

Phototransformation of pesticide by UV, H₂O₂/UV and the combination of moroccan natural phosphate and UV radiation in dilute aqueous solution

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The degradation of oxamyl in purified water has been studied in the process of photolysis under polychromatic radiation ($\lambda > 285$ nm), process of photolysis in homogeneous media using a combination of ultraviolet light ($\lambda = 253.7$ nm) with hydrogen peroxide H₂O₂/UV and process of photolysis in heterogeneous media using a quasi-monochromatic irradiation ($\lambda = 365$ nm) in aqueous suspensions containing natural phosphate (NP). Upon polychromatic excitation, apparent first-order kinetic constants have been determined. For oxidation by H₂O₂/UV the rate constant of the reaction of hydroxyl radicals HO[•] with oxamyl, determined by kinetic experiments, was evaluated to be equal to $2,45 \cdot 10^9$ L.mol⁻¹.s⁻¹. The same primary photoproducts: the isomer (E) and nitrile derivative (N,N-dimethyl-2-nitrilo-acetamide) have been formed in the process of photolysis under polychromatic radiation and the process H₂O₂/UV. In the case of the phototransformation of oxamyl in the presence of NP, a single photoproduct was identified by LC/MS analysis as the derivative of oxime.

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1. Introduction

There has been a considerable interest in the photooxidation reactions of pesticide in aqueous solution. Indeed, widespread use of pesticides for agriculture production has led to their accumulation in soil, surface and ground water, resulting in serious environmental problems [1]. Direct and indirect sunlight-induced photochemical reactions contribute to the transformation of pesticides in water. Indirect photo-degradation may be due to the presence of chemical transients, mainly the hydroxyl radical HO[•] which is an extremely reactive oxidant [2]. This work is a contribution to the study of the phototransformation of oxamyl by the direct photolysis at $\lambda > 285$ nm, by the combination of hydrogen peroxide and ultraviolet radiation ($\lambda = 253,7$ nm) and by the combination of NP and monochromatic radiation ($\lambda = 365$ nm). The choice of NP was dictated by its abundance in our country (Morocco), its low price and non-aggressive nature towards the environment like its use by certain authors to removal some heavy metal ions [3-6]. In our work, we studied the photosensitizer effect of NP on the degradation of oxamyl. Oxamyl belongs to the carbamate family of pesticides. It has been classified as a restricted use pesticide (RUP) by the The U.S. Environmental Protection Agency due to its acute toxicity to humans and its toxicity to birds and mammals. Oxamyl is highly soluble in water (280 g/l, 25°C) and therefore causes groundwater contamination.

2. Materials and methods

L'oxamyl was a Riadel-de Haën product. All solutions were prepared with purified water (resistivity 18

M Ω .cm⁻¹, DOC <0,1 mg.l⁻¹) obtained using a Millipore device (Milli-Q). A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco). The irradiation set-up was a batch photoreactor (volume of irradiated solution = 3.7 L, optical reactor pathlength = 6,75 cm). The lamp was located at the center of the reactor, in a quartz sleeve. Three radiation source were used: polychromatic light ($\lambda > 285$ nm) (Vilbert et Lourmat T6M see figure 1), quasi-monochromatic light at $\lambda = 365$ nm (Sylvania (Black Light Blue) see figure 2) and monochromatic light at $\lambda = 253,7$ nm (Vilbert et Lourmat T6C) where the number of photons was evaluated with hydrogen peroxide actinometry as described elsewhere [7]. The value obtained was 10^{-6} Einstein. L⁻¹. s⁻¹ during the period of experiments.

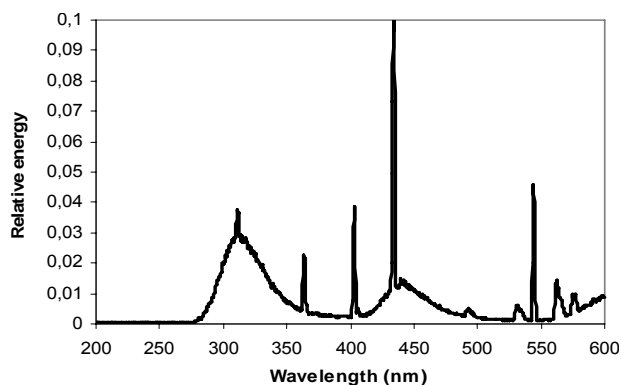


Fig. 1. Emission spectrum of T6M lamp.

