„ALEXANDRU IOAN CUZA” UNIVERSITY OF IASI
FACULTY OF CHEMISTRY,
THE CHEMISTRY AND LIFE AND EARTH SCIENCES DOCTORAL SCHOOL

The major environmental pollutants: uncoupling agents, mechanisms of toxicity and decontamination

ABSTRACT

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Iaşi, 2015

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Mr/Mrs……………………………………………

Please note that on September **24th 2015**, at **11:00 o'clock,** in the, în **P3 Amphitheatre,** Mr. **ZAHARIA I. MARIUS-MIHAI** there will be held the public defence of the PhD Thesis entitled „ **The major environmental pollutants: uncoupling agents, mechanisms of toxicity and decontamination**", in fulfilment of the requirements for obtaining the degree of Doctor of **CHEMISTRY**.

The doctoral committee is comprised of the following members:

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We hereby send you the abstract of the PhD Thesis, with the kind request to send us your written appreciations and observations.

On this occasion we invite you to attend the public defense of the PhD Thesis.

The thesis can be accessed at the library of the **Faculty of Chemistry.**

Acknowledgments

Sincere and warm thank to d-l ***Prof. Dr. GABI DROCHIOIU,*** *the scientific supervisor of this thesis for his trust and goodwill that guided me both in making this work and for talks with senior scientific and professional content which contributed to my training and integration in research.*

The elaboration of this thesis was made possible by the financial support of the project ***POSDRU/159/1.5/S/137750***

I thank Mr. ***Lect. Dr. Robert Vasile Grădinaru*** *for sharing with me his invaluable volume of knowledge and for his constant encouragements!*

Many thanks to Mr. ***Prof. dr. Aurel Pui*** *for support for FT-IR spectroscopy measurements, Mr.* ***Conf. dr. Gheorghiţă Zbancioc*** *to obtain measurements and support the interpretation of FTIR spectra and GC-MS.*

I thank Mrs. ***Olga Pintilie*** *for support in the conduct germination tests.*

Thank you to the teachers and colleagues at the University Al. I. Cuza University for their contribution to my formation as a man, chemist and researcher and for scientific and professional discussions.

Thank Biochemistry and Toxicology group for atmosphere collegial and warmth that they received and them support and permanent encouragement offered.

Thanks to everyone who helped me during this PhD thesis.

I thank my wife and my family for their support, attention, guidance, patience and love.

My mother and my father's belief that up there, see me and be happy for me, my prayers direct them.

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KEYWORDS: dinitrophenols compounds, decontamination, yeast, toxicity, uncoupling agents, oxidative phosphorylation, germination tests, UV-Vis, photocatalysis, spectroscopy and spectrometer method, FT-IR, GC-MS.

The abstract presented in a brief form chapter, personal research results, conclusions and selective references. In drawing up chapters, subchapters, figures, charts and tables was kept the same notation according with PhD thesis.

ABBREVIATIONS

ADP adenosine diphosphate

ATP adenosine triphosphate

Krt. 2,4-dinitro-6-octylphenyl crotonates and 2,6-dinitro-4-octylphenyl crotonates, Dinocap, Karathane

2,4-DNA 2,4-dinitroanisole

2,4-DNB 2,4-dinitrobenzoic acid

DNCB 1-chloro-2,4-dinitrobenzene, 2,4-dinitrochlorobenzene

DNED 2,4-dinitrophenylethylenediamine, N- dinitrophenyl-ethylenediamine

DNFGA 2-(2-fluoro-5-nitrofenilamino)-acetamidă

DNG 3-(2,4-dinitrophenyl)propane-1,2-diol, 2,4-dinitrophenilglicerine

DNOC 3,5-dinitro-*o*-cresol

2,4-DNP 2,4-dinitrophenol

2,5-DNP 2,5-dinitrophenol

DNP-GSH dinitrophenyl-S-glutation

DNSA 3,5-dinitrosalicylic acid

Drjd. yeast *Saccharomyces cerevisiae*

FADH$_2$ flavin adenine dinucleotide

FT-IR infrared spectroscopy

GC-MS gas chromatography–mass spectrometry

Glc glucose

GL freedom degree

NADH nicotinamide adenine dinucleotide

NAD$^+$ nicotinamide adenine dinucleotide phosphate

pNBA *p*-nitrobenzaldehyde

rpm spins per minute

TNF 2,4,6-trinitrophenol, picric acid

UV-Viz ultraviolet–visible spectroscopy

INTRODUCTION

The PhD research refers to the investigation, the monitoring the concentration and finding out antipollution measures of some major environmental pollutants (nitroderivatives, nitrophenol pesticides, metabolic inhibitors, aromatic nitro ethers, other organic pollutants). The solutions by which extremely toxic compounds will be transformed in some harmless and even useful ones could contribute to the transformation of the contaminated technologies in some ecological ones. Recent research shows that these pollutants are highly toxic, without existing antidote, is accumulate in the body or converted into more toxic compounds and, with many fatalities due to their ingestion. The relationship between these persistent pollutants and the physiological processes is still little known at the molecular and cellular level.

