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Phototransformation of pesticide in the presence of moroccan natural phosphate in aqueous solution

L. EL GAINI, A. MEGHEA[a], M. BAKASSE[*]
Faculty of Science, University Chouaib Doukkali, 24000, El Jadida, Morocco
[a]University POLITEHNICA of Bucharest, Romania

Natural phosphate is a natural rock formed through geological processes. The use of phosphates is widespread in both industry and agriculture**.** Moroccan reserves account for around 50% of the world total. The aim of this work is to study the photosensitizer effect of natural phosphate on the degradation of oxamyl under polychromatic light. Oxamyl is not amenable to direct photolysis. Indeed the UV-Visible spectrum of oxamyl shows no absorbance at these wave radiations. We have also verified that there was no reaction in the mixture oxamyl - natural phosphate in the dark and thermostatically controlled temperature of 25 °C. The irradiation of oxamyl in the presence of natural phosphate, leads to its degradation. The photodegradation rates were compared by varying substrate and inducer concentrations. A single photoproduct was found and identified by LC/MS analysis as the derivative of oxime.

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Keywords: Oxamyl, Natural phosphate, Photodegradation

1. Introduction

Natural phosphate is a general term that describes naturally occurring mineral assemblages containing a high concentration of phosphate minerals. About 80 percent of world natural phosphate production is derived from deposits of sedimentary marine origin mainly composed of apatites.

Natural phosphate that account for most of world natural phosphate production are in Morocco, the United States of America, the Near East and China [1]. Moroccan reserves account for around 50% of the world total [2]. Natural phosphate is the commercial source of phosphorus used as the raw material for manufacturing phosphorus fertilizers and certain other chemicals like the production of animal feed supplements and food products and detergents.

The abundance of natural phosphate in Morocco, its low price and non-aggressive nature towards the environment are advantages for its utilization in wastewater treatment like its use by certain authors to removal some heavy metal ions [3-6]. In our work, we studied the photosensitizer effect of natural phosphate 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 $M\Omega.cm^{-1}$, 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) (figure 1). The lamp was located at the center of the reactor, in a quartz sleeve. A high pressure mercury lamp (Philips HPK, 125 W) which emitted a maximum radiation at 365 nm was used as radiation source (Fig. 2).

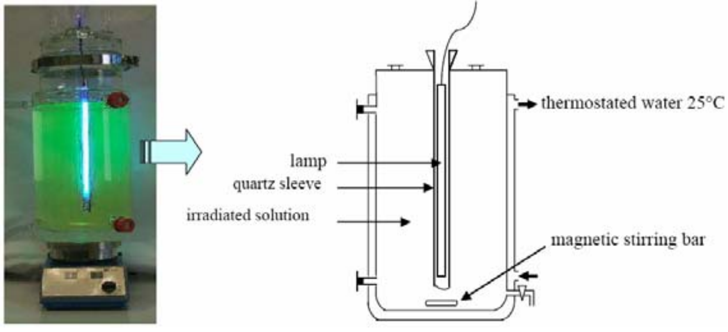


Fig. 1. Photograph and schematic diagram of the batch photoreactor.

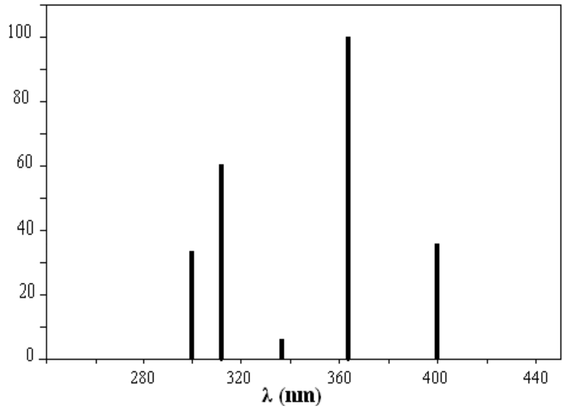


Fig. 2. Emission spectrum of HPK 125 lamp.

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 (5µm), eluant Methanol 25% + water 75%, flow 0,3 ml.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 natural phosphate were obtained by XPERT-PRO diffractometer with Cu K_α radiation (45 kV and 40 mA) and a Bruker Vertex 70 spectrophotometer. The BET surface area of natural phosphate 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. Preparation and characterisation of natural phosphate (NP)

The NP is treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and recalcination. The structure of NP is similar to that of fluorapatite ($Ca_{10}(PO_4)_6F_2$), as shown by X-ray diffraction and IR data (Figure 3 and 4). The IR spectra present the absorption bands corresponding to the vibration modes characteristic of PO_4^{3-} groups in the apatite structure (ν_1, ν_2, ν_3 and ν_4). The doublet at 1420 cm^{-1} and 1455 cm^{-1} correspond to the ν_3 starching vibrations of the carbonate group (CO_3^{2-}), while the band at 865 cm^{-1} is assigned to ν_2 CO_3^{2-} mode. The band at 726 cm^{-1} corresponds to the shifting OH^- liberation mode. This is caused by the increase of F^- content of in the (OH^- , F^-) chain of apatite with predominant configuration of …FHO:OHF… [7,8].

