness of the oxidation process, a kinetic of the fenamiphos transformation in aqueous medium has been studied to determine the conditions for the oxidation of fenamiphos using experimental design.

Key words: Environment, Experimental design, Fenamiphos, Kinetics, Photodegradation.

1. Introduction
Various organic compounds such as pesticides, industrial chemicals and dyes can be introduced into the environment as a result of several human activities. They can be present in groundwater, rivers [1, 2], soils and atmosphere. Their negative ecological consequences are often assigned to their persistence in these media. In recent years, different methods for water or air purification as well as soil decontamination have been developed including chemical, electrochemical or photochemical processes [3-5]. Photodegradation can result either from a direct process if the pollutant absorbs solar light or by a photo-induced process [6, 7].
Fenamiphos (IUPAC NAME: ethyl 4-methylthio-m-tolyl isopropylphosphoramidate) belongs to the organophosphorus class of insecticide which is mostly used to control soil nematodes in turf and horticultural crops [8-10]. Fenamiphos is oxidized rapidly to give rise to fenamiphos sulfoxide (IUPAC NAME: N-Isopropylamidophosphoric acid ethyl 4-(methylsulfinyl)-3-methylphenyl ester) which can also slowly oxidized to give rise to fenamiphos sulfone (IUPAC NAME: isopropyl-, ethyl 4-(methylsulfonyl)-m-tolyl ester) [11, 12]. Fenamiphos sulfoxide and fenamiphos sulfone have similar pesticide activity and toxicity like fenamiphos [13], but higher mobility and persistent. Its photodegradation process follows pseudo first order kinetic and depends on the pH and temperature [14].
The aim of this study is to optimize photocatalytic degradation conditions of fenamiphos using the methodology of experimental research and to determinate the main effects and interactions of different parameters (pH, concentration of fenamiphos and concentration of Fe^{2+}).

2. Material and Methods
2.1. Reagents and kinetic
Fenamiphos with 99.5% purity is used as received. All other chemicals were analytical grade and were used without further purification. Solutions were prepared with high purity water. A 10 ppm working standard solutions in water was prepared.

2.2. Irradiation experiment

The kinetic experiments were performed by following the disappearance of insecticide by means of HPLC with Diode Array UV detector. The solutions were irradiated in a reactor (a cylindrical Pyrex glass vessel of 250 mL) using the lamp: High-pressure mercury lamp HPLK 125W-Phillips (high level of UV radiation, provide maximum energy at 365 nm, with substantial radiation also at 435, 313, 253 and 404 nm) (Figure 1). All solutions were stirred using magnetic stirrer and samples from considered solutions were taken at regular time intervals, centrifuged and then analyzed directly without preconcentration by HPLC.

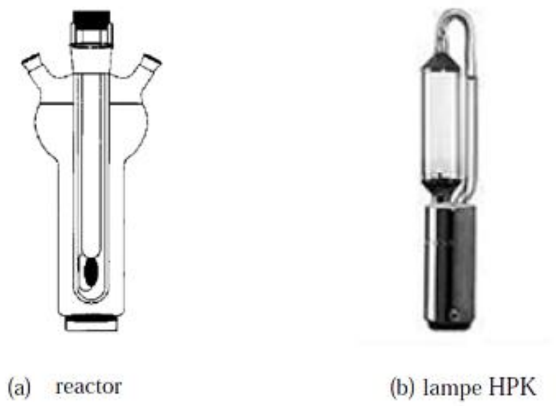


Figure 1. Irradiation system (a) equipped with a 125W Philips HPK lamp (b).

All experiments were performed in duplicate. Test controls were incubated in the dark to ensure that the transformation of fenamiphos was only due to light absorption. The concentrations were determined from the calibration curve (area vs concentration) produced from known concentrations. The absorbance spectrum of Fenamiphos in aqueous solution is presented in Figure 2.

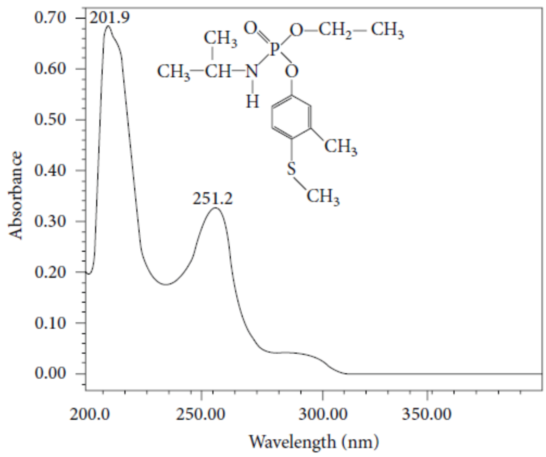


Figure 2. Absorbance spectrum and the chemical structure of fenamiphos.