The present doctoral research aims at elaborating and applying new selective and sensitive analytical metods for the identification and cuantification of organic major pollutants in the environment (soil, waters etc) such as dinitrophenol pesticides and metabolic inhibitors. As well, the toxicological mechanisms of these pollutants at the molecular and cellular level are being investigated toxicokinetically and toxicodinamically. The real pollution and intoxication with dinitrophenol pesticides will be prevented; people will be awarded on the excessive use of chemical pesticides. People will be awared of a healthy agriculture, the need to use highly biological products, and the project will improve the health of population, reducing the risk of degenerative diseases.

PhD thesis „**The major environmental pollutants: uncoupling agents, mechanisms of toxicity and decontamination**” contains **251** pages divided into **3** chapters which include **28** Tables, **52** Figures, **7** Schemes and **234** references.

Thesis is structured in two parts: first part contains information about literature (**Chapter I**), and the second part contains original results (**Chapter II and III**), divided in experimental part, materials and methods, conclusion and references.

Chapter I comprise general considerations on the current state of scientific research on dinitrophenol pesticide (structure, use, stability, toxicity, action mode, characterization methods, decontamination, etc.).

In the **Chapter II** are presents tools, materials and method used in developing the PhD thesis.

Chapter III was aimed at presenting original results and the related discussion was conducted in this thesis.

Original researches carried out have been focused on several directions:

1. The study of dinitrophenols decontamination methods using microorganisms, using commercial yeast *Saccharomyces cerevisiae*.

2. Was studied photocatalytic decontamination of dinitrophenol using nanoparticles of zinc ferrite ($ZnFe_2O_4$) as catalyst, synthesized in the Faculty o Chemistry.
3. Establishing an emphasizing action method of uncoupling oxidative phosphorylation by respiration
4. Research on uncoupling agents action in glucose consumption and them study in the near-infrared.
5. Results dissemination and establishing new collaboration within international specialists in environmental research.

The carrying out of the present project has a major scientific technical impact by solving the problem of ultrarapid and ultrasensitive detection and monitoring the nitrophenolderivatives. It also proposed revolutionary microbiological methods of soil remediation, which will help increase crop quality, reducing quanty of pesticide content and also increasing the value of agriculture products.

PART I. Literature study

CHAPTER I. The current state of scientific research

I.1. General considerations about the structure, use, stability, toxicity and action mode of dinitroderivatives

Nitroaromatic compounds constitute a major class of widely distributed environmental contaminants. Many of these pollutants have been widely used pesticides that persist in some contaminated soils, and have been found in ground-waters, causing health and environmental hazards. Dinitrophenols have multiple biological effects, being used in agriculture as insecticides, fungicides, herbicides and acaricides or in medicine and biology as metabolic inhibitors. These hazardous compounds in the contamination of the food supply from agricultural waste are an increasing concern worldwide. Trace amounts of nitrophenols have been found in spiked tap water, reservoir water and stream water [40]. Dinitrophenols (DNP) and their derivatives are known to be toxic to the environment, being potent uncoupling agents [63, 85]. Despite their overwhelming toxicity, some dinitrophenols are still used as pesticides with an important role in the chemical protection of plants [50]. Dinitrophenols have been used as body building drugs or analytical tools [7]. However, they may be hazardous materials when are largely used in agriculture and biology.

These compounds act on respiratory process by blocking the reactions of oxidative phosphorylation, which results in the inhibition of ATP formation from ADP [139]. Many hypotheses and theories tried to explain their toxicity based on the properties of dinitrophenyl moiety, which can inhibit the energy transfer from excited molecules in the cell to ATP synthase [63].

