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DOCTORAL SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

PhD THESIS

SUMMARY

MATERIALE OXIDICE CU PROPRIETĂȚI CATALITICE AVANSATE OBȚINUTE PRIN VALORIFICAREA UNOR DEȘEURI INDUSTRIALE

OXIDIC MATERIALS WITH ADVANCED CATALYTIC PROPERTIES OBTAINED FROM INDUSTRIAL WASTES

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INTRODUCTION

The doctoral thesis entitled *"Oxidic materials with advanced catalytic properties obtained from industrial wastes"* aims to develop new materials from wastes and their functionalization for environmental protection applications. These new materials are important in the context of the circular economy and sustainable development by restoration in the economic circuit of some wastes into functional products which have wastewater treatment applications, supporting the preservation of one of the most important resources-water but also in the context of the smart waste management.

The scientific research activity of this thesis was focused on the synthesis and characterization of a new type of material, a support material obtained from waste and its photocatalytic functionalization by covering with different concentrations of ZnO films. The obtained materials have been tested for applications in the field of environmental protection. It has been successfully used for degradation through heterogeneous photocatalysis from aqueous solutions contaminated with persistent organic compounds.

The doctoral thesis entitled *"Oxidic materials with advanced catalytic properties obtained from waste"* can be structured in 3 parts: a theoretical part, an experimental part and a part in which the general conclusions, further research directions and the author's scientific contributions are presented, totaling **6 chapters, 60 figures and 16 tables.** At the end of each chapter are presented the partial conclusions and the thesis ends with bibliographic references.

In **chapter 1** entitled *"Current state of the oxidic materials used in the photocatalytic processes for wastewater treatment"*, a bibliographic study was conducted on national and international level in the field of oxidic materials, focusing on the types of materials used as immobilization supports but also on the presentation of the techniques and methods of immobilization of oxides on the support surfaces.

In the **chapter 2** entitled *"General objectives and experimental research methodology for achieving the objectives"* it was made a presentation regarding the objectives, the experimental research methodology and also the used equipments.

In **chapter 3** with the title *"Achievement of an oxidic material from waste"*, it was presented my own contributions in the doctoral researched field, which consisted in the synthesis of a new functionalized oxidic material for water treatment applications, by capitalization of glasd, food waste and an agricultural fertilizer as well as patenting the process of obtaining it by the submission of a patent application at State Office for Inventions and Trademarks (OSIM), with the registration number A/00386/2019.

In **chapters 4 and 5** entitled *"Morphological, compositional and structural characterization of photocatalytically functionalized spongy oxide material"* and respectively *"Tests of photocatalytic degradation of an pharmaceutical organic compound using the spongy oxide material obtained"*, the morphological, compositional and structural characterization of the synthesized oxidic material was performed, respectively some efficiency photocatalytic degradation tests of some organic compounds from aqueous solutions, especially on a pharmaceutical compund, it was tested the reuse capacity of the obtained material and the degradation efficiency in the VISIBLE spectrum.

The **main objective** of this thesis is represented by the synthesis of a new support material based on waste recovery and its functionalization, which would allow the use of the material as a catalyst, for photocatalytic degradation of refractory organic compounds from wastewater. Therefore, the main objective of my thesis is to obtain new reusable zinc-based catalysts on porous substrates, using optimized preparation methods - deposition of oxide film on the surface of the substrate by immersion, orbital agitation and then by autoclaving and drying fixing the oxide film on the substrate.

The research topic proposed in this doctoral thesis has as **specific objectives**:

- Study of the techniques of immobilization of semiconductors on fixed supports;

- Synthesis of a new support material for environmental applications through waste recovery;
- ZnO immobilization on the porous surface of the support material obtained;
- Morphological and structural characterization of the synthesized- SpongeMat/ZnO oxidic material;
- Testing the applicability of the oxidic material in the degradation of the organic compounds from wastewater through Advanced Oxidation Processes (AOPs) - heterogeneous photocatalysis.

The most recent studies in the field of catalysis are directed towards the preparation of immobilized catalysts on fixed functionalized supports, in order to obtain photocatalytic activities and high selectivities and thus to avoid reaction mixtures that require the separation of secondary reaction products. Also, a very important aspect is the decrease of the number of steps necessary for the preparation of catalytic materials and the use of economic precursors based on oxides, which will not have a negative effect on the environment. Generally speaking, when discussing the catalytic properties of ZnO, the interactions they form with the support used, the ratio between the active surface and the total surface of the support are taken into account.

The researches in the field of catalysis have shown that, in order to obtain immobilized catalysts on fixed substrates, with high photocatalytic activity, an important factor to consider is the choice of an efficient support that allows the anchoring of the oxide particles on the surface of the material host. In order to deposit ZnO, there are a number of techniques, of which the most commonly used in industrial practice is impregnation/spraying. These method involves contacting the support with the precursor solution, followed by drying, calcining and activating the catalyst. Depending on the volume of the precursor solution used, this process is found under various names, namely: wet impregnation- when the volume of the precursor solution is greater than the volume of the support pores or impregnation with incipient, wetting- when the volume of the precursor solution is equal to pore volume.

Due to the importance of the catalytic processes in the chemical industry and the continuous need for them to be improved, in order to reduce environmental pollution, but also to reduce costs, many efforts are being made to develop new synthesis pathways that allow the improvement of physico- chemical properties of the catalysts and which maximize their activities. One of the current concerns in the field of photocatalysis is to develop fixed catalysts immobilized, so that the problem of recovering the particles of classical catalysts can be avoided.