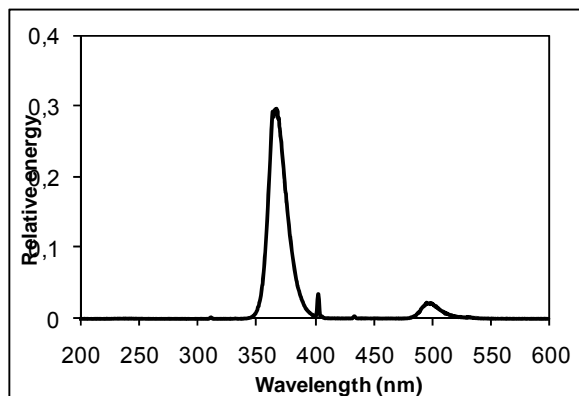


Fig. 2. Emission spectrum of Sylvania lamp

UV-Vis spectra were recorded on a SECOMAM SF0086 single-beam spectrometer, using either 1 or 5 cm cell. The disappearance of oxamyl was quantified by HPLC using a Waters system equipped with a UV absorbance detector (uptisphere column 250×3 mm ($5\mu\text{m}$), eluant Methanol 25% + water 75%, flow $0,3 \text{ ml}\cdot\text{min}^{-1}$). The apparatus of HPLC/mass spectrometry (HPLC/MS) was a Thermo-Electron LC Surveyor equipped with a detector mass spectrometer LCQ Deca XP and with SURVEYOR photodiode array detector.

The diffractogramme X and the IR spectrum of NP were obtained by XPERT-PRO diffractometer with $\text{Cu K}\alpha$ radiation (45 kV and 40 mA) and a Bruker Vertex 70 spectrophotometer. The BET surface area of NP was determined by N_2 adsorption (QuantaChrome Instruments). For SEM a Philips scanning electron microscope was utilized. The accelerating voltage was 25 kV.

3. Results

3. 1. Electronic absorption properties of oxamyl

The UV-Vis spectra of oxamyl in aqueous solution were recorded. The molar absorption coefficients are $151 \text{ M}^{-1} \text{ cm}^{-1}$ and $5042 \text{ M}^{-1} \text{ cm}^{-1}$ respectively at 285 nm and 254 nm. No absorption is recorded at 365nm. The irradiation at $\lambda > 285$ nm or at 254 nm of a solution of oxamyl leads to a degradation of the compound whereas it is not degraded at 365 nm, from where the use of NP to induce its degradation.

3.2. Photolysis of oxamyl

The evolution of the concentration of oxamyl as a function of the time of irradiation is shown in figure 3.

The concentration of oxamyl as a function of the time of polychromatic irradiation in dilute aqueous solution is given by the following relation:

$$-\frac{d[\text{oxa}]}{P_2} = 2.3l \sum_{\lambda} \Phi_{\lambda} I_{0,\lambda} \varepsilon_{\lambda} [\text{oxa}] = k_{\text{app}} [\text{oxa}]$$

where Φ_{λ} and $I_{0,\lambda}$ are the quantum yield and the rate of light absorption at the wavelength λ respectively, ε_{λ} the molar absorption coefficient, k_{app} the apparent rate constant, $[\text{oxa}]$ and l are the concentration of oxamyl and the reactor optical pathlength, respectively.

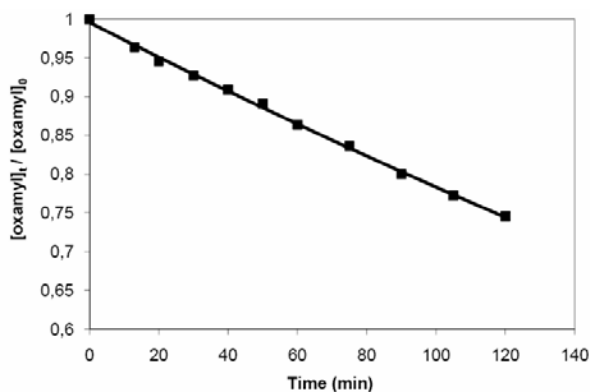


Fig. 3. The kinetics of photolysis of oxamyl under polychromatic in purified water ($[\text{oxamyl}]_0 = 10 \mu\text{M}$).

