



MBNA Publishing House Constanta 2021



## Proceedings of the International Scientific Conference SEA-CONF

SEA-CONF PAPER • OPEN ACCESS

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To cite this article: Octavian-Gabriel CHIRIAC, Oana-Elisabeta HOZA, Nicușor CHIRIPUCI, Adriana AGAPE, Andrei BURSUC and Edith-Hilde KAITER, Proceedings of the International Scientific Conference SEA-CONF 2021, pg.233-242.

Available online at [www.anmb.ro](http://www.anmb.ro)

ISSN: 2457-144X; ISSN-L: 2457-144X

doi: 10.21279/2457-144X-21-031

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# Decontamination of High Toxicity Organophosphorus Compounds by Means of Photocatalytic Methods

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**Abstract:** The hereby paper aims at investigating the photocatalytic behaviour of some titanium dioxide-based catalysts in the photocatalytic degradation reaction of organophosphorus compounds. Using conventional synthesis methods, new photocatalytic systems were prepared, which were tested in the mineralization of four simulants of organophosphorus chemical warfare agents. All these preparation methods aimed at modifying the photocatalytic properties of TiO<sub>2</sub> in order to visible absorb, by doping TiO<sub>2</sub>, with transition metal ions. The exhaustive characterization of the photocatalytic behaviour of the synthesized materials led to a comparative study between the photocatalytic activity under conditions of irradiation in the visible range and that in the UV domain for the photodegradation of organophosphorus compounds. To achieve this goal, a set of techniques capable of providing the necessary information was used.

## 1. Introduction

Chemical warfare agents (CWA) are the most toxic and lethal chemical compounds that mankind has ever created, their main purpose being to temporarily or permanently incapacitate one of the parties to a military conflict [1]. In terms of their chemical structure, the main CWAs are currently divided into three major groups, namely: G series (soman GD, sarin GB, tabun GA), V series (Vx, VX, VA, VR, VE, VG, VM and EA-3148) and H series (mustards). Of these, the most toxic are those belonging to the first two series, known generically as neurotoxic chemical agents, their main role being to inactivate the action of acetylcholinesterase in the central nervous system [2].

Eliminating the danger posed by these war chemicals requires the use of quickly and easily applicable decontamination systems, which should ideally be non-corrosive and produce as few environmental problems as possible. There are already a number of scientific papers and reviews that contain detailed descriptions of the methods currently used in the CWA decontamination process. Of these, hydrolysis and oxidation are the most widely used methods of CWA decontamination. G-series chemicals are typically decontaminated by aqueous hydrolysis. However, in terms of the efficiency of the decontamination process, hydrolysis is not suitable for all CWAs, such as Vx or VX of Russian origin, both toxic substances leading during the decontamination process to the appearance of reaction products, hydrolytically stable secondary acids such as thioic acids. Moreover, chemical warfare agents are generally combined with a polymer, the main purpose of which is to adhere as closely as possible to the surface of the environment in which they were deliberately released. Unfortunately, these CWA "thickening" polymers have an extremely low solubility in aqueous medium. To actively respond to such problems, hydrolysis catalysed in basic environment at high temperature is currently widely used in order to achieve the highest possible degree of decontamination [3]. Although from a practical point of view basic catalysed hydrolysis of neurotoxic chemicals is seen as an appropriate way to decompose these toxic compounds with maximum yields, the hydrolysed compounds must continue to be exposed to a secondary step (supercritical oxidation) in order to become harmless. In addition, all the steps involved in the decomposition process involve high temperatures and large amounts of water and decontaminating chemicals, while the decomposition products must be stored and treated as hazardous waste. In addition, such procedures reduce the number of possible

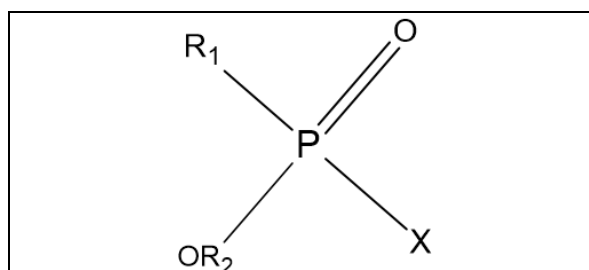
applications in the field, and the decontamination of sensitive equipment or human skin becomes an impractical process due to the increased corrosivity of the decontamination systems used.

In this context, researchers around the world have focused on the development of innovative technologies for the decontamination and detoxification of CWA and other highly toxic chemicals, together with the development of appropriate application equipment.