In **chapter 6** with the title *"General conclusions, Original contributions and Future research directions"* are presented the general conclusions regarding the experimental results presented in this thesis in the field of the synthesis of an oxidic material with catalytic properties from waste as well as the degradation yield of some emergent compounds from aqueous environment.

Additionally, chapter 6 describes the "*Original contributions and Future research perspectives"* where are presented the author's contributions in the field of research, scientific achievements that reflect the elements of originality in the field of doctoral thesis approaches completed by the submission of a patent application at the State Office for Inventions and Trademarks (OSIM), dissemination of the results by publishing scientific articles and by participating at national and international scientific events. The doctoral thesis ends with *Bibliography* and *Scientific Achievements in the research domain.*

Key words: oxide materials, photocatalysts immobilized on the substrate, waste recovery, ZnO, heterogeneous photocatalysis, UV, VISIBLE light, Advanced Oxidation Processes (POA), wastewater treatment, organic compounds

CHAPTER 1. The current state of the oxidic materials used in the photocatalytic processes for wastewater treatment

1.1. The main purpose of the doctoral researches

The aim of the research topic is to obtain some oxide materials by waste recovery, in order to use them in the removal of emergent compounds from wastewater, especially pharmaceutical compounds thorugh Advanced Oxidation Processes (POAs) by heterogeneous photocatalysis. In this chapter we focused on a brief presentation of the current state of the water resources conservation in Romania and their high level of contamination with pollutants from the emergent organic compounds, from which resulted the need to find out new oxide materials in order to contribute to wastewater treatment.

1.2. Motivation of the research topic

The need for continuous development of new support materials for the immobilization of photocatalytic semiconductors used in the degradation of organic pollutants from wastewater, has gained an important place in the last decade, due to the many advantages they have compared to suspended catalytic powders.

Based on these premises, in this chapter, were presented the types of support materials, techniques and methods used nationally/internationally in immobilization of photocatalytic oxides on the surface of support materials and the use of Advanced Oxidation Processes by heterogeneous photocatalysis with zinc oxide semiconductors in water treatment.

At national and international level, previous studies present as materials used as support for the immobilization of photocatalytic oxides various types of substrates, including industrial waste that through minimal processing can be reused in various applications. In this thesis, a special attention has been paid to support materials obtained from industrial waste due to the convergence to the principles of a circular economy but also from environmental considerations in terms of sustainable development. In particular, special attention was paid to waste with high oxide content, due to the multiple possibilities of using it in useful by-products.

The growing environmental problems caused by the improper storage of industrial waste has led to the need to develop processes for either recycling or recovery that turn this waste into materials with potential use in various fields of activity.

In recent years, interest in waste recovery/recycling has grown globally, currently standing at around 60%. Lately, the use of waste as a raw material in obtaining new products has become increasingly studied due to the high composition of elements suitable for reuse.

Wastes with oxide compositions that could be used as raw material in obtaining support materials, according to the literature, are presented in *table 1.1* .:

Table 1.1. *General industrial waste with high oxide content suitable for recovery*

GENERAL INDUSTRIAL WASTES AND RECYCLABLE MATERIALS, %							
Materials	**SiO_2**	**CaO**	**Fe_2O_3**	**MgO**	**Na_2O**	**SO_3**	**Al_2O_3**
Construction and demolition	72	9.84	1.28	0.26	0.22	2.09	1.88

Concrete waste	71	12.76	2.43	0.39	1.04	0.33	2.84
Glass waste	76.42	9.70	0.20	3.30	13.7	-	0.4
Brick waste	50.95	9.92	6.68	5.62	0.55	3.37	16.92

Another category of waste that can be a valuable source of reusable material refers to waste from the food industry. Poultry waste is one of the most emerging problems in the food industry due to the high costs of disposing of it. Eggshells are wastes generated not only from agro-industrial activities (from poultry farms), large quantities also resulting from the food industry, from the manufacture of various products containing eggs. According to EU regulations, eggshell waste is considered hazardous waste, however, hundreds of thousands of tonnes are dumped worldwide every year and more than 250,000 tonnes of eggshells are estimated to be produced daily. The potential of this waste to be recovered is high, as it has a high content of calcium, bound in the form of calcium carbonate (over 95% $CaCO_3$), so that this eggshell waste could be a valuable source of reusable material, which can be used in various fields of activity including as an anchoring medium for photocatalytic semiconductors [19, 20].

1.3. Techniques and methods for obtaining photocatalytic functional surfaces on fixed supports

The method chosen for immobilizing the photocatalyst on the support material plays a significant role in determining the photocatalytic activity of the photocatalyst and its yield. Therefore, in the proper choice of the support material it is often necessary to take into account the type of catalyst used and the pollutant molecule to be degraded. The technique followed by deposition must be done so as not to reduce the photocatalytic activity of the photocatalyst.

Many of these types of methods have been presented in the literature, some of these methods include:

- sol-gel method, which consists of immersion coating (*dip coating*) [44, 45];
- chemical vapor deposition (CVD) which includes techniques such as chemical vapor deposition at atmospheric pressure (APCVD);
- increased chemical vapor deposition in plasma (PECVD), deposition of metalorganic chemical vapors (MOCVD);
- hybrid physico-chemical vapor deposition (HPCVD);
- heat treatment method, electrophoretic deposition [46, 47];
- sol-spray method [48] etc.