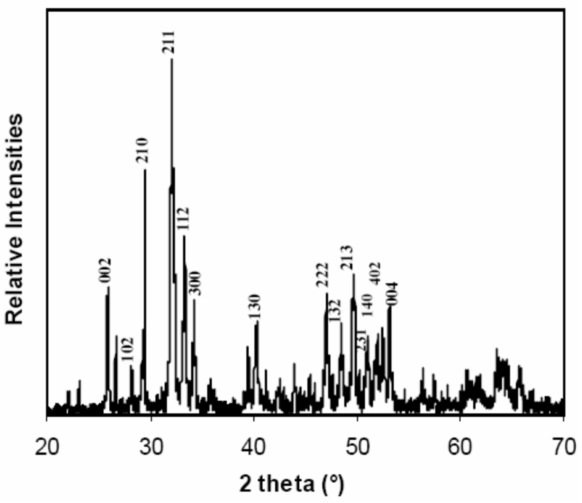


Fig. 3. XRD patterns of natural phosphate.

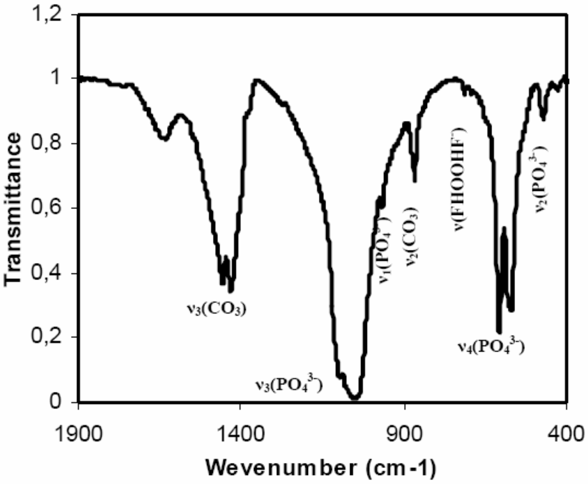


Fig. 4 . IR spectra of natural phosphate.

The BET surface area of NP is measured as 1.8 m^2 g^{-1}. The surface structure of natural phosphate was observed using Scanning Electron Microscopy (Fig. 5). The treatment of NP describes above lead to a fraction between 100 µm and 400 µm that is rich in phosphate and as can be seen that compact natural phosphate appearance was evident. The treated NP has following chemical composition: CaO (54.12%), P_2O_5 (34.24%), F^- (3.37%), SiO_2 (2.42%), SO_3 (2.21%), CO_2 (1.13%), Na_2O (0.92%), MgO (0.68%), Al_2O_3 (0.46%), Fe_2O_3 (0.36%), K_2O (0.04%) and several metals in the range of ppm.

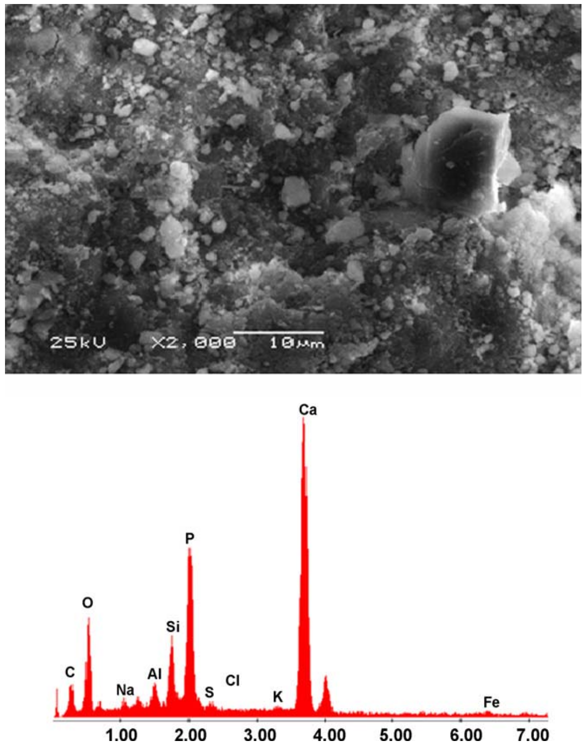


Fig. 5. Scanning electron micrograph of natural phosphate

3.2. Phototransfomation of oxamyl in the presence of natural phosphate

The UV-visible absorption spectra of oxamyl show no absorption at the UV radiation of the polychromatique lamp (Fig. 6) then it will not be amenable to direct photolysis at this radiation (Fig. 7).