In the case of decontamination of organophosphorus compounds with high toxicity, it should be noted that the effectiveness of a catalytic / photocatalytic decontamination system has already been identified and demonstrated by combining two different decontamination techniques: basic catalysed alcoholism (especially methanolysis) and heterogeneous photocatalysis, which gives us a much clearer picture of what we might call the “golden key” in developing an effective system for the decomposition / detoxification of organophosphorus war chemicals.

Organophosphorus compounds are a category of highly toxic chemical compounds that attack both the central nervous system and the peripheral nervous system, which is why they are also called “neurotoxic” or “neuromuscular”. The category of organophosphorus compounds includes neurotoxic CWAs and their simulants (organophosphorus pesticides and a number of industrial toxic substances). In order to achieve an efficient decontamination of organophosphorus compounds from the CWA category and their simulants, it is very important to know the structure of these particularly dangerous compounds, the way they act on organisms and the mechanisms by which they can be decontaminated.

The structure of neurotoxic agents is as shown in Figure 1 and Table 1:



**Figure1.** General structure of neurotoxic agents.

**Table 1.** The structure of neurotoxic agents.

Agent	X	R <sub>1</sub>	R <sub>2</sub>
Tabun (GA)	CN	N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>
Sarin (GB)	F	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
Soman (GD)	F	CH <sub>3</sub>	CH(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>3</sub>
Cyclosarin (GF)	F	CH <sub>3</sub>	Cyclohexyl
VX	SCH <sub>2</sub> CH <sub>2</sub> N[CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>

In the experimental research presented in this study we used four **toxic chemical agents, simulants of neurotoxic CWA: Paraoxon, Methyl-paraoxon, Parathion, Methyl-parathion, which were subjected to photocatalytic decontamination.** Paraoxon and Methyl-paraoxon fall into the category of phosphates (contain bonds of type -P=O), and their analogues, Parathion and Methyl-parathion, fall into the category of phosphorothioates (containing bonds of type -P=S).

## 2. Materials and experimental study

The hereby study involved experimental laboratory research on:

- the synthesis of photocatalytic decontamination compositions, which should ensure the efficient decontamination of organophosphorus compounds from the CWA category and their simulants;
- structural and morphological characterization of the synthesized compositions;
- testing the synthesized compositions in the decontamination of some organophosphorus compounds and determining the degree of their decontamination.

Synthesized decontamination compositions may be intended for the photocatalytic decontamination of weapons, military techniques, equipment, interior and exterior of vehicles, aircraft and ships, including their sensitive equipment.

The experimental part involved the preparation of photocatalytic systems based on the use of TiO<sub>2</sub> obtained by depositing different concentrations of metal nanoparticles on porous materials (Au/TiO<sub>2</sub>). The article describes the synthesis and photocatalytic properties of highly efficient, non-toxic systems for the environment, capable of detoxifying surfaces contaminated with neurotoxic CWAs only by simply irradiating with light from the visible range. Other alternatives, such as incineration or chemical degradation, are aggressive and polluting, requiring the use of toxic and corrosive chemicals and, in addition, not using recyclable components. Therefore, the use of a non-toxic solid catalyst in ambient light conditions in the visible range is an extremely advantageous alternative.

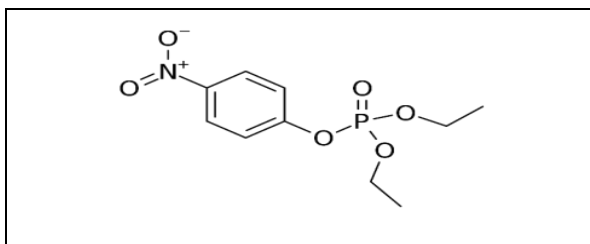
The photocatalytic systems used are based on the dual ability of semiconductors to simultaneously adsorb both chemical compounds and photons. When a photocatalyst is irradiated with photons of energy greater than or equal to the energy of its forbidden band, the separation of electrons and photo created voids occurs. In the reaction fluid medium, the reactants can be adsorbed on the surface of the semiconductor and react with either electrons (acceptor molecules such as O<sub>2</sub>) or voids (electron donor molecules).