However, most of these techniques are not widely used, as they require a high calcination temperature which can cause the decomposition of the complex substrate leading to expensive procedures and tools. Sol-gel and sputtering methods are popular methods for researchers. These are the main low temperature deposition techniques for immobilizing nanophotocatalyst particles on various inert media. It has been observed in many cases that the photocatalytic activity by using immobilized TiO_2 obtained by the sol-gel method is generally restricted due to the formation of the amorphous TiO_2 phase after sol-gel synthesis, this can be explained by the fact that the separation of the photo-induced charge takes place effectively only in the crystalline phase (anatas). If this crystalline phase is recovered from amorphous TiO_2 films synthesized by the sol-gel method, heat treatment at relatively high temperatures are required after the coating process. This illustrates how certain versatile

immobilization techniques are also prevented by the final heat treatment, which requires support for high thermal stability. Immobilized catalytic materials exist in different forms, and their preparation can be done using a multitude of experimental protocols, following different synthesis schemes.

1.3. Advanced Oxidation Processes. The mechanism of heterogeneous photocatalysis of zinc oxide

1.3.1. Contamination of water resources with emerging pollutants

A rapidly growing population and a constantly improving industrialization have made the wastewater problem vital in recent years and have therefore led to the need to develop researches on Advanced Oxidation Processes (POAs). There is a lot of research into the development of sustainable water treatment techniques that can improve water quality. Unavailability of drinking water is a crucial issue especially in region where conventional drinking water treatment systems fail to degrade emerging pollutants, toxic metal ions and industrial waste present in the aquatic environment. Research & developments from this field have given rise to a new class of processes called POAs, especially heterogeneous photocatalysis, which converts photonic energy into chemical energy. Technological advances in this field have improved the ability to specifically develop and adapt the properties of photocatalytic materials used in this area.

Clean and safe water, free of toxic materials, carcinogens and harmful bacteria, is necessary for human health. According to the 2018 United Nations World Water Development Report, the demand for clean water will increase by almost a third by 2050 [65]. Clean water is an elementary primary requirement in a variety of crucial industries, for example electronics, food and pharmaceuticals. Therefore, in order to meet the demand for water supply, more and more efforts are being made to develop new methods and materials for wastewater treatment.

Thus, in this context, the use of techniques that facilitates the reuse of the catalyst meet this shortcoming, making the photocatalysis process more environmentally friendly. Many authors have reported the feasibility of using immobilized catalyst on the substrate for photocatalytic degradation of polluting organic molecules [90, 91, 92, 93, 94, 95].

Various techniques have been successfully used in the approaches performed for the immobilization of catalysts on different support materials such as glass substrates, zeolites, metal supports and photoelectrodes, etc., these techniques have been extensive presented in *Chapter 1.*

1.3.2. Heterogeneous photocatalysis of zinc oxide

Heterogeneous photocatalysis of zinc oxide (ZnO) belongs to the class of Advanced Oxidation Processes that use light energy to produce highly reactive intermediates with a high oxidation or reduction potential, which eliminates the target compounds [96]. The high interest for this method is due to the fact that the process can be performed in ambient conditions and can lead to the total mineralization of organic carbon to CO_2 [97].

Recently, **zinc oxide (ZnO)** has been used extensively as a photocatalyst for the decomposition of emerging pollutants by heterogeneous photocatalysis processes as a possible alternative to conventional water treatment technologies, as the potential value of its valence and conduction bands allows water oxidation and adsorption on their surface of several organic substances and with the reduction of oxygen.

The reason why we chose the presentation of the zinc oxide semiconductor is that this paper presents studies on the photocatalytic functionalization by coating with zinc oxide of a support material obtained from waste with activity in VISIBLE and UV-A light spectrum.

CHAPTER 2. General objectives and methodology of the experimental researches

2.1. General and specific objectives

The **general objective** of this paper is to obtain new support materials by waste recovery and functionalization with catalytic oxides, which would later allow the use of the material as a photocatalyst, in order to degrade the refractory organic compounds from wastewater from the class of pharmaceutical compounds. The present study focused on obtaining new reusable catalysts based on zinc oxides on porous substrates, using simple optimized preparation methods - depositing the oxide film on the surface of the substrate by orbital agitation and then applying an autoclaving and drying process for its immobilization on the substrate.

The specific objectives set in this thesis were:

- Carrying out a documentary study on the current state of recent research at national and international level in the field of photocatalyst systems immobilized on support materials used for wastewater treatment;
- Presentation of immobilization techniques of photocatalysts on substrates;
- Optimization of working parameters in the process of synthesis of photocatalytic oxide materials;
- Obtaining a support material by recovering some waste and by coating with a zinc oxide layer on its surface;
- Compositional, morphological and structural characterization of the SpongeMat/ZnO oxide material obtained (SEM, XRD analyzes, 2D and 3 D roughness profilometric determinations, Vickers micro-indentation);
- Evaluation of the photocatalytic degradation capacity of the spongy material coated with zinc oxide, for different types of organic compounds present in wastewater;
- Dissemination of the obtained results and future research directions.

2.1. Experimental research program

The experimental research program took place in the laboratories of the National Institute for Research and Development in Environmental Protection - Bucharest (INCDPM-Bucharest), École Nationale Supérieure de Chimie de Rennes (ENSCR), Université de Rennes 1, France, Polytechnic University of Bucharest, Romania and University of Lille 1, Materials and Transformation Unit - Faculty of Sciences and Technologies, France.

In the following are presented separately the scientific contributions during the development of the Doctoral Research Program:

Obtaining the spongy material coated with zinc oxide with photocatalytic properties was carried out in the Laboratories of the National Institute for Research and Development in Environmental Protection - Bucharest (INCDPM-Bucharest), within PN 18 26 02 03 NUCLEU Program entitled: *"Contributions on improvement wastewater quality through the use of modern technologies in order to eliminate hazardous organic compounds"*, phases 1, 2 and 3, researches conducted as project director, with a grant of the Ministry of Education and Research.