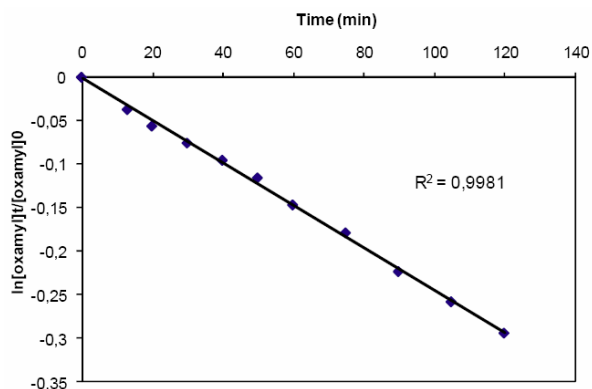


Fig. 4. Semi-logarithmic representation of the disappearance of oxamyl

Fig. 4 shows that the kinetics of photolysis of oxamyl under polychromatic radiation obey to an apparent first order kinetics law, in agreement with the preceding relation. The value of the apparent rate constant is $2,4 \times 10^{-3} \text{ min}^{-1}$ and the half-life time is 4,8 hours.

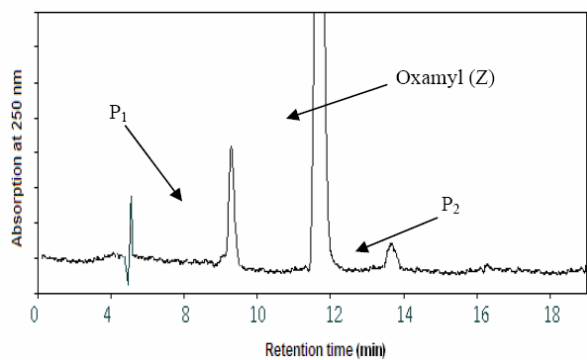
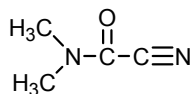
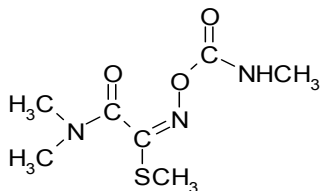


Fig. 5. The chromatogram of irradiated solution of oxamyl

Two chromatographic peaks appear in the chromatogram of irradiated solution of oxamyl (Figure 5). The analysis of P₁ product by HPLC/MS in positive mode APCI reveals the presence of two pseudomolecular peaks at *m/z* 99 and 131, corresponding to [M+H]⁺ and [M+H+MeOH]⁺ respectively. In negative mode, we observe the ion [M-H]⁻ with *m/z* 97. These results lead us to conclude that this compound is the nitrile derivative (N,N-dimethyl-2-nitrilo-acetamide) with a molecular mass 98 g/mol of which the structure is indicated below.



The mass spectrum in positive mode APCI of the photoproduct P₂ indicates the presence of the pseudomolecular peak at *m/z* 237, which corresponds to [M+NH₄]⁺. It is the isomer E of oxamyl represented below.



The study of the influence of the oxygen dissolved on the polychromatic photolysis shows that it does not intervene in the phototransformation of the oxamyl (Figure 6). What lets us to suggest the same mechanisms established by MAZELLIER et al. [8], who are the homolytic cleavage of the N-O bond and the photoisomerisation of oxamyl leading respectively to nitrile and isomer E.

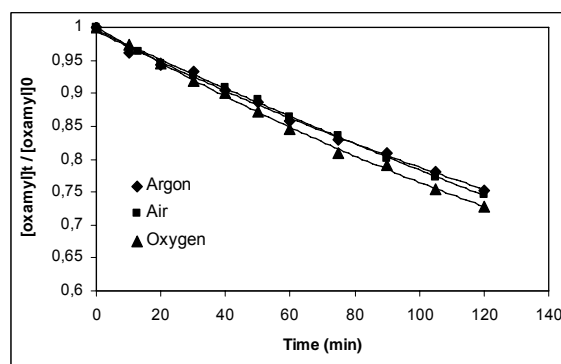


Fig. 6. Kinetics of oxamyl photodegradation in the presence of various dissolved oxygen contents (according to the sparging gas).