2.3. Instrumental analysis

HPLC was performed using a GBC equipped with a UV diode array detector set at 249 nm. The column was a 250mm x 4.6 mm agilent Zorbax SB C18 column. The mobile phase was a mixture of water and methanol (30/70, v/v). The flow rate of isocratic elution was 1mL/min and the injection volume was 20µL.

The HPLC coupled to mass spectrometer (HPLC/MS) used in this study is equipped with HPLC LC type Surveyor brand Thermo-Electron, C18 column (4.6 * 150 mm), quaternary gradient pump with integrated degasser, oven included in the ferryman, stable between 5 and 95 °C, UV detector diode array SURVEYOR (spectral range from 190 to 800nm) and a detector mass spectrometer LCQ Advantage MAX ion trap type.

3. Results and discussion

The objective of the methodology of experimental research (MER) is to search an optimal strategy which allows obtaining the largest number of good quality information concerning a studied phenomenon, while carrying a limited number of experiments. The main purpose of a screening study is to identify the most influential factors and those that may be regarded as inert. Fractional factorial designs [15] were chosen to evaluate the factors that significantly influence photodegradation of fenamiphos. For each problem formulated, the first problem is the choice of the factors which are the parameters that we can control. We must choose the variation limit of these factors which determines the experimental domain. These variations may have very different orders of magnitude, so that, to be able to compare the factor effects, it is necessary to work with the code levels of variation of each factor. For the present work, we have to evaluate the influence of 3 factors, each at two levels (high (+1)) and low (-1)). The selected parameters are listed in Table 1.

Table 1: Factors and their levels for the experiments

level	Concentration of fenamiphos ppm	Concentration of Fe^{2+} Mole/L	pH
-1	**5**	**10^{-4}**	**3**
+1	**20**	**10^{-2}**	**9**

The Fractional Factorial Design consists in expressing the estimated effects in contrast. We used a 2^3 experiment: 3 factors each at two levels (+1, -1) were investigated; 8 trials were necessary for this fractional factorial design (Table 2). All experiments were performed in random order and the calculation was obtained by the NEMROD program [16]. In order to show the effect of each factor. Experimental matrix and the results obtained are shown in Table 3, the studied response is the kinetic of photodegradation of fenamiphos.

Table 2: Complete factorial design 2^3: theoretical values of coded variables

Exp	X_1	X_2	X_3
1	**-1**	**-1**	**-1**
2	**+1**	**-1**	**-1**
3	**-1**	**+1**	**-1**
4	**+1**	**+1**	**-1**
5	**-1**	**-1**	**+1**
6	**+1**	**-1**	**+1**
7	**-1**	**+1**	**+1**
8	**+1**	**+1**	**+1**

Table 3: Experimental design and responses

Exp	X_1	X_2	X_3	k (min^{-1})
1	**5**	**10^{-4}**	**3**	**0.016**
2	**20**	**10^{-4}**	**3**	**0.006**
3	**5**	**10^{-2}**	**3**	**0.011**
4	**20**	**10^{-2}**	**3**	**0.015**
5	**5**	**10^{-4}**	**9**	**0.004**
6	**20**	**10^{-4}**	**9**	**0.007**
7	**5**	**10^{-2}**	**9**	**0.003**
8	**20**	**10^{-2}**	**9**	**0.006**

Processing of the data led to the estimation of 8 coefficients for the polynomial equation for the response as follows and is given in Table 4:

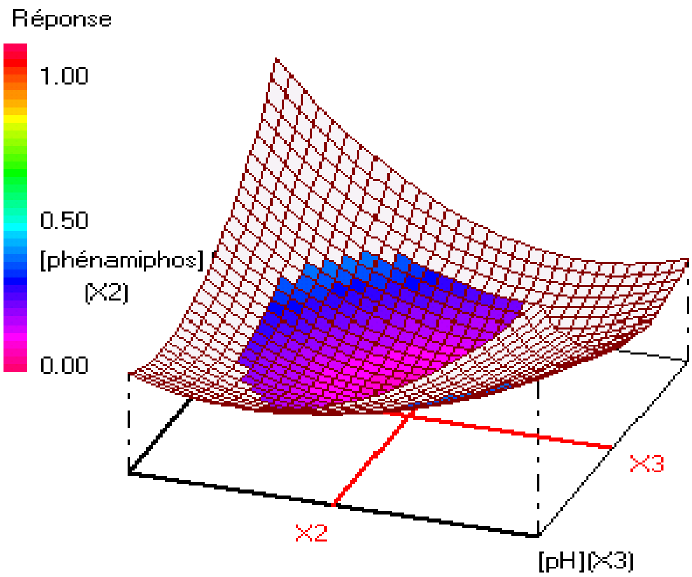
$$\mathbf{Y = 0 .0085- 0.0011x_1+ 0.0025x_2 - 0.0035x_3 + 0.0017x_1x_2 + 0.0015x_1x_3 - 0.00075x_2x_3 -0.0017x_1x_2x_3.}$$

The study of these results indicates that the process can be explained by the strong effects corresponding to the pH of the medium and concentration fenamiphos. The Fe^{2+} ions have no influence of the process.