The obtained materials were appropriately characterized and tested in decontamination reactions of high toxicity organophosphorus chemical compounds with chemical structure similar to organophosphorus war chemicals (paraoxon PO, methyl-paraoxon MPO, parathion PT, methyl-parathion MPT), because in the context due to the pandemic caused by the SARS-CoV-2 coronavirus, we no longer had the opportunity to perform experiments on real chemical agents. Thus, in agreement with the project team, we decided to study the mechanisms of photocatalytic degradation of organophosphorus CWA on these four simulants and to compare the results obtained on the degree of decontamination of toxic compounds.

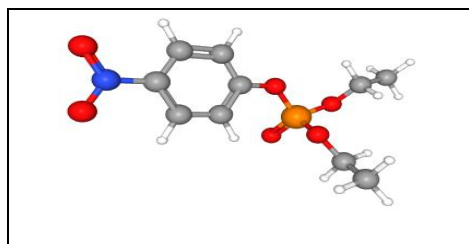
The characterization of the synthesized photocatalytic compositions was performed within CCSA CBRNE (SEM and EDX analyses) and within INCDFM (National Research-Development Institute for Materials Physics).

### 2.1. Properties of toxic organophosphorus compounds subjected to photocatalytic decontamination

#### Paraoxon (CAS 311-45-5)



**Figure 2.** The chemical structure of Paraoxon.

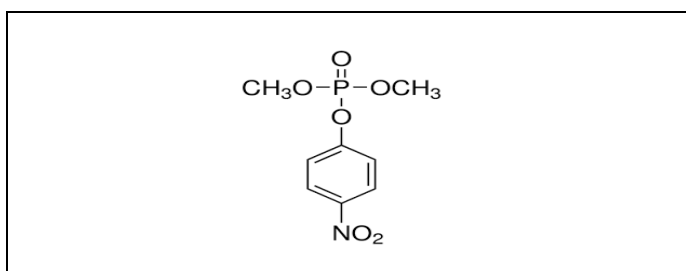


**Figure 3.** 3D structure of Paraoxon.

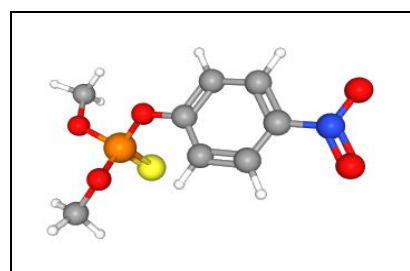
Paraoxon has the following physicochemical and toxicological properties:

- Chemical formula: C<sub>10</sub>H<sub>14</sub>NO<sub>6</sub>P;
- Molecular weight: 275,19 g/mol;
- Appearance: Reddish oily liquid, with a faint fruity odour;
- Miscible with water and polar organic solvents;
- Density: 1,274 g/mL at 25 °C;
- Freezing temperature: 6 °C;
- Boiling point: 169-170 °C;
- Water solubility: 3,640 mg/l at 20°C;
- Toxicity: TDLo = 14 mg/kg oral administration method to humans;
- Danger phases: fatal in contact with skin, fatal if inhaled, fatal if swallowed, very toxic to aquatic life.

### Methyl-paraoxon (CAS 950-35-6)



**Figure 4.** The chemical structure of Methyl-paraoxon.

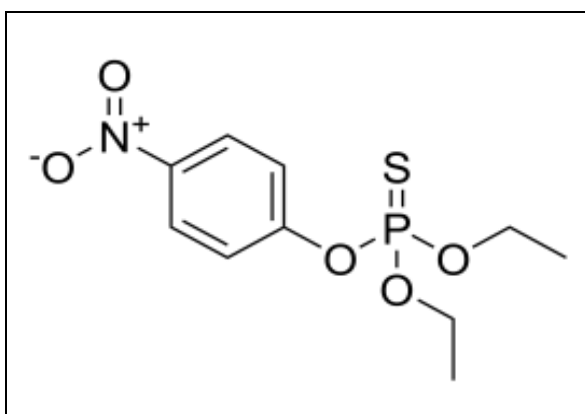


**Figure 5.** 3D structure of MPO.

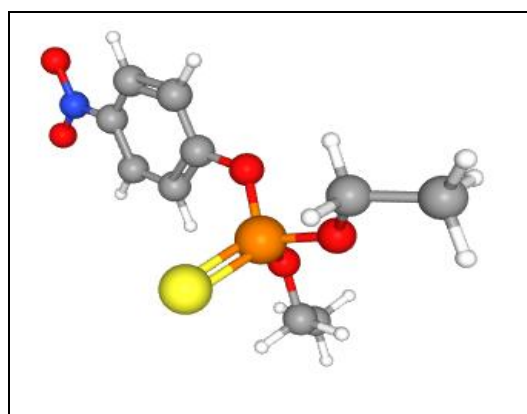
Methyl-paraoxon has the following physicochemical and toxicological properties:

- Chemical formula: C<sub>8</sub>H<sub>10</sub>NO<sub>6</sub>P;
- Molecular weight: 247,14 g/mol;
- Appearance: Reddish oily liquid, with a faint fruity odour;
- Miscible with water and polar organic solvents;
- Density: 1,274 g/mL la 25 °C;
- Freezing temperature: 6 °C;
- Boiling point: 169-170 °C;
- Water solubility:3,640 mg/l la 20°C;
- Toxicity: TDLo = 14 mg/kg oral administration methodto humans;
- Danger phases: fatal if inhaled, fatal if swallowed.

### Parathion (CAS56-38-2)



**Figure 6.** The chemical structure of Parathion.

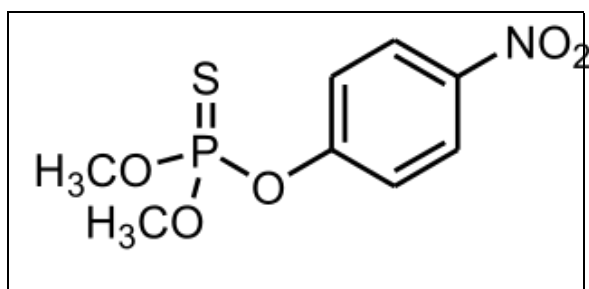


**Figure 7.** 3D structure of Parathion.

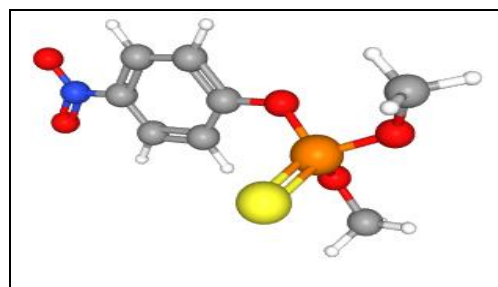
Parathion has the following physicochemical and toxicological properties:

- Chemical formula: C<sub>10</sub>H<sub>14</sub>NO<sub>5</sub>PS;
- Molecular weight: 291,26 g/mol;
- Appearance: yellow liquid with a faint smell of garlic;
- Miscible with water and polar organic solvents;
- Density: 1,26 g/ml la 25 °C;
- Freezing temperature: 6,1 °C;
- Boiling point: 375 °C;
- Water solubility:11 mg/l la 20 °C;
- Toxicity: TDLo = 196 mg/kg oral administration method in pigs;
- Danger phases: fatal in contact with skin, fatal if inhaled, fatal if swallowed, very toxic to aquatic life.

## Methyl-parathion (CAS 298-00-0)



**Figure 8.** The chemical structure of MPT.



**Figure 9.** 3D structure of MPT.

Methyl parathion has the following physicochemical and toxicological properties:

- Chemical formula:  $C_8H_{10}NO_5PS$ ;
- Molecular weight: 263,21 g/mol;
- Appearance: white crystalline solid;
- Miscible with water and polar organic solvents;
- Density: 1,4 g/cm<sup>3</sup>;
- Freezing temperature: 35,5 °C;
- Boiling point: 289 °C;
- Water solubility: 37,7 mg/L at 20 °C;
- Toxicity: TDLo = 0,286 g/kg oral administration method to humans;
- Danger phases: fatal in contact with skin, fatal if inhaled, fatal if swallowed, very toxic to aquatic life.

### 2.2. Photocatalytic systems obtained by depositing different concentrations of metallic nanoparticles on porous materials (Au/TiO<sub>2</sub>)

#### 2.2.1. Synthesis of Au/TiO<sub>2</sub> photocatalytic systems

Systems were designed and synthesized that consisted of the deposition of gold nanoparticles on the surface of anatase-type titanium dioxide. The reference photocatalyst at this time is titanium dioxide. Numerous studies to date have shown that the anatase form is much more active than the rutile form. Degussa P25 TiO<sub>2</sub>, which is a titanium dioxide with a predominantly anatase content, is generally used as a reference material.

Titanium dioxide is very close to being the ideal photocatalyst. Its only disadvantage, however, is that it cannot absorb light from the visible realm. Doping of the semiconductor with various ions of transition metals can lead to an increase in the efficiency of the photocatalytic system.