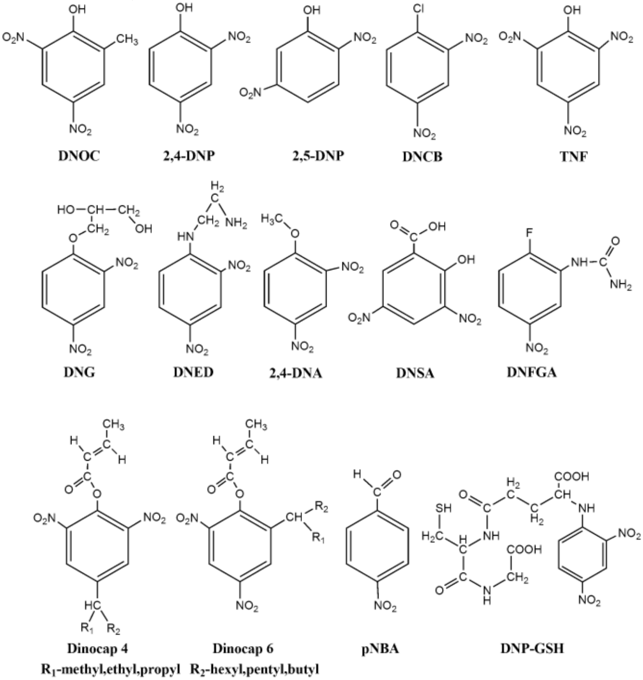


Fig. II.1. The chemical structure of investigated dinitrophenolic pesticides

II.2.1. Decontamination of dinitroderivatives by yeast Saccharomyces cerevisiae suspensions

The microorganisms used in the dinitrophenols decontamination were yeast suspensions 5g/L in the presence or absence of glucose [73, 74]. The yeast suspensions in the presence of glucose were prepared as follow: were mixed 10 g of yeast, 50 g glucose and 0.40 g/L KH_2PO_4, and was dissolved with 1000 mL distilled water. The investigated dinitrophenols had at concentration ranging from 10^{-4} M to 10^{-2} M. In 300 mL Erlenmeyer flasks, in three replicates, were introduced 100 mL yeast suspensions, which were prepared as described above, over that 100 mL the investigated compounds. The biodegradation process occurs 7 days on an IKA-KS 4000 ic control orbital stirrer at 30 ºC and 50 rpm (**Fig. II.4**).

Fig. II.4. Microbiological degradation of dinitroderivatives by yeast *Saccharomyces cerevisiae* suspensions

Seven days after the starting of the biodegradative process of investigated compounds, yeast suspensions were centrifuged for 10 min at 6000 rpm. Separately, the content of supernatants with the resulted compounds in the degradation process was analyzed in thin layer chromatography. The supernatants were used in spectroscopic measurements and in germination experiments

Germination tests with supernatants containing degraded DNOC. As low as 10^{-3} M aqueous solutions of DNOC inhibit wheat growth, while DNOC-treated yeast suspensions were completely non-toxic to wheat seeds and seedlings (**Fig. III.4.**). Yeast suspensions lacking glucose could have a stimulatory effect on wheat development during germination experiments. In contrast, the glucose induced a less stimulatory effect on wheat seedlings. Possibly, glucose depleted in the presence of yeast in suspensions, and some by-products could have a toxic effect on wheat seeds and seedlings.

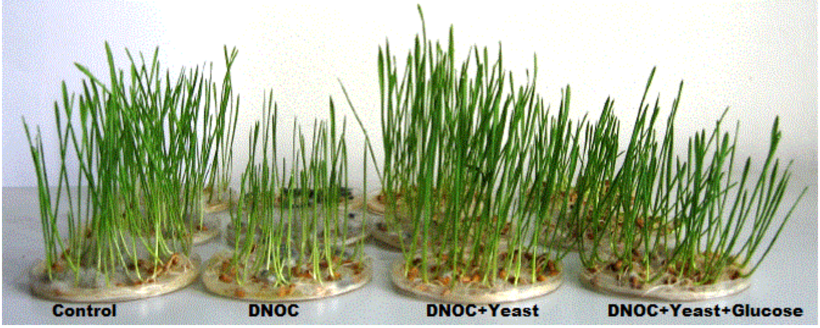


Fig. III.4. Effect of DNOC and supernatants from DNOC biodegradation on wheat seeds during the 7-day germination process

To prove chemical transformation of the investigated dinitrophenols as well as to follow the degradation process, we measured the UV-visible spectra of supernatants (**Fig. III.21.**). The pesticide DNOC at a concentration of $5 \cdot 10^{-3}$ M displayed three absorbance maxima at 212 nm, 263 nm, 370 nm, and a shoulder at 411 nm. The supernatant from DNOC-treated yeast suspensions containing glucose, displays the following absorbance values: A = 0.343 (212 nm), A = 0.183 (268 nm), A = 0.283 (370 nm), and A = 0.277 (410 nm), respectively. Moreover, in the absence of glucose, the following values were measured: A = 0.696 (212 nm), A = 0.204 (268 nm), A = 0.137 (370 nm), and A = 0.277 (411 nm), respectively. In brief, the band at 212 nm disappeared due to yeast biodegradation, while the maxima at 268 nm and 410 nm of pure DNOC in solution were shifted to 263 nm and 411 nm, on using yeast. In the presence of glucose the above mentioned maxima shifted toward 272 nm and 431 nm, respectively. In addition, the absorbance at 268 nm decreased from 0.566 to 0.203. The spectra were normalized in order to compare the supernatants (**Fig. III.21.**).