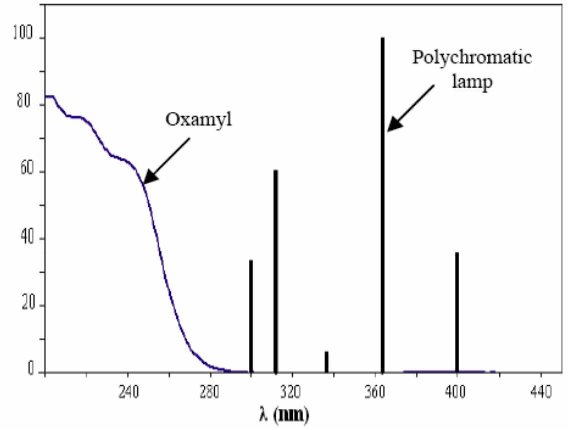


Fig. 6. The UV-visible absorption spectra of oxamyl and emission spectrum of HPK lamp.

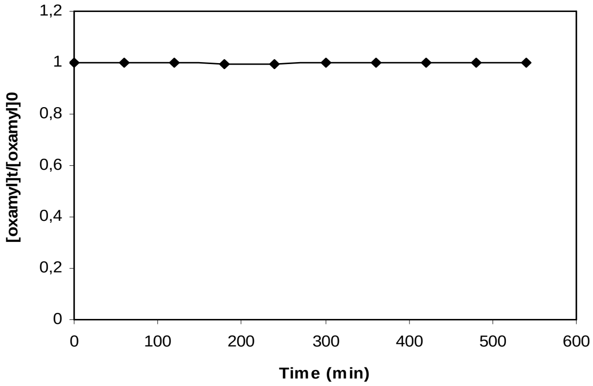


Fig. 7. The kinetic of direct photolysis of oxamyl ([oxamyl]$_0$ = 10µM; pH = 6.0; T = 25°C)

The kinetic of reaction of oxamyl with natural phosphate (Fig. 8) under dark conditions shows a slow degradation. Under radiation, oxamyl is degraded quickly in the presence of natural phosphate; its kinetics of degradation is represented in the Fig. 8.

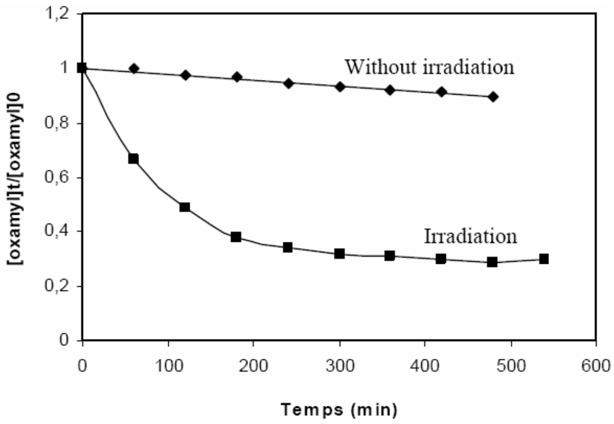


Fig. 8. The kinetics of degradation of oxamyl (10µM) in the presence of natural phosphate (500mg/L) with and without irradiation (pH=7.4).

The chromatogram of a solution of oxamyl in the presence of natural phosphate with or without irradiation shows the formation of a unique degradation product (Fig. 9).

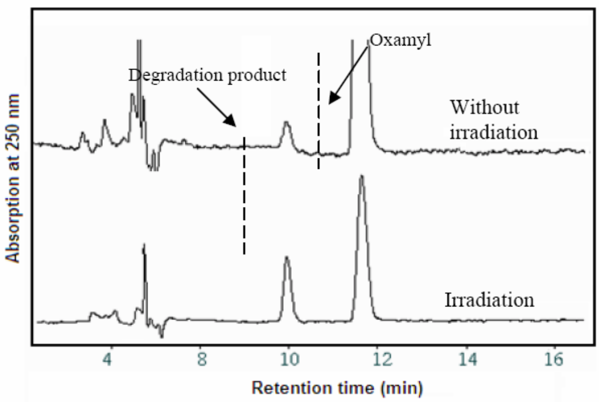


Fig. 9. The chromatogram HPLC/UV (λ = 250 nm) of a solution of oxamyl (10µM) in the presence of natural phosphate (500mg/L) with and without irradiation (pH=7.4).