Researches on the morphological and structural characterization of the obtained spongy material was carried out at the *University of Lille 1, Unité Matériaux et Transformation- Faculty of Sciences and Technologies*, France under the coordination of Prof. Dr. Eng. Guy REUMONT, Prof. Dr. Eng. Ingrid PRORIOL- SERRE, Prof. eng. David BALLOY and within the Polytechnic University of Bucharest, Faculty of Materials Science

and Engineering, Romania under the coordination of Prof. univ. dr. eng. Cristian PREDESCU and Prof. univ. Dr. chem. Ecaterina MATEI. The financing of the high-level training mobility, of one month within the Université de Lille 1, was possible with the support of the Ministry of Foreign Affairs through the French Romanian Institute.

The evaluation of materials obtained from the point of view of photocatalytic activity, in the presence of ultraviolet light and visible spectrum light using advanced oxidation processes through heterogeneous photocatalysis, was performed at the *École Nationale Supérieure de Chimie de Rennes (ENSCR), Université de Rennes 1,* France, Department of Chemistry and Process Engineering, under the coordination of Prof. Dr. Lidia FAVIER. The financing of the 2 doctoral mobility of 4 months each (2018 and 2019), carried out in France was possible through the French Government Scholarships Program (BGF) - 2017 edition funded by the French Embassy in Romania.

2.2. Experimental research methodology

In order to achieve the established objectives, an experimental research methodology was drawn up that combines three of the fundamental branches of research, namely: *fundamental research, applied research* and *experimental development* in order to obtain a unique and innovative result, consisting of an oxide material with photocatalytic properties as follows:

✓ *fundamental research* - achieving of a *State of the art* regarding the types of materials used as support for the immobilization on their surface of some oxide films and which have applications in wastewater treatment by heterogeneous photocatalysis, as well as the presentation of techniques and methods of obtaining it;

✓ *applied research* - following the bibliographic synthesis, followed the generation and testing of some hypotheses in order to put into practice the obtaining of a new oxided material immobilized by capitalizing some waste;

✓ *experimental development* - stage in which we obtained a series of oxide materials from waste and tested their functionality in wastewater treatment applications loaded with organic pollutants.

In the applied and experimental research, a series of *support materials* (MS) were developed by recovering glass waste from fluorescent lamps, eggshells and Epsom agricultural fertilizer and subsequently photocatalytic functionalization with a zinc oxide film in order to photocatalytic degradation of organic compounds in wastewater. Glass waste, eggshells and Epsom salt with the composition presented in *table 2.1* were used for the elaboration of the support material as it follows:

Table 2. 1. *The composition of the spongy support material (MS)*

Glass waste		**Eggshell waste $CaCO_3$**		**Epsom salt $MgSO_4$**	
(%)	**g**	**(%)**	**g**	**(%)**	**g**
86-94	6.51	5-10	0.49	1-4	-
	6.44		0.49		0.07
	6.16		0.49		0.35
	6.93		0.07		-
	6.86		0.07		0.07
	6.58		0.07		0.35
	6.79		0.21		-
	6.72		0.21		0.07
	6.44		0.21		0.35

The scheme of the experimental research methodology is represented in figure 2.1 .:.:

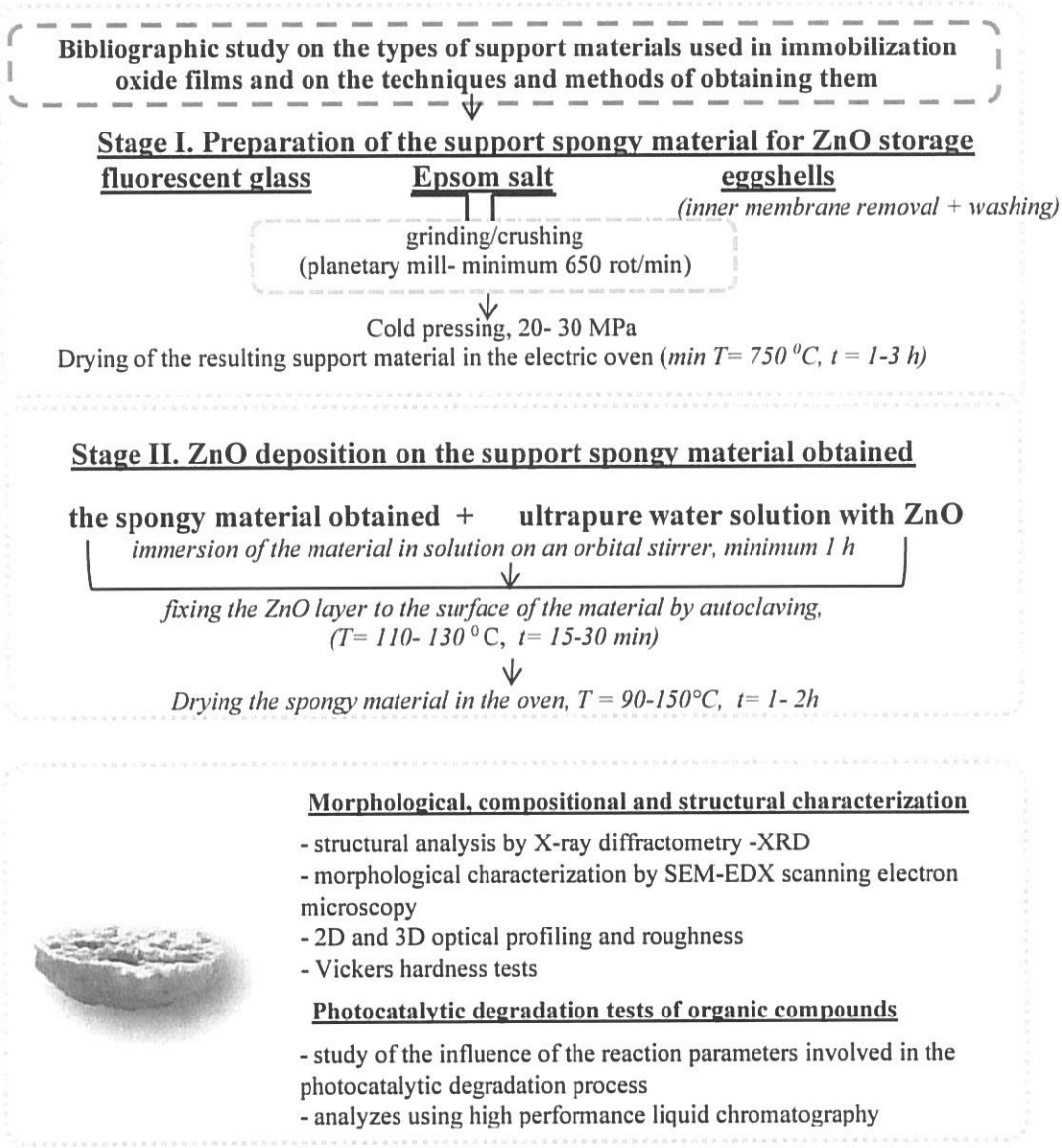


Figure 2. 1 - Experimental research methodology regarding the spongy material coated with zinc oxide, with photocatalytic activity in the UV and VISIBLE field - SpongeMat/ZnO

For photocatalytic functionalization, it was immobilized on the surface of the obtained MS with the unique composition $CaCO_3$= 0.21 g, $MgSO_4$ = 0.07 g, glass = 6.72 g the following quantities of ZnO presented in *tabel 2.2.* resulting a number of 7 samples :

Table 2. 1 *The amounts of ZnO in order to photocatalitically functionalization of the MS*

oxidic films	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
ZnO	*20*	*50*	*100*	*250*	*500*	*1000*	*1750*

Sponge Mat/ZnO oxide materials used for experimental research were obtained by encapsulating the powder by cold pressing, synthesized at 750^0 C in a calcining oven HTCT 08/14 for 1- 3h from INCDPM- Bucharest and subsequently photocatalytic functionalization by depositing a zinc oxide film on the sample surface by immersion, orbital shaking and then autoclaving and cooling in electric arc furnace at a temperature between 90- 150^0 C.

The steps for the development of Sponge Mat/ZnO oxide material samples can be divided into two major steps as it follows:

1. Obtaining the support material from waste and agricultural fertilizer;
2. Immobilization of the catalyst on the surface of the obtained support material.

2.3. Equipment used and analysis techniques used to achieve the objectives

2.3.1. Structural analysis by X-ray diffraction (XRD)

The structural characterization of the oxide material synthesized at different concentrations of ZnO by autoclaving was performed using the X-ray diffraction method (XRD) using the equipment Bruker D8 type, from the University of Lille 1, Unité Matériaux et Transformation- Faculty of Sciences and Technologies, France.

2.3.2. Scanning electron microscopy (SEM) and energy scattering X-ray spectroscopy (EDX)

The FLEXSEM 1000-HITACHI electron microscope from the *University of Lille 1, Unité Matériaux et Transformation- Faculté Sciences et Technologies, France,* was used to capture high-resolution images.

Before performing the analyzes, the sectioned samples were prepared by polishing the surface with SiC paper and subsequently a diamond polishing paste of 6, 3 and 1 μm was used to remove any scratches, and the samples of glass powder and eggshell were were embedded in the resin.

Due to the fact that the porous layers of zinc oxide on the surface of the support material are electrical insulators, all samples analyzed were coated with a thin layer of chromium to prevent electrically charged non-conductive samples that can be induced by the beam of incident electrons, this coating was made using the sprayer device model GATAN-682, with deposition values in the range of 30 - 100 Å.

2.3.3. Optical profiling

Optical profiling and 2 D and 3D roughness measurements were performed using the Contour GT-K 3D optical microscope from the *University of Lille 1, Unité Matériaux et Transformation- Faculté Sciences et Technologies, France.*

2.3.4. Microhardness analysis

The determination of the microdurity by the Vickers method on the surfaces of the samples was performed with the help of the automatic microdurimeter, BUEHLER device, the load used was 500 g for 10 s for each sample.

2.3.5. High Performance Liquid Chromatography (HPLC)

The water samples treated with the photocatalytic oxide material obtained - SpongeMat/ZnO, were analyzed using High Performance Liquid Chromatography (HPLC), equipment from the laboratory of the *Ecole Nationale Superieure de Chimie de Rennes (ENSCR),* France. The HPLC system using a mobile phase consisting of a mixture of acetonitrile/water/formic acid (60/40/0.1), column used type WAT054275 reference C18 with a diameter of 5 mm and 25 cm in length.

CHAPTER 3. Obtaining a photocatalytic oxide material from waste

This chapter presents the own contributions made in the field of doctoral research, as follows:

- identification of the optimal synthesis parameters of a new support material obtained by capitalizing on some waste;
- photocatalytic functionalization, by depositing a film of zinc oxide on the surface of the synthesized support material, as well as testing it for applications in wastewater treatment through advanced oxidation processes;
- elaboration of a process for obtaining the functionalized spongy material and its patenting, by filing and registering a patent application at the National Office of Inventions and Trademarks (OSIM).