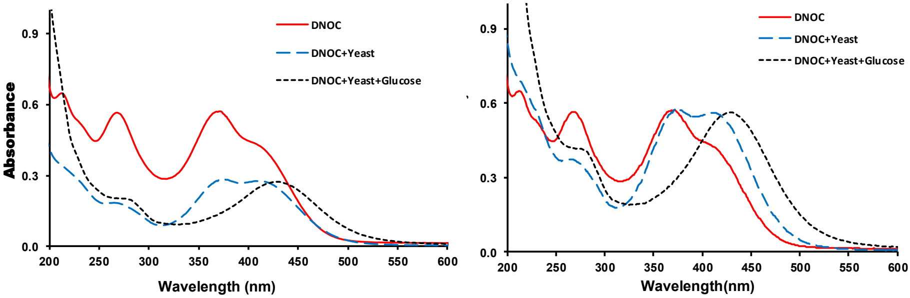


Fig. III.21. Degradation of DNOC ($5 \cdot 10^{-3}$ M) by yeast suspensions in absence/presence of glucose. Original spectra (left) and normalized (right).

III.2. Photocatalytic degradation of dinitrophenols by $ZnFe_2O_4$ nanoparticles in aqueous solution

The photocatalytic degradation experiments were performed in a Pyrex cylindrical photo-reactor [80] (**Fig. II.3.**). A low pressure UV light Hg lamp emitting a wavelength of 254 nm was used for photoreaction.

Fig. II.3. Pyrex cylindrical photo-reactor

III.2.1. Germination tests

An aqueous solution of 2,4-DNP completely inhibited wheat germination and growth, whereas the supernatant that resulted from 2,4-DNP photodegradation was not toxic to wheat seeds and seedlings. We interrupted the biological experiment since the results were already conclusive (**Fig. III.24.**).

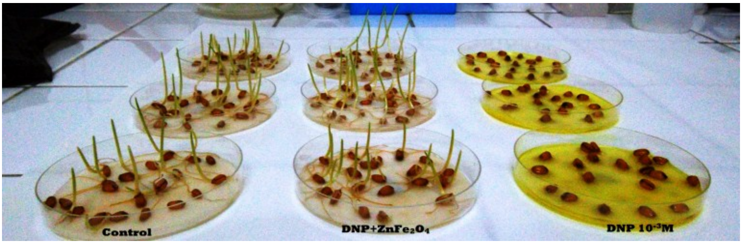


Fig. III.24. Effect of 2,4-DNP-degradation solution resulted after the photocatalytic process on wheat seed germination

Since the 10^{-3} M solution of 2,4-DNP had a toxic effect on wheat seeds, whereas the resulted supernatant from the UV-irradiated heterogeneous suspension of $ZnFe_2O_4$ catalyst in phenolic solution was not hazardous, we concluded that 2,4-DNP was mostly photodegraded. Moreover, this solution even had a slightly stimulatory effect on wheat germination since the height of plantlets increased from 35.66 cm to 40.36 cm. We supposed that the photocatalytic-treated solution may contain degradative compounds with a nutrient effect on the seeds, or that they can be used as a nitrogen source by the wheat plantlets. (**Table III.21.**).

Table III.21. The effect of 2, 4-DNP solutions on wheat germination before and after photodegradation catalyzed by $ZnFe_2O_4$

Treatment *)	**Seedlings**	**Germinated seeds**	**Dead seeds**	**Seedlings height (cm)**	**Seedlings weight (g)**
Control, H_2O	12±1	1	7±1	35,7±12,2	0,39±0,09
2,4-DNP + $ZnFe_2O_4$	14±2	0	6±1	40,3±7,7	0,42±0,08
2,4-DNP 10^{-3} M	0	0	0	0	0

III.2.3. Spectral analysis

III.2.3.1. UV-Vis spectroscopy

The 2, 4-DNP degradation efficiency on the zinc ferrite $ZnFe_2O_4$ catalyst was enhanced by reduced degradation time (15 min). The reaction was carried with a yield of 82%. The DNP absorption spectrum is dominated by a strong absorbance band at 356 nm due to the n-π* transition of the nitro group, $–NO_2$. Besides, characteristic bands are usually observed at 260 nm and 290 nm, being assigned to the π-π^* transitions related to the aromatic ring, and at 400 nm due to the charge transfer. The degradation reaction was followed based on the disappearance of the characteristic band at 356 nm (not shown). The changes in the optical densities at 260 nm and 296 nm (benzene ring) also suggested the benzene-core opening. (**Fig. III.26.**).