LC–MS analyses of this product in positive mode APCI indicates the presence of the pseudomolecular peaks of MH^+ = 163 Da and MNa^+ = 185 Da (Fig. 10). 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. [9].

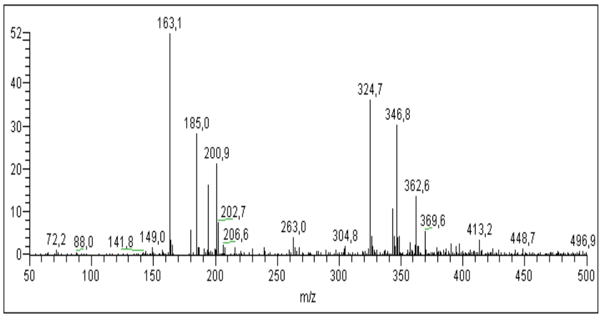
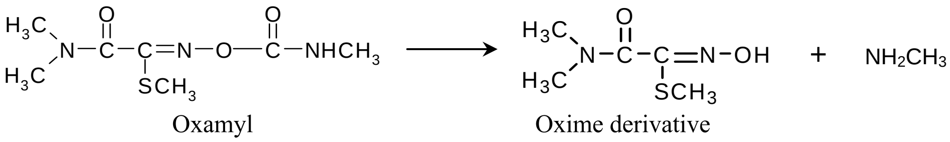


Fig. 10. The mass spectrum in positive mode APCI of the degradation product.

The formation of the oxime derivative in the case of the degradation of oxamyl in the presence of natural phosphate under dark conditions is due to hydrolysis at pH 7.4 like mentioned by Harvey and Han [10]. 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 [9]. The reaction of hydrolysis of the oxamyl is represented on the Fig. 11.



$$(H_3C)_2N-\overset{O}{\overset{||}{C}}-\underset{SCH_3}{\underset{|}{C}}=N-O-\overset{O}{\overset{||}{C}}-NHCH_3 \longrightarrow (H_3C)_2N-\overset{O}{\overset{||}{C}}-\underset{SCH_3}{\underset{|}{C}}=N-OH + NH_2CH_3$$

Fig. 11. Oxamyl hydrolysis [10]

The effect of the natural phosphate quantity on the initial rate of degradation showed the decreases of the initial rate of degradation when the natural phosphate quantity is higher than 500 mg may be caused by a screen effect of the high concentration of natural phosphate. The initial rate of degradation of oxamyl increases when the concentration of oxamyl is increased for all natural phosphate quantity (Fig. 12).

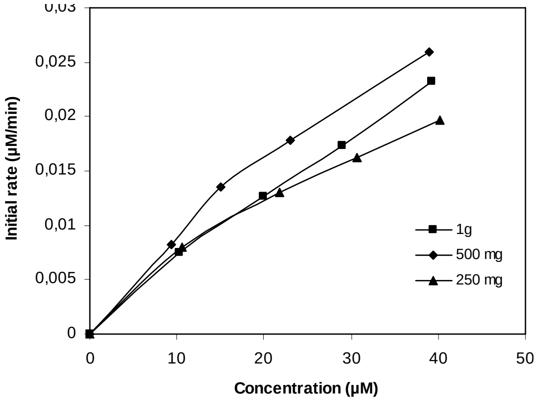


Fig. 12. The initial rate of oxamyl degradation as a function of pesticide and natural phosphate concentrations

4. Proposal of phototransfomation 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 [11]. In our work, photodegradation of oxamyl by natural phosphate is probably due to the presence of semiconductor in natural phosphate, such as $Fe_2 O_3$, 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. The natural phosphate is a Lewis acid, according to Alahiane et al. [12], 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^- with the formation of hydroxyl radicals. The $OH^\cdot$ radicals are highly active for the oxidation of organic substances.

5. Conclusions

The irradiation of oxamyl in the presence of natural phosphate, leads effectively to its degradation. The photodegradation rates compared by varying substrate and inducer concentrations show the increases of the initial rate of degradation of oxamyl when the concentration of oxamyl is increased. The use of the natural phosphate quantity higher than 500mg decreases the initial rate of degradation of oxamyl may be because of a screen effect of the high concentration of natural phosphate. A single photoproduct was found and identified by LC/MS analysis as the derivative of oxime. Photodegradation of oxamyl by natural phosphate is probably due to the presence of semiconductor in natural phosphate, such as Fe_2O_3.

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[*] Corresponding author. bakassem@yahoo.fr