In the field of heterogeneous catalysis research, Au/TiO<sub>2</sub> is one of the preferred catalysts in aerobic oxidation reactions, including in this category oxidative degradation reactions of chemical weapon simulants. Many of these studies have shown that the photocatalytic activity shown by this material, under visible light irradiation conditions, is due to the absorption of photons by gold particles on the surface, as well as the induction of an electronic flux to the TiO<sub>2</sub> valence band.

#### 2.2.2. Preparation of photocatalysts

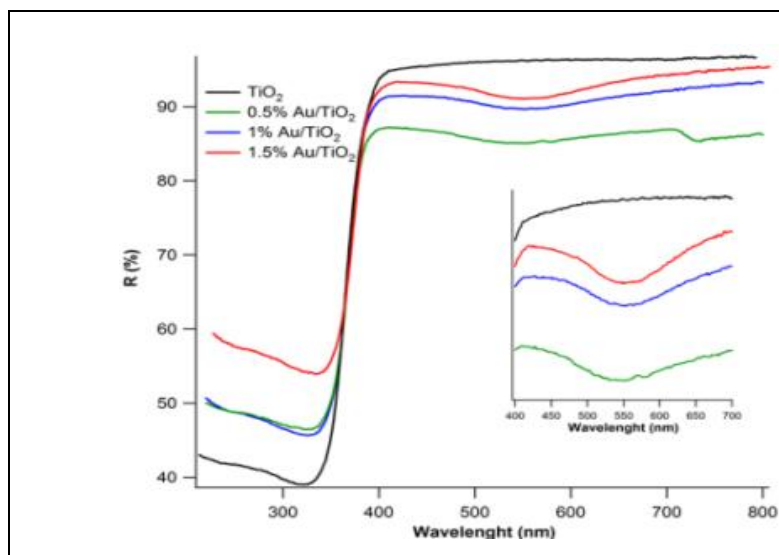
In practice, the synthesis of Au/TiO<sub>2</sub> photocatalysts involved the use of the deposition-precipitation method. To summarize, the samples 0.5, 1 and 1.5% by weight deposited on TiO<sub>2</sub> were obtained by adding one gram of TiO<sub>2</sub> anatase in 100 mL aqueous solution containing 10, 20 and 30 mg of gold precursor (chloroauric acid H[AuCl<sub>4</sub>] • 3H<sub>2</sub>O) in previously adjusted to a pH of 8.5 with a 0.2 M NaOH solution. In order to obtain a better dispersion of gold nanoparticles, the formed mixtures were heated at 80°C for at least 5 hours and under vigorous magnetic stirring.

After performing this step, the mixtures were cooled to room temperature, and the solid samples were filtered and washed thoroughly with deionized water until complete removal of the chloride ion. After performing this step, the samples were dried at 80°C for 48 hours.

### 2.2.3. Characterization of photocatalysts

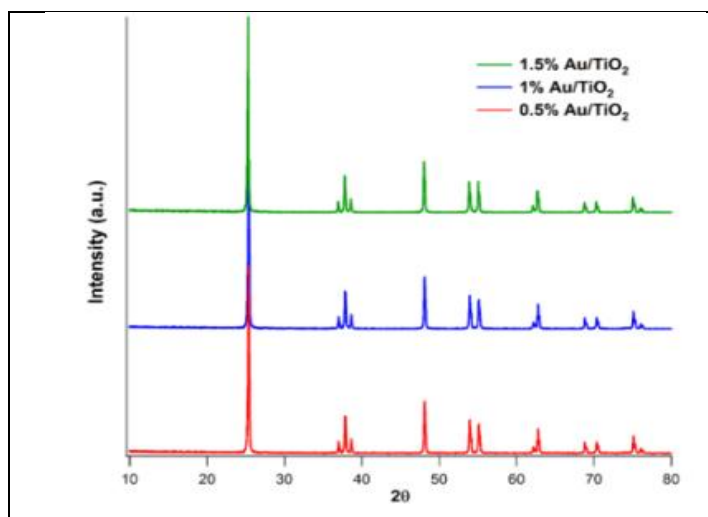
The amount of gold deposited on the TiO<sub>2</sub> surface was determined by the ICP-OES technique using an Optima 9300 spectrophotometer from PerkinElmer. The nominal values were found to be 0.35, 0.9 and 1.3%, respectively; the solid samples were then investigated using UV-Vis spectroscopy (PerkinElmer Lambda 950 spectrophotometer equipped with an integrating sphere). Spectra were recorded in the range of 200–800 nm using BaSO<sub>4</sub> as a baseline. The structural, morphological and surface properties of the Au/TiO<sub>2</sub> samples were characterized by XRD, SEM and XPS. XRD measurements were performed with a Bruker-AXS D8 diffractometer equipped with one-dimensional LynxEye detector using Cu K $\alpha$  radiation (0.1541 nm). SEM images of the samples were taken using a Tescan Vega II LMU microscope equipped with an EDX BrukerQuantax 200 spectrometer, using the following operational parameters: 30 kV acceleration voltage, 1200 seconds measurement time, approx. 10.5 mm working distance, 0.4 kcps scanning speed. XPS measurements were performed with a surface study cluster from Specs, using Al K $\alpha$ 1 radiation (1486.74 eV) produced by a monochrome X-ray source (Al / Mg K $\alpha$ ) operational at a total power of 300W (12.5 kV  $\times$  24 mA) and a pressure of  $2 \times 10^{-8}$  Pa. The photoelectrons extracted from the sample were recorded using a hemispherical analyser (Phoibos 150) fixed in the 20 eV energy step transmission mode. In addition, an electron cannon at an energy of 1 eV and 0.1 mA was used to avoid charging the sample during the measurements. The presented parameters were optimized in order to obtain the C1s peak of the sample contamination carbon at a value of  $284.6 \pm 0.05$  eV.