Fig. 7 gives the evolution of the peak areas of the photoproducts of oxamyl as measured using HPLC area versus the irradiation time. The two resulting compounds as products of photolysis seem to be primary photoproducts, since they appear in the first minutes. It appears that the nitrile derivative accumulate in the irradiated solution and is very stable even after several days of irradiation. It seems that the nitrile derivative is the major photoproduct.

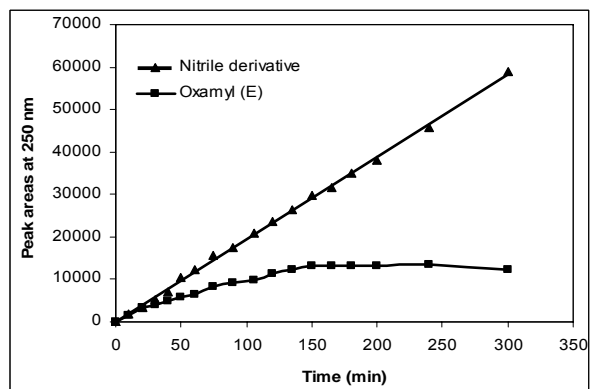


Fig. 7. Formation of nitrile derivative and the isomer E of oxamyl during the photodegradation of 50% of oxamyl ($C_0 = 10 \mu\text{M}$).

The photolysis reactions of oxamyl are represented in the Fig. 8.

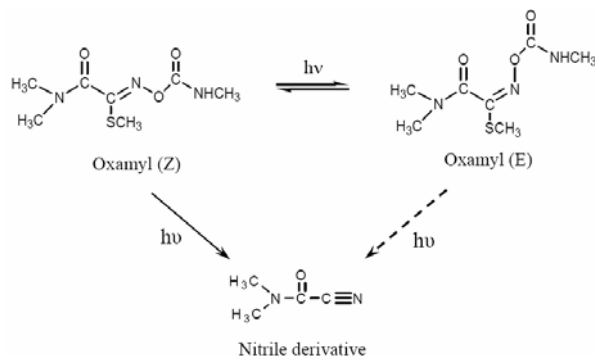
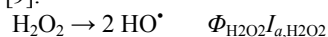


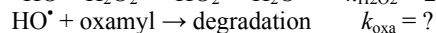
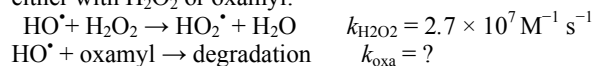
Fig. 8. The photolysis reactions of oxamyl

3.3. Transformation of oxamyl by an H_2O_2 /UV process

The irradiation ($\lambda_{exc} = 253.7$ nm) of hydrogen peroxide in aqueous solution leads to the production of HO^\bullet radicals [9].



In the presence of oxamyl, hydroxyl radicals react either with H_2O_2 or oxamyl:



The steady-state concentration of hydroxyl radicals at a given time t is:

$$[HO^\bullet] = \frac{2 \Phi_{H_2O_2} \times I_{a,H_2O_2}}{k_{H_2O_2} [H_2O_2] + k_{\text{oxa}} [\text{oxa}]} \quad (I)$$

where $\Phi_{H_2O_2}$ is the initial quantum yield of hydrogen peroxide disappearance, equal to 0.5, I_{a,H_2O_2} , the rate of light absorption by H_2O_2 .

If hydrogen peroxide concentration is high enough to consider that:

1. the incident light is completely absorbed by hydrogen peroxide;
2. the decrease in H_2O_2 concentration is low (<5%) in the time scale of the experiments;

Table1. Values of the apparent rate constant k_{app} for each initial concentration of H_2O_2

$[H_2O_2]_0$ (M)	0,05	0,07	0,1	0,2	0,3
k_{app} (s^{-1})	$3,52 \cdot 10^{-3}$	$2,79 \cdot 10^{-3}$	$1,89 \cdot 10^{-3}$	$1,12 \cdot 10^{-3}$	$0,709 \cdot 10^{-3}$

The representation of k_{app} as a function of $1/[H_2O_2]_0$ (Figure 10) gives access to the rate constant of the reaction of hydroxyl radicals HO^\bullet with oxamyl according to the relation (IV).