3.1. Waste recovery into a new catalytic material

The material obtained in the thesis converges the principle from waste to functional by-product by the fact that it involves the recovery of a series of waste in a support material and then its coating with an oxide semiconductor. We started from the premise that Romania is invaded by mountains of waste, which, for various reasons (financial, legislative, technical, etc.), remain undervalued and continue to degrade the environment. Apart from the aspects related to the environment, these mountains of waste occupy enormous spaces and swallow large sums of money, given that they could be valuable sources of recyclable/recoverable material.

Increasing the recovery of glass waste is currently one of the objectives of Directive (EU) 2018/852 of the European Parliament and of the Council of 30 May 2018. In this context it is necessary to develop new technologies and materials based on the concept of glass waste recovery [106].

The spongy composite material resulting from this thesis was obtained by recovering a series of wastes as follows: glass waste from fluorescent tubes, eggshells and agricultural fertilizer Epsom salt ($MgSO_4$). This support is subsequently covered with a layer of ZnO which gives it photocatalytic properties. Both the synthesized composite material and the production process were developed based on 2 principles converging towards good practices in the field of environmental protection:

- ⇨ the process does not generate secondary components and involves the recovery of waste (glass from fluorescent tubes, eggshells) and Epsom salt to obtain the spongy support material (MS), thus helping to reduce the impact on the environment generated by the volume of waste stored improperly ;
- ⇨ zinc oxide-coated spongy composite material (SpongeMat/ZnO) has potential for application in the field of environmental protection, having the capacity for photocatalytic degradation of organic compounds in wastewater in the UV and visible range.

The spongy material coated with zinc oxide synthesized based on glass waste (glass content between 86-94%), is used to obtain the support spongy material for the deposition of ZnO with photocatalytic properties on its surface. The glass waste used is not potentially toxic, X-ray fluorescence analyzes showing the presence of glass-specific chemical elements - Si, Na, Ca, Mg, K, Ba, Al, and an insignificant proportion of heavy elements (sum of Pb element concentrations, Sr, Cr, Mn is below 0.5%). Due to the porous structure, spongy materials are of interest due to the large specific surface that can be functionalized with different metal oxides for their use as materials with photocatalytic properties, and applications in the field of environmental protection.

SpongeMat/ZnO spongy material presents photocatalytic activity in the UV and VISIBLE field and it was obtained by a simple method of ZnO deposition and autoclaving.

The opportunity and necessity of the present spongy material coated with ZnO results from the fact that compared to other types of synthesized materials, this material was obtained based on waste recovery and has high efficiency of degradation of organic compounds in the UV field (over 97%), having in addition, photocatalytic activity in the VISIBLE field (efficiency over 43%). The material can be reused up to 5 times in a row with the same degradation efficiency of organic compounds, thus avoiding the problem of difficult recovery of conventional catalysts, in powder form, in Chapter 5 being presented in detail the study on the efficiencies of the degradation material of organic compounds in the class of pharmaceutical compounds, dyes and phenols present in wastewater.

In the following will be presented the two technological steps applied to obtain the SpongeMat/ZnO material consisting of *Step 1. Obtaining the support material* and *Step 2. Deposition on the surface of the support material of zinc oxide film, for catalytic functionalization.*

3.2. Obtaining the support material for coating with ZnO. Stage 1

3.2.1. Preparation of samples and elaboration of powder for obtaining the support material

For Technological Stage 1 in order to obtain the spongy support material (MS) were used: glass waste from fluorescent tubes for gas discharges, from light sources, anhydrous Epsom salt (MgSO4) and eggshells, from farms poultry. The glass was washed to remove fluorescent powder from inside the tubes and then dried. The eggshells were prepared by removing the inner shell membrane and then washed in a stream of water to remove organic traces (egg white or yolk). Anhydrous Epsom salt, added as a binder, did not require prior preparation. The components of the mixture according to the recipe presented in *table 3.1.* were ground and finely ground in a planetary ball mill, until the total passage through the 63 μm mesh sieve. Eggshells, due to the high content of calcium carbonate ($CaCO_3$), were used as a foaming agent (AS). $CaCO_3$ in the composition of the eggs causes the formation of the spongy structure of the material due to the decarbonation at temperatures between 600-750°C, CO_2 released determines the formation of pores characteristic of the material.

Table 3.1. *Composition of glass-based support material (MS)*

Glass waste (%)	Eggshell waste (%)	Epsom salt (%)
86-94	5-10	1-4

3.2.2. Cold pressing and heat treatment

The powder obtained after grinding was cold pressed using a hydraulic press (at a pressure of up to 25 tons) to obtain the support material (ϕ = 4 - 6 cm), after that it was dried in an electric oven at a temperature between 100- 150°C, for up to 24 h. The spongy structure was obtained by sintering the material at a temperature of 750°C, between 1-3 h.

In order to synthesize the support spongy material, a series of laboratory tests were performed varying different compositional reports for the components that make up the samples, these reports and the labeling of the samples are presented in *table 3.2.*

Table 3.2. *Labeling of synthesized support material samples*

		Sample labels for the Support Material (MS)								
		A	B	C	D	E	F	G	H	I
$CaCO_3$	[g]	0.49	0.49	0.49	0.07	0.07	0.07	0.21	0.21	0.21
$MgSO_4$		-	0.07	0.35	-	0.07	0.35	-	0.07	0.35
glass		6.51	6.44	6.16	6.93	6.86	6.58	6.79	6.72	6.44

3.3. Photocatalytic functionalization by coating with zinc oxide films the surfaces of the support materials. Stage 2

In **technological Stage 2**, the Support Materials (MS), obtained in the first stage, are used as supports for the deposition of different amounts of zinc oxide semiconductor, in order to photocatalytic functionalization.