Figure 10 shows the DR-UV-Vis spectra of the prepared samples. The undoped sample of titanium dioxide shows an absorption threshold in the UV region at approx. 370 nm, which corresponds to a value of the forbidden band energy of 3.2 eV, specific to anatase. The DR-UV-Vis spectra of the Au/TiO<sub>2</sub> samples are characterized by the presence of an absorption band at approx. 550 nm, which is typical of these materials, this absorption being caused by the surface plasmonic vibrations induced by the gold nanoparticles present in the process. The presence of this absorption band induces the photoactivity of these materials when they are exposed to irradiation with light from the visible range and, implicitly, sunlight.

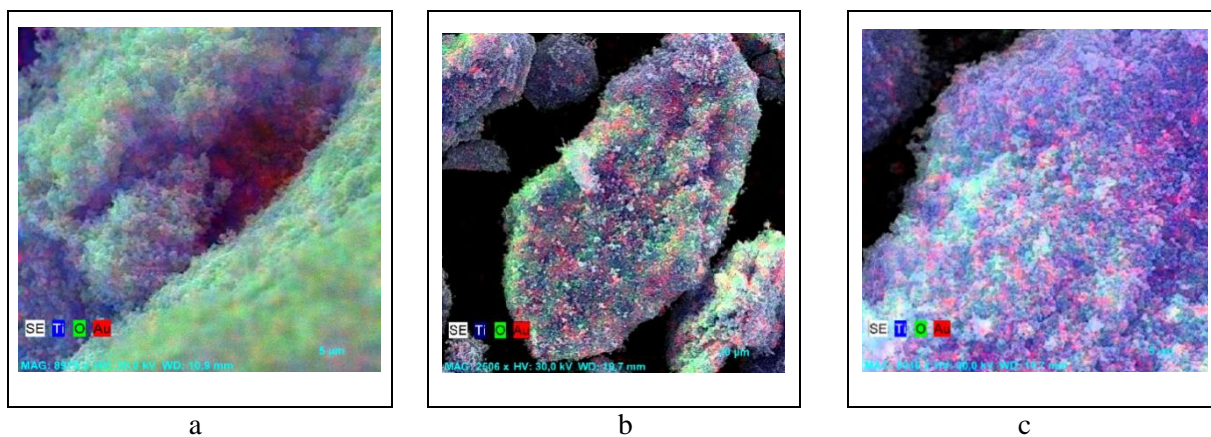


**Figure 10.** DR-UV-Vis spectra of prepared photocatalysts. The inserted image shows the 400–700 nm region of the spectra.

All Au/TiO<sub>2</sub> samples were characterized by X-ray diffraction, and the corresponding diffractograms are shown in Figure 11. As it can be seen, apart from the diffraction lines typical of the crystallographic phase of the anatase, no other diffraction lines were detected, suggesting that gold nanoparticles are well dispersed on the surface of titanium dioxide and do not form clusters.