3. $k_{H_2O_2} [H_2O_2]_0 \gg k_{\text{oxa}} [\text{oxa}]_0$.

Then equation (I) becomes:

$$[HO^\bullet] = \frac{2 \Phi_{H_2O_2} \times I_0}{k_{H_2O_2} [H_2O_2]_0} \quad (II)$$

The rate of oxamyl disappearance can be written according to relation (III) (the direct photolysis at 253.7 nm being negligible) and the integrated form is equation (IV).

$$-\frac{d[\text{oxa}]}{dt} = k_{\text{oxa}} [HO^\bullet][\text{oxa}] \quad (III)$$

$$-\ln \frac{[\text{oxa}]_t}{[\text{oxa}]_0} = \frac{k_{\text{oxa}} \times 2 \Phi_{H_2O_2} \times I_0}{k_{H_2O_2} [H_2O_2]_0} t = k_{app} t \quad (IV)$$

The Fig. 9 representing $\ln [\text{oxa}]_t / [\text{oxa}]_0$ as a function of time allows to determine the values of the apparent rate constant k_{app} (Table 1).

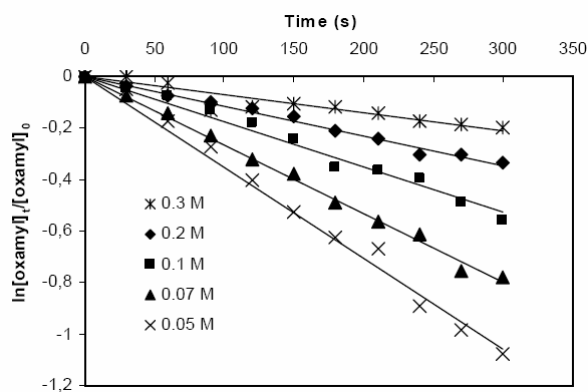


Fig. 9. The kinetics of photodegradation of oxamyl in the presence of various concentrations of H_2O_2 ($[\text{oxamyl}] = 1 \mu M$, $I_0 = 1,019 \cdot 10^{-6} E \cdot L^{-1} \cdot s^{-1}$).

We can deduce:

$$k_{\text{oxa}} = 2,45 \cdot 10^9 L \cdot mol^{-1} \cdot s^{-1}$$

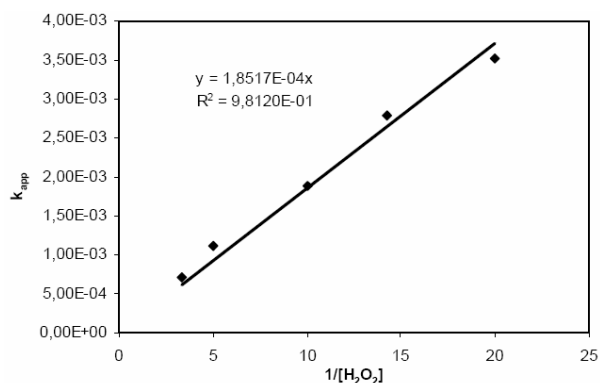


Fig. 10. The representation of k_{app} as a function of $1/[H_2O_2]_0$

The rate constant of the reaction of hydroxyl radicals HO[•] with oxamyl is in agreement with a high reactivity of the radicals HO[•] with the oxamyl. The same order of reactivity of the radicals HO[•] was observed for another pesticide of the family of the oxamyl: carbendazime (2-methyl benzimidazole carbamate) $2,2 \pm 0.3 \cdot 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$.

Two chromatographic peaks appear in the chromatogram of the photodegradation of oxamyl by the process H₂O₂/UV (Figure 11). The analysis of P₁ and P₂ photoproducts by HPLC/MS in positive mode APCI shows the same photoproducts the nitrile derivative and isomer (E) of oxamyl respectively, as those observed under polychromatic radiation ($\lambda > 285 \text{ nm}$).