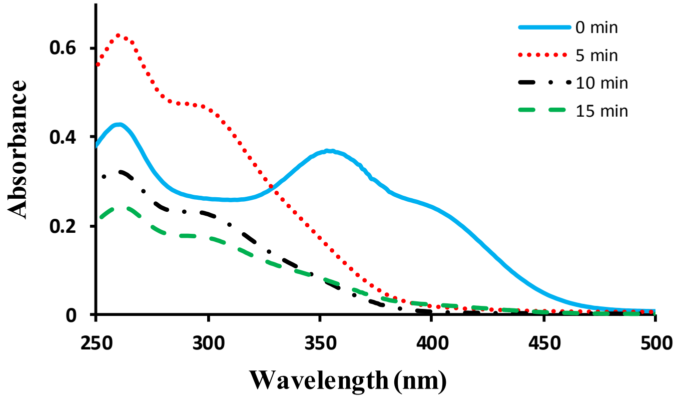


Fig. III.26. Absorption spectra of pure 2,4-dinitrophenol (2,4-DNP; 250 µM) and the resulted supernatants after different UV irradiation times in presence of $ZnFe_2O_4$

To prove the mechanism of photocatalytic process, GC-MS and FT-IR spectra of 2,4-DNP and the degradation products by $ZnFe_2O_4$-assisted UV irradiation were obtained.

III.2.3.2. FT-IR spectroscopy

The most important bands occurring in the FT-IR spectrum of 2,4-DNP were observed at 1348 cm^{-1} and 1535 cm^{-1}, respectively, being attributed to symmetric and asymmetric stretching vibrations of the nitro groups. Besides, the stretching vibration of hydroxyl (-OH) was observed at 3434 cm^{-1} (**Fig. III.29.**). The C–O stretching vibration band of 2,4-DNP was found at 1238 cm–1, whereas the benzene ring appeared at 725 cm^{-1} and 842 cm^{-1}.

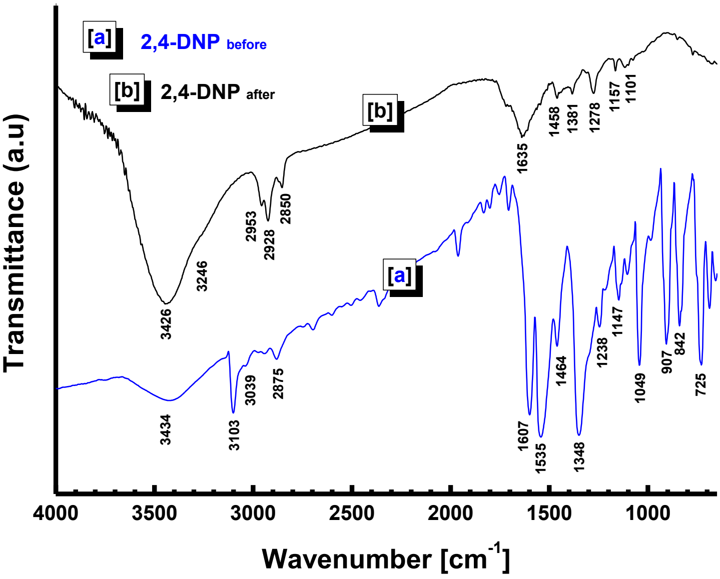


Fig. III.29. Infrared spectra before (a) and after (b) photocatalytic degradation of 2,4-DNP

After photodegradation process the signal at 3434 cm^{-1} characteristic to OH group were shifted at 3426 cm^{-1}. The weak signal at 1381 cm^{-1} showed that nitro groups are still present in the resultant molecule, but that a C=O group appeared with a characteristic absorption at 1635 cm^{-1}. In fact, this band was characteristic of the –CH=CH–CH=O structure, which was effectively found in our measurements. In addition, the strong signal at 2928 cm^{-1} indicated the CH stretch vibration. Moreover, all the signals in the fingerprint area characteristic for the benzene ring disappeared.

III.2.3.3. GC-MS spectrometry

The highest signal in the chromatogram, which appeared at 9.28 min, was subjected to MS analysis (**Fig. III.30.**). The molecular peak at *m/z* 203 was assigned to 6-hydroxy-3,5-dinitrohexa-2,4-dienal (M) since the other peaks confirm the proposed structure. The other peaks were found at *m/z* = 186 (M-HO), *m/z* = 174 (M-CHO), *m/z* = 153 (M-HNO_2), *m/z* = 109 (M-$2NO_2$), *m/z* = 79 (M-$2HNO_2$-CH_2O)$^+$ etc.