Procedure

For this purpose, the zinc oxide was dispersed in ultrapure water, in a mass ratio of 1/1000 - 5/1000. The spongy materials were immersed in the obtained solution and kept under continuous stirring for 1-2 h, using an orbital stirrer. Due to the flotability of the support material, it was kept completely immersed in the solution throughout the stirring by placing a counterweight on its surface.

After the end of the period allocated to the deposition of the ZnO layer, the container containing the solution and the spongy material were subjected to an autoclaving heat treatment, for fixing the oxide layer, for up to 1h, at a temperature of 110- 150°C. ZnO-coated spongy composite materials (SpongeMat/ZnO) were oven dried at a temperature between 90-150°C, for 1- 2h.

In *table 3.3.* the ZnO concentrations that were deposited on the surface of the chosen Support Materials (MS) are presented.

Table 3.3. *Photocatalytic functionalization of MS by deposition of zinc oxide film*

Samples labeling SpongeMat/ZnO [%]	Concentration of ZnO solution in which MS is immersed [mg/L]
J/ ZnO 0.2%	20
K/ZnO 0.5%	50
L/ ZnO 1%	100
M/ ZnO 2.5%	250
N/ ZnO 5%	500
O/ ZnO 10%	1000
P/ ZnO 17.5%	1750

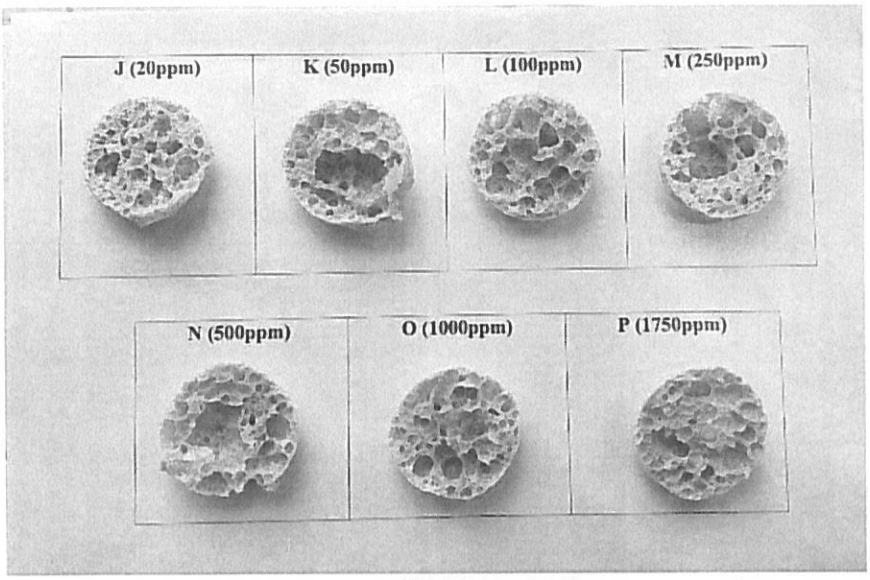
In figure 3.2. the procedure for coating with zinc oxide film on the MS surface is presented, as follows:



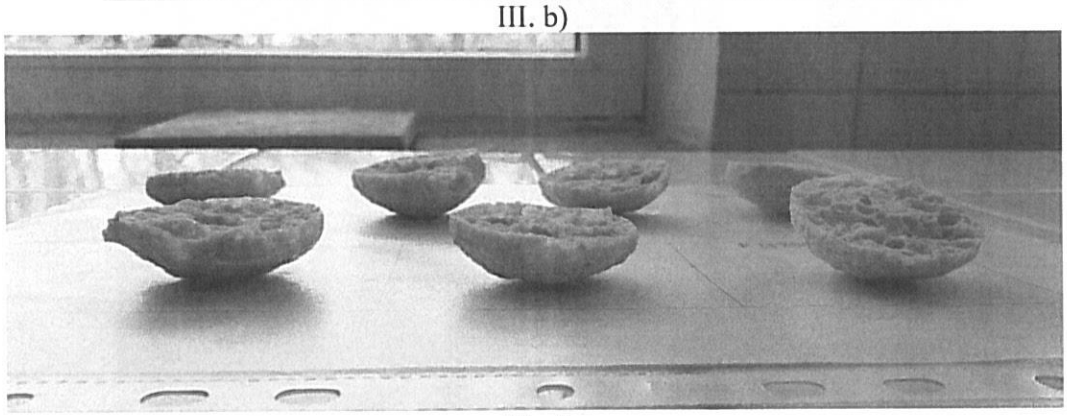
I. Autoclaving of MS/ZnO samples to fix the zinc oxide layer at a temperature of T= 110° – 150 °C, t = 15- 30 min


II. Oven drying of samples, Support Materials functionalized with ZnO (SpongeMat/ZnO), t= 24 h

III. a)



III. b)



III. c)

III. Support spongy material (MS), obtained by waste recovery and photocatalytically functionalized through ZnO coating (SpongeMat/ZnO); a) top layer of SpongeMat/ZnO; b) lower layer of SpongeMat/ZnO; c) side view of SpongeMat/ZnO

Figure 3.2. The process of support materials coating with zinc oxide films

The oxide-SpongeMat/ZnO material obtained was characterized morphologically and microstructurally by scanning electron microscopy, X-ray diffractometry and roughness, hardness and profilometry measurements were determined, subsequently it was tested in the laboratory to evaluate the degradation efficiency of organic compounds of the pharmaceutical and other classes, in the UV and VISIBLE field.