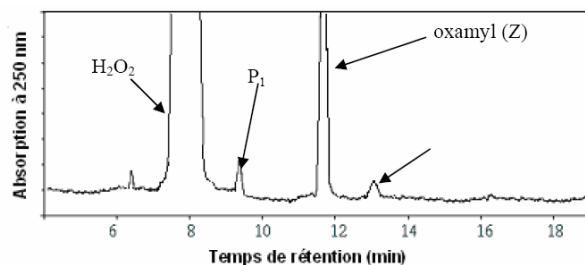


Fig. 11. The chromatogram of photodegradation of oxamyl in the presence of H₂O₂

The Fig. 12 shows that the evolution of the photoproducts of oxamyl by H₂O₂/UV process is identical to the direct photodegradation process.

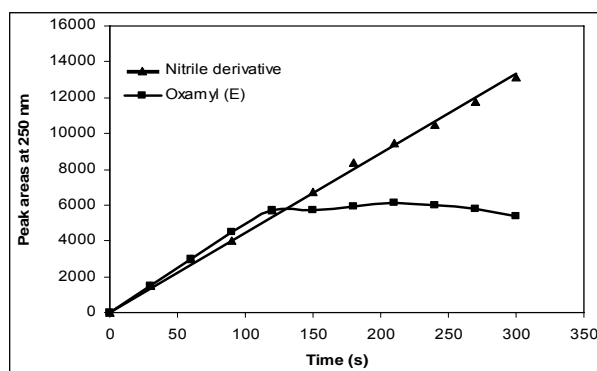


Fig. 12. Formation of nitrile derivative and the isomer E of oxamyl during the photodegradation of 70% of oxamyl ($C_0 = 1 \mu\text{M}$) at $0,05\text{M H}_2\text{O}_2$.

3.4. Phototransformation of oxamyl in the presence of NP

3.4.1. Preparation and characterisation of NP

The preparation and characterisation of NP used in this study was published in Journal of optoelectronics and advanced materials [10].

3.4.2. Analysis of the elements leached by NP

In order to use NP in the photodegradation of oxamyl we verified that it does not reject harmful elements. To analyze the elements leached by NP, a suspension of 500 milligrams of NP in 1L of water was magnetically stirred at room temperature for 72 h and filtered through a filter membrane of $0,45\mu\text{m}$. The filtrate was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP/OES). As shown in Table 2, the results of this analysis show that the concentration of the elements leached by NP is lower than the Maximum acceptable values (MAV) required for the quality of the water intended for human consumption.

Table 2. Analysis of the elements leached by NP in aqueous solution by ICP/OES.

Elements	Concentration ($\mu\text{g/L}$)	The Maximum acceptable values (MAV) required for the quality of the water intended for human consumption
		Concentration ($\mu\text{g/L}$)
Al	11,8	200*
B	71,2	300*
Na	2010	200 000**
Ca	3090	100 000***
K	1530	12 000**
Mg	80	50 000***
Fe	2,64	300*
Mn	0,62	500*
Zn	7,05	3000*
P	188	5000**
S	677	-
Cd	2,85	3*
Co	0,17	-
Ni	6	20*
Cu	10,4	2000*
Pb	0,75	10*
Ba	1,82	700*
Cr	0,67	50*
Mo	1,54	70*
Si	180	-
F	1200	1500*

* Moroccan standard (NM 03.7.001) concerning water used for human consumption.

** European Directive 98/83/EC on the quality of water intended for human consumption 03/11/1998.

*** French Decree no. 2001-1220 of 20 December 2001 concerning water used for human consumption.

3.4.3 Phototransformation of oxamyl in the presence of NP

The UV-visible absorption spectra of oxamyl show no absorption at the UV radiation of the monochromatic lamp (Figure 13) then it will not be amenable to direct photolysis at this radiation (Fig. 14).

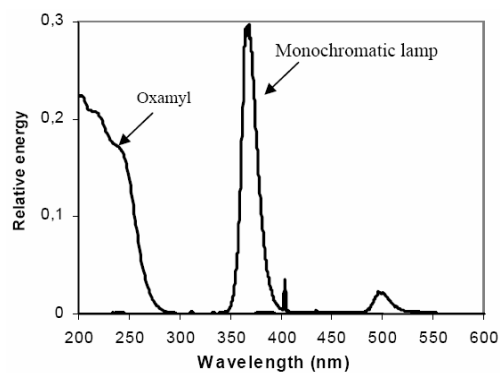


Fig 13. The UV-visible absorption spectra of oxamyl and emission spectrum of Sylvania lamp