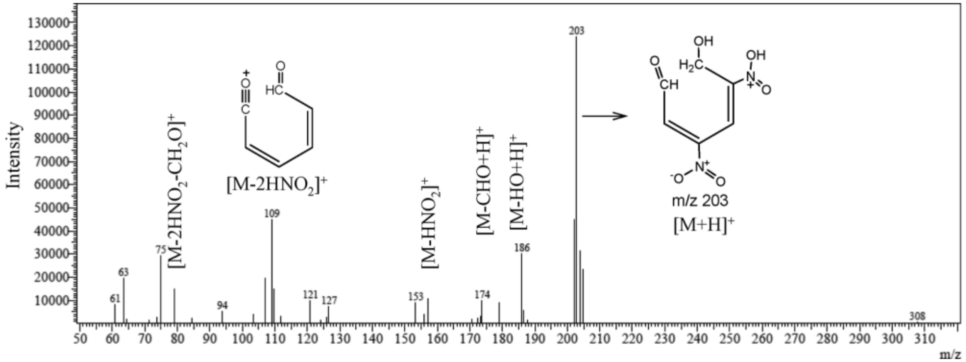
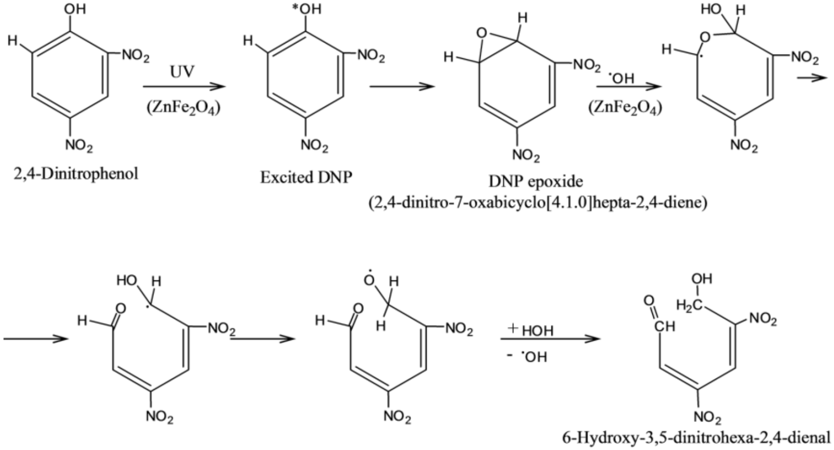


Fig. III.30. GC-MS spectrum of the main photodegradation product of 2,4-DNP

To explain the formation of 6-hydroxy-3,5-dinitrohexa-2,4-dienal starting from 2,4-DNP, we have taken into consideration two findings, namely epoxide[232] and HO• formation [77] under rather similar conditions (Scheme 4). Under UV irradiation, 2,4-DNP is excited, and this affords an epoxide, by binding of the excited oxygen atom to the adjacent carbon atom. This epoxide reacts with the radical HO• species to form a large and rather stable molecular radical. In its turn, the molecular radical undergoes some rearrangements and splitting to afford the final product of degradation with the liberation of HO• species, which continues the degradation process.



Schema 4. Proposed reaction mechanism of 2,4-DNP photodegradation catalyzed by $ZnFe_2O_4$ ferrite.

III.3.3. Chemical method for identifying the uncoupling agents based on ethanol formation

For emphasizing uncoupling agents effect of investigated compounds was used an indirect method based on the quantifying alcohol produced in fermentation. As vegetative samples were used yeast *Saccharomyces cerevisiae* or fresh plantlets or roots. The procedure was made in a closed container glass with a lid provided with a second internal smaller dish (Conway type) **(Fig. II.2)**.

Fig. II.2. Conway dish

This method can be used to identifying the uncoupling agents of oxidative phosphorylation, as well as quantifying the intensity of their action by determining the ethanol produced in living cells of some biological materials. Thus, the action of uncoupling agents, such as dinitrophenols, results in the inhibition of respiration of eukaryotic cells whereas the alcohol formed can be colorimetrically determined by the reduction in the presence of sulfuric acid (H_2SO_4) of the orange colored potassium dichromate ($K_2Cr_2O_7$) to green colored salts of chromium (III). A well-defined volume of sample is taken from the green colored solution, diluted with distilled water, and its absorbance measured in a spectrophotometer or colorimeter. The calibration curve is carried out with different concentrations of ethanol.