**Figure 11.** XRD diffractograms of Au/TiO<sub>2</sub> photocatalysts



**Figure 12.** SEM images of 0.5% Au/TiO<sub>2</sub> (a) 1% Au/TiO<sub>2</sub> (b), and 1.5% Au/TiO<sub>2</sub> (c) photocatalysts.

The images obtained by the SEM technique are presented in Figure 12. EDX mapping of surfaces confirms the presence of Au nanoparticles (color code: red), which are well distributed on the TiO<sub>2</sub> surface, which is consistent with XRD data.

#### 2.4.4. Testing of photocatalysts obtained in the photocatalytic degradation of simulants of chemical warfare agents

The effects of photocatalytic activity of Au/TiO<sub>2</sub> on the same toxic compounds were studied: PO, MPO, PT, MPT, solubilized in methanol.

The photocatalytic activity was investigated comparatively, under UV light irradiation, using a natural aerated quartz reactor and under visible light irradiation. As radiation sources, a 125 W high-pressure mercury lamp (HQV 125W, Osram, Germany) with a maximum emission at 365 nm and a radiant power of 3.0 W UVA, and a neon lamp of 200 W (F74-765, Tungsram, Hungary) with a maximum emission at 600 nm. The light intensity at the distance where the sample was placed was 810 and 4300 Lx, respectively. Intensity measurements were performed using an 840006 Speer Scientific luxmeter. The tests were performed as follows: an initial solution was prepared by dissolving the toxic organophosphorus compound in anhydrous methanol (5 µl toxic: 1 ml methanol). The initial toxic solution was analysed by GC-MS.

From this solution a quantity of 2 ml was taken which was brought into contact, in a quartz cuvette, with 20 mg of photocatalyst, leaving it in contact in the dark for about 10 minutes, to allow the adsorption of the toxic compound on the surface of the photocatalytic material. The photocatalyst cuvette and the toxic compound solution were further introduced into the reactor and exposed to visible light and UV light. The whole assembly was exposed to irradiation perpendicular to the direction of light propagation.



The evolution of the photocatalytic reaction was followed by taking samples of the quartz cuvette contents at regular intervals (30 minutes, 120 minutes), extracting the photocatalyst with methanol, stirring, filtering and analysing the resulting solution by GC-MS.

The initial sample, not exposed to irradiation, and the irradiated samples were subjected to derivatization treatments to produce volatile trimethylsilyl derivatives of the degradation products. For derivatization, the procedure is as follows: the toxic solution is eluted with a volume of 500  $\mu$ l ACN (acetonitrile) and 500  $\mu$ l BSTFA (N, N-bis (trimethylsilyl) trifluoroacetamide), is stirred for homogenization, and is introduced into the preheated oven at 60°C for 30 minutes. The sample is removed from the oven, it is allowed to reach room temperature and then the GC-MS is analysed.

The photocatalytic degradation yield was calculated as a percentage of the compound consumed from the entire initial amount introduced into the reaction.

#### 2.4.5. Results and discussions

**Table 2.** PO degradation yield in the presence of Au/TiO<sub>2</sub> catalysts.

Irradiation source	Exposure time (min.)	Photocatalysts		
		0.5% Au/TiO <sub>2</sub>	1% Au/TiO <sub>2</sub>	1.5% Au/TiO <sub>2</sub>
UV	30	25	32	33
	120	38	45	49
VIS	30	48	73	75
	120	75	100	100

**Table 3.** MPO degradation yield in the presence of Au/TiO<sub>2</sub> catalysts.

Irradiation source	Exposure time (min.)	Photocatalysts		
		0.5% Au/TiO <sub>2</sub>	1% Au/TiO <sub>2</sub>	1.5% Au/TiO <sub>2</sub>
UV	30	28	35	39
	120	39	48	50
VIS	30	52	77	78
	120	79	100	100

**Table 4.** PT degradation yield in the presence of Au/TiO<sub>2</sub> catalysts.

Irradiation source	Exposure time (min.)	Photocatalysts		
		0.5% Au/TiO <sub>2</sub>	1% Au/TiO <sub>2</sub>	1.5% Au/TiO <sub>2</sub>
UV	30	13	22	21
	120	21	34	37
VIS	30	30	56	65
	120	60	87	90

**Table 5.** MPT degradation yield in the presence of Au/TiO<sub>2</sub> catalysts.

Irradiation source	Exposure time (min.)	Photocatalysts		
		0.5% Au/TiO <sub>2</sub>	1% Au/TiO <sub>2</sub>	1.5% Au/TiO <sub>2</sub>
UV	30	19	30	28
	120	33	41	42
VIS	30	39	70	75
	120	66	92	100

As it can be seen, Au/TiO<sub>2</sub> samples are less active under conditions of UV irradiation than light radiation. This remarkable result indicates that the higher photocatalytic efficiency is due to the gold nanoparticles that are responsible for the appearance of the radiation absorption process in the visible range. The results show that, at a relatively short exposure time (two hours), except for parathion, the other toxic organophosphorus compounds can be completely degraded.