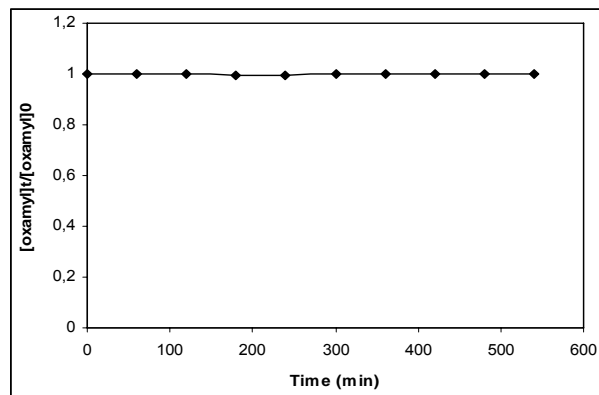


Fig. 14. The kinetic of direct photolysis of oxamyl ($[oxamyl]_0 = 10\mu M$; $pH = 6.0$; $T = 25^\circ C$)

The kinetic of reaction of oxamyl with NP (Fig. 15) under dark conditions shows a slow degradation. Under irradiation, oxamyl is degraded quickly in the presence of NP; its kinetics of degradation is represented in the Fig. 15.

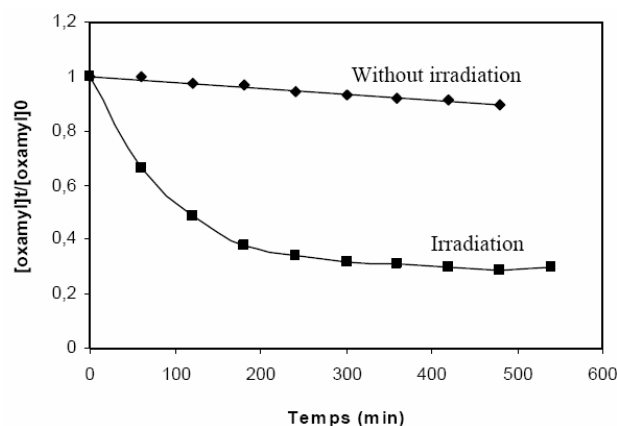


Fig. 15. The kinetics of degradation of oxamyl ($10\mu M$) in the presence of NP ($500mg/L$) with and without irradiation ($pH=7.4$)

The chromatogram of a solution of oxamyl in the presence of NP with or without irradiation shows the formation of a unique degradation product (Figure 16).

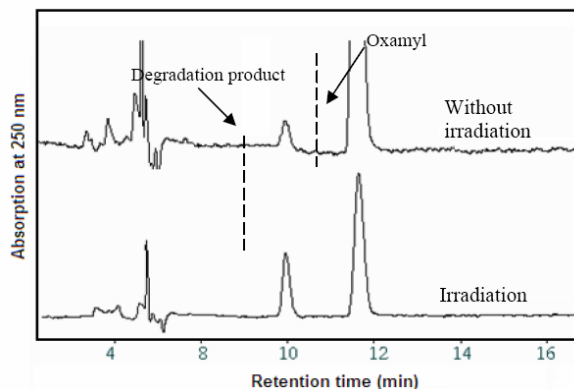


Fig. 16. The chromatogram HPLC/UV ($\lambda = 250\text{ nm}$) of a solution of oxamyl ($10\mu M$) in the presence of NP ($500mg/L$) with and without irradiation ($pH=7.4$).

LC-MS analyses of this product in positive mode APCI indicates the presence of the pseudomolecular peaks of $MH^+ = 163\text{ Da}$ and $MNa^+ = 185\text{ Da}$ (Figure 17). This is in agreement with the structure of the oxime derivative (2-dimethylamino-N-hydroxy-2-oxo-thioacetimidic acid methyl ester-R-OH derivative) as mentioned by Zamy et al. [11].

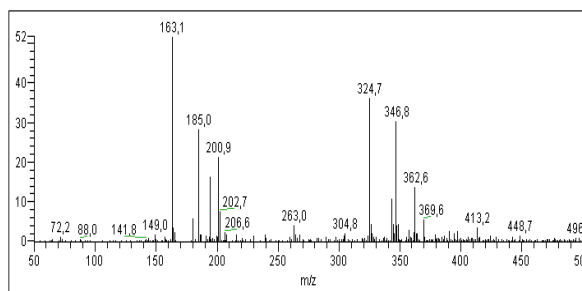


Fig. 17. The mass spectrum in positive mode APCI of the degradation product.