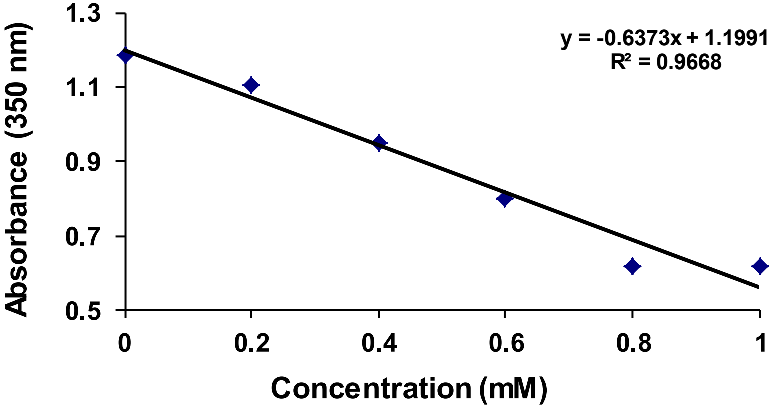


Fig. II.5. Calibration curve for ethanol determination

GENERAL CONCLUSIONS

The study of decontamination methods of dinitrophenols using microorganisms such as using commercial yeast, Saccharomyces cerevisiae:

- ✓ yeast *S. cerevisiae* can be degrade / decontaminate of pesticides dinitrophenol, and dinitrophenol, that at concentrations below 10^{-3} M;
- ✓ following the research supernatants action on germination of wheat, yeast can be an effective agent for dinitrophenols derivatives degradation.
- ✓ generally, yeast suspensions containing glucose proved to be less effective in decreasing pesticide dinitrophenol toxicity than those without glucose.

- ✓ biodegradation compounds were isolated and studies were performed using FT-IR, UV-Vis and GC-MS to establishing their structure;
- ✓ GC-MS analysis technique was proposed a microbiological decontamination mechanism, whereby commercial yeast can reduce nitro groups, the toxically dinitrophenols compounds were converted in quinone imidic compounds rich in nitrogen (fertilizer source);
- ✓ we consider yeast can be used both *in situ*, in the contaminated area, and in some collecting devices for residual waters from the field Our results are in best agreement with those obtained by other authors, that measured CO_2 amount produced by yeast fermentation in the presence of various dinitrophenyl derivatives and related compounds.

For the first time we studied 2,4-dinitrophenol degradation by using $ZnFe_2O_4$ in the presence of ultraviolet radiation.

- ✓ the decontamination of 2,4-DNP efficiency, using zinc ferrite, it was demonstrated by degradation reduced tim (15 minutes) and high efficiency (η= 82%), compared to using TiO_2 as a catalyst;
- ✓ infrared spectroscopy and the germination test, also confirmed the disappearance of the toxicity;
- ✓ to prove the mechanism of photocatalytic process, GC-MS and FT-IR spectra of DNP and the degradation products by $ZnFe_2O_4$-assisted UV irradiation were obtained;
- ✓ GC-MS was for the first time used to demonstrate the photocatalytic opening of the benzene core of 2,4-DNP with the formation of 6-hydroxy-3,5-dinitrohexa-2,4-dienal in short reaction using zinc ferrite as a catalyst;
- ✓ although the reaction mechanism is complex, DNP degradation suggests an unusual benzene-core hydrolysis. However, further research is needed to understand the fate of this compound over time under the photocatalytic conditions investigated here.

Achieving a method emphasizing the ucounplig action of respiration to the oxidative phosphorylation:

- ✓ this study is most important to understanding the transition from respiration to the fermentation action mechanism of dinitrophenyl ethers are conducted in a energy way, perhaps by formation of radicals and triplet state and the transport of protons as a secondary phenomenon in the oxidative phosphorylation process;

- ✓ ethanol formation can be colorimetrically determined, since the resulted color solution is green due to the reduction of chromium (VI) to chromium (III). The determination of alcohol produced is dependen with the action of uncoupling oxidative phosphorylation, such as dinitrophenol derivatives or other compounds with similar uncouplied action, and also with their concentration and the action time;
- ✓ according with the absorbance intensity at the 350 nm was realized a database with the main substances who have uncoupling properties;
- ✓ further research aimed to establishing a ne correlations (if any) between the studied compounds acidity and their uncoupling ability, or between the last parameter and the membrane lipids solubility. Also to be estimated electron density for each molecule and to be observed a correlation between the absorb radiation ability of these compounds at different wavelengths and if they absorb in infrared.

SCIENTIFIC ACTIVITY DURING DOCTORAL STUDIES (2012-2015)

Scientific papers supporting with PhD thesis:

The original results obtained from thesis research were published in national and international journal, or presented as oral presentation or posters at scientific events.