The photocatalytic activity of Au/TiO<sub>2</sub> materials grows with the increase in the amount of gold in their composition and, in some cases, these materials are able to destroy more than 70% of chemical compounds even after 30 minutes of light irradiation in the visible range.

These data demonstrate that the system used is based on the double capacity of the photocatalyst Au/TiO<sub>2</sub> both to adsorb toxic chemicals on its surface and to absorb photons simultaneously.

### 3. Conclusions

The purpose of the hereby study is to investigate the photocatalytic behaviour of some titanium dioxide-based catalysts in the photocatalytic degradation reaction of organophosphorus compounds. Using conventional synthesis methods, photocatalytic systems were prepared and tested in the mineralization of four simulants of organophosphorus warfare chemicals. All the preparation methods used aimed at modifying the photocatalytic properties of TiO<sub>2</sub> in order to visibly absorb, by doping TiO<sub>2</sub> with transition metal ions. The characterization of the photocatalytic behaviour of the synthesized materials allowed the realization of a comparative study between the photocatalytic activity in conditions of irradiation in the visible domain and that in the UV domain for the photodegradation of organophosphorus compounds. To achieve this goal, a set of techniques capable of providing the necessary information was used.

The degradation of organophosphorus compounds was studied by comparing the action of Au/TiO<sub>2</sub> photocatalytic systems prepared by the deposition method that degrades the toxic molecule under irradiation with light from the visible field, over a longer period, up to the mineralization of these compounds (resulting compounds which are non-toxic or very non-toxic).

Regarding the Au/TiO<sub>2</sub> system, the progressive increase of the amount of Au in the structure of the photocatalytic material led to increasing degrees of degradation, the most active photocatalyst being 1.5% Au/TiO<sub>2</sub>.

The degradation system by heterogeneous photocatalysis on Au/TiO<sub>2</sub> can degrade all organophosphorus compounds, both those with double bond P=O and those with double bond P = S, with different yields and speeds. This investigated system is an efficient one defining a stable and recyclable catalyst, capable of destroying all organophosphorus agents at short exposure times.

The data presented in this paper demonstrate the efficacy of synthesized photocatalysts in the complete degradation of known CWAs. The experiments allowed to highlight the applicability of Au/TiO<sub>2</sub> systems as efficient photocatalysts, under irradiation with light in the visible field, in the detoxification reaction of organophosphorus compounds. Thus, compared to incineration processes and chemical degradation processes, the photocatalytic degradation process of CWAs can be considered a clear example of "green chemistry". Given that the proposed technology uses only a stable and recyclable gold catalyst supported on titanium oxide, light that can come even from the sun and does not involve solvents, we can admit that this type of photocatalytic process can be considered a destruction economical way of a very wide range of organic pollutants.

Synthesized decontamination compositions may be intended for the photocatalytic decontamination of weapons, military techniques, equipment, interiors and exteriors of vehicles, aircraft and ships, including their sensitive equipment or military troops.

### Acknowledgments

*We would like to thank to all those who, directly or indirectly, have contributed to the evolution of this scientific approach and to its completion.*

We would like to thank Mrs. SR I, Dr. Chem. Nicoleta PETREA and her team from the Scientific Research Center for CBRN Defense and Ecology in Bucharest for their support and the possibility of testing photocatalysts on simulants of chemical warfare agents.

We would also like to thank to all the military and civilian personnel from the Diving Center staff for their support and encouragement.

### List of Acronyms

**CWA** = chemical warfare agents;

**EDX** = energy dispersive x-ray;

**MPO** = methyl-paraoxon;

**MPT** = methyl-parathion;

**PO** = paraoxon;

**PT** = parathion;

**SEM** = scanning electron microscope;

**UV** = ultraviolet radiation;  
**VIS** = radiation in the visible range;  
**XRD** = X-ray diffraction.

## Reference

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