The formation of the oxime derivative in the case of the degradation of oxamyl in the presence of NP under dark conditions is due to hydrolysis at $pH\ 7.4$ like mentioned by Harvey and Han [12]. The mechanism of this hydrolysis is induced by an addition of HO^- onto the carbonyl with a further elimination of the RO^- leaving group or an abstraction of the hydrogen of the methyl carbamate moiety again evolving with elimination of the RO^- group [11]. The reaction of hydrolysis of the oxamyl is represented on the figure 18.

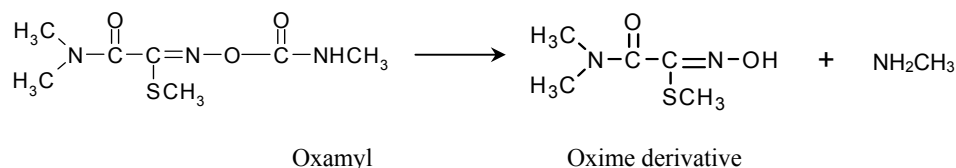


Fig. 18. Oxamyl hydrolysis [12].

3.4.4 Proposal of phototransformation mechanism

Evstratov et al. was studied in a patent the role of the materials which have a Lewis acid or Lewis base property to neutralize the free current carriers of a first type, positive electrons or holes, so as to protect current carriers of second type against recombination of a semiconductor component in amorphous state excited by light radiations [13]. In our work, photodegradation of oxamyl by NP who leads to the formation of oxime derivative (Figure 19) is probably due to the presence of semiconductor in NP, such as Fe_2O_3 , which absorb the light and promotes an electron from the valence band to the conduction band. Such process leads to the formation of a positive hole (h^+) in the valence band.

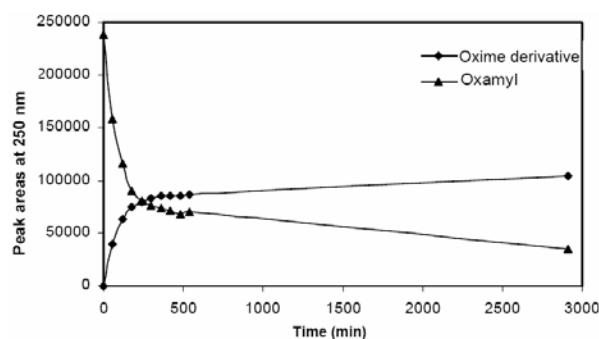


Fig. 19. The kinetics of photodegradation of oxamyl ($10\mu\text{M}$) in the presence of NP (500mg/L) and the kinetics of formation of its photoproduct: oxime derivative.

The NP is a Lewis acid, according to Alahiane et al. [14], playing a role of electrons trap which allows the forced separation of the free charge carriers (electrons, holes) preventing their immediate recombination, giving more time to the positive holes to oxidize water molecules or HO^\cdot with the formation of hydroxyl radicals. The OH^\cdot radicals are highly active for the oxidation of organic substances.

4. Conclusion

This present study shows that the photolysis of oxamyl under polychromatic radiation ($\lambda > 285\text{ nm}$) lead to the formation of two photoproducts: the isomer (E) and nitrile derivative. The half-life time of oxamyl is 4,8 hours. No dependence of the oxygen dissolved on the photolysis was noted. In the case of oxidation of oxamyl by $\text{H}_2\text{O}_2/\text{UV}$ the same photoproducts (the isomer (E) and nitrile derivative) as those observed under polychromatic radiation ($\lambda > 285\text{ nm}$) were observed.

The rate constant of the reaction of hydroxyl radicals HO^\cdot with oxamyl, determined by kinetic experiments, was evaluated to be equal to $2,45 \cdot 10^9\text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. In the case of irradiation under quasi-monochromatic irradiation ($\lambda = 365\text{ nm}$) in the presence of NP, the oxamyl undergoes an indirect transformation due probably to the presence of semiconductor in NP, such as Fe_2O_3 . A single photoproduct was found and identified by LC/MS analysis as the derivative of oxime.

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