7 ISI paper were published:

1. **Marius Zaharia,** Adrian Borhan, Daniel Gherca, Aurel Pui, Robert Gradinaru, Gheorghita Zbancioc, Gabi Drochioiu, Letter: Study on the mechanism of ferrite-associated dinitrophenol photodegradation, *European Journal of Mass Spectrometry*, **20**, 193-197, **2014**, **(IF$_{2014}$ = 1,165).**
2. Cristina-Amalia Dumitraş Huţanu, **Marius Zaharia** and Olga Pintilie, Quenching of Tryptophan Fluorescence in the Presence of 2,4-DNP, 2,6-DNP, 2,4- DNA and DNOC and Their Mechanism of Toxicity, *Molecules*, **18**(2), 2266-2260, **2013**, **(IF$_{2013}^{=}$ 2,095).**
3. **Marius Zaharia**, Dan Maftei, Cristina Amalia Dumitras-Hutanu, Aurel Pui, Zomi Claude Lagobo, Olga Pintilie and Robert Gradinaru, Biodegradation of pesticides DINOCAP and DNOC by yeast suspensions in a batch system, *Revista de Chimie. (Bucharest)*, **64**(4), 388-392, **2013**, **(IF$_{2013}^{=}$ 0,677).**
4. **Marius Zaharia**, Stefana Jurcoane, Dan Maftei, Aurel Pui, Cristina-Amalia Dumitraş Huţanu and Robert Gradinaru, Yeast biodegradation of some pesticide dinitrophenols, *Romanian Biotechnological Letters*, **18**(2), 8144-8151, **2013**, **(IF$_{2013}^{=}$ 0,363).**

5. **Marius Zaharia,** Dumitru Ganju, Catalin Blegescu, High selectivity of supported oxo-trinuclear compounds in styrene epoxidation, *REV. CHIM. (Bucharest),* **66**(6), 829-832, **2015**, (**IF$_{2014}^{=}$ 0,810).**
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2. **Marius Zaharia,** Lucia Tudorachi, Olga Pintilie, Cristian Drochioi, Robert Gradinaru, Manuela Murariu, Banned dinitrophenols still trigger both legal and forensic issues, *Environ. Forensics,* **(IF$_{2014}^{=}$ 0,732).**

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1. **Marius Zaharia**, Olga Pintilie, Adelina Cosma, Robert Gradinaru, Gabi Drochioiu, Manuela Murariu, Ion Sandu, Toxicitatea şi utilitate compuşilor dinitrofenolici ca medicament, *REVISTA TEHNOCOPIA*, (ISSN 1857-3843), **2**(11), 12-17, **2014**.

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1. O. Pintilie, **M. Zaharia**, A. Cosma, R. Gradinaru, I. Sandu. Both toxic and stimulatory effect of dinitrophenol derivatives on seed germination, *19th Romanian International Conference on Chemistry and Chemical Engineering,* Sibiu, România, 2-5 Septembrie **2015**, (Poster).
2. S. Bancila, E. Ciornea, E. Ciubotariu, **M. Zaharia,** R. Stefanescu, G. Drochioiu. Effect of potasium iodate and 2,4-dinitrophenol on enzymes

involved within the oxidative stress, *19th Romanian International Conference on Chemistry and Chemical Engineering,* Sibiu, România, 2-5 Septembrie **2015**, (Poster).

3. O. Pintilie, **M. Zaharia**, A. Cosma, G. Drochioiu, V. Vasilache, I. Sandu. The nature of life: dinitrophenolic pesticides-induced biostructural alteration of enzyme activity. *European Exhibition of Creativity and Innovation (EUROINVENT),* Iași, Romania 14-16 May 2015, (Poster), gold medal.
4. **M. Zaharia,** A. Cosma, R. Gradinaru, M. Murariu and G. Drochioiu. The effect of some dinitrophenol pollutants on microorganism suspensions, *Annual Scientific Meeting "Biodiversity conservation in context of sustainable development*", Faculty of Biology, Alexandru Ioan Cuza University of Iasi, 23-25 Octombrie **2014**, (Poster).
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1. **M. Zaharia,** A. Cosma, A. Pui, R. Gradinaru, G. Zbancioc, M. Murariu and G. Drochioiu. High yield photocatalytic degradation of pesticide contaminants by ferrite nanoparticles, "*Alexandru Ioan Cuza" University Days, Faculty of Chemistry Conference*, Iasi, 31 Octombrie -1 Noiembrie **2014**, (Poster).
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1. Cristian Drochioi, Victor Vlad Costan, **Marius Zaharia,** Otilia Boisteanu, Ioan Gabriel Sandu, Kamel Earar, Eugenia Popescu, FT-IR caracterization of some biological materials used in reconstructive surgery, *REV. CHIM. (Bucharest),* **66**(9), 1302-1305, **2015**, **(IF_{2014}= 0,810).**

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