Table 4. Main effects and interactions effects calculated from Factorial Fractional Design 2^3.

b_0	**+0.0085**	b_2	**+ 0.0025**	b_{12}	**+ 0.0017**	b_{23}	**- 0.00075**
b_1	**- 0.0011**	b_3	**- 0.0035**	b_{13}	**+ 0.0015**	b_{123}	**- 0.0017**

Based on these experimental data, the kinetic of transformation of the fenamiphos is higher when the medium is acidic (-1) and the concentrations in the pesticide (-1) and in ions Fe^{2+} (-1) are low.
The figure 3 is an example of 2D and 3D representation showing the variation of the response as a function of the concentration of Fe^{2+} and fenamiphos.



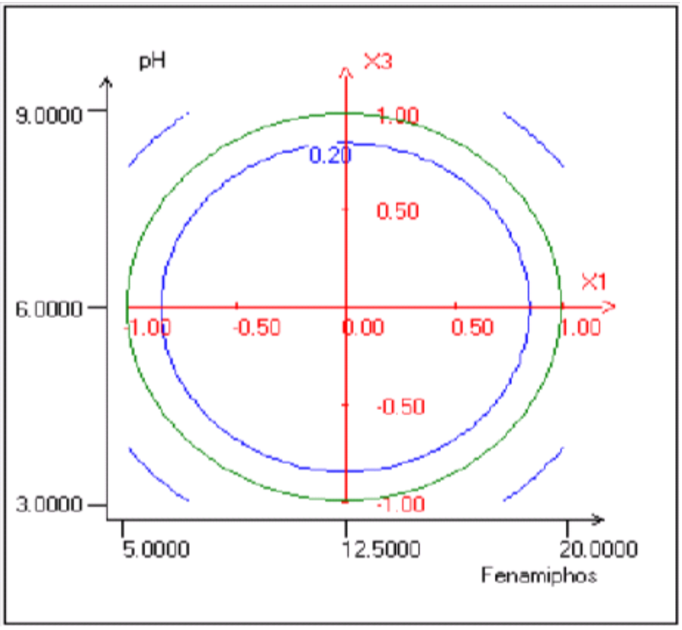


Figure 3. 2D and 3D representation of the variation of the degradation kinetics of the interaction depending fenamiphos concentration / pH.

Pareto chart (Fig. 4) shows the percentage effect of each factor influencing the kinetics of transformation of Fenamiphos. According to this result, the most effect is attributed to the pH. We noticed that all interactions have approximately the same effect on the transformation kinetic of fenamiphos in water.

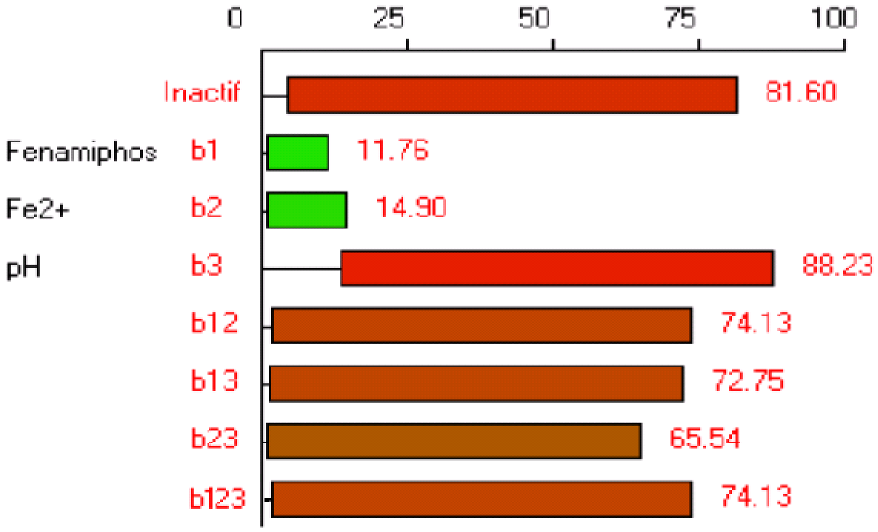


Figure 4. The pareto diagram.

Conclusion

The aim of this study is the optimisation of the photodegradation of fenamiphos. The present work has demonstrated that the experimental domain that we defined appears suitable for this optimisation. The complete factorial design allows a rapid overall study of phototransformation process, under relatively strong experimental constraints. The primary conclusion of this study is that pH and interactions between bath compounds and pH have an important influence on the degradation process. The experimental designs used for these experiments led to the optimum conditions being obtained.

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