The technological process for obtaining the spongy oxide material - SpongeMat/ZnO, which is also the subject of a patent application submitted at OSIM with registration number A/00386/2019.

The researches on obtaining the spongy oxide material - SpongeMat/ZnO were carried out in the laboratories of the National Institute for Research and Development in Environmental Protection - Bucharest, within the NUCLEU Project PN 18 26 02 03, Phases 1, 2 and 3, in 2018, project with title: *"Contributions on improving wastewater quality through the use of modern technologies in order to eliminate hazardous organic compounds"*, as Project Director and funded by the Ministry of Education and Research. These involved laboratory determinations to obtain an innovative material with photocatalytic properties with applicability in environmental protection. At the same time, from this study resulted a patent application submitted at OSIM with registration number A/00386/2019 and publication number 11 in the BOPI Inventions Catalog for 2019

CHAPTER 4. Morphological, compositional and structural characterization of photocatalytically functionalized spongy oxide material

This chapter is dedicated to the morphological and structural characterization of the synthesized SpongeMat/ZnO oxide material and to the presentation of the obtained results. X-ray diffractometry (XRD) was used for the structural characterization of the material surface, the surface and elemental morphological characterization was performed using the X-ray analyzer coupled scanning electron microscope (SEM-EDX) and finally performed 2D and 3D measurements of profilometry, roughness and Vickers hardness.

4.1. Structural analysis by X-ray diffractometry (XRD)

The structural characterization of the support material coated with zinc oxide was performed using the X-ray diffraction method (XRD) to observe the phase changes of the surface of the material obtained by the method of immersion and autoclaving. In the following is presented the XRD diffractogram the solid spongy composite material.

4.1.1. Structural analysis of the powder of spongy oxide material obtained

In figure 4.3. is represented by the XRD diffractogram for the synthesized SpongeMat/ZnO oxide material, we observe that the intensity band is between 20° and 40° which is characteristic of an amorphous material and is normal due to the presence of more than 90% of fluorescent lamp residues in the composition of the synthesized oxide material.

We also notice some peaks at 29° and 39°, which could be associated with diffractograms of eggshells, present in small quantities and in the composition of the synthesized SpongeMat/ZnO material.

In addition, we can observe the appearance of small peaks at 24°, 31°, 32° and 33° due to the presence of the element Yttrium and a corresponding peak at 36.5° due to the ZnO coating of the support material.

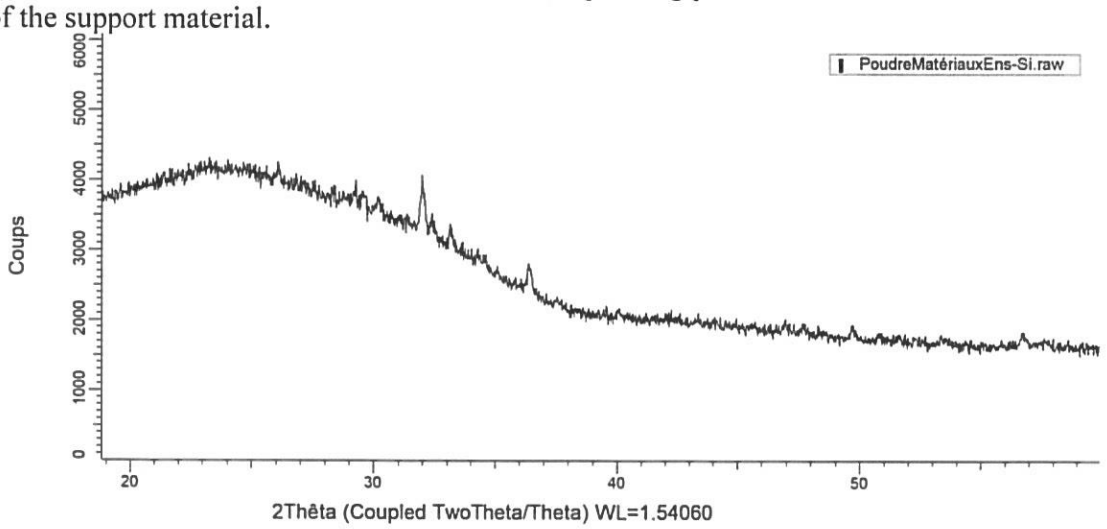


Figure 4.3. XRD spectrum at room temperature for the synthesized SpongeMat/ZnO oxide material

Moreover, a number of changes were observed near the peak 29°, this could be due to the presence of eggshells in the composition of the spongy material. A small peak in size is observed around 36.5°, it could be associated with the presence of ZnO according to data from the literature [115].

4.2. Morphological characterization by scanning electron microscopy (SEM)

The morphological characterization was performed using the scanning electron microscope (SEM) on the surface of SpongeMat/ZnO samples of different concentrations of zinc oxide, but also for the components in the composition of the obtained material.

4.2.1. SEM analyzes of the synthesized oxide material -SpongeMat/ZnO

The most interesting of the specimens of synthesized oxide materials (SpongeMat/ZnO) and presented in *Chapter 2*, were studied to investigate microstructural development using scanning electron microscopy (SEM), the analyzed samples are centralized in *table 4.1.* as follows :

Table 4.1. *SpongeMat/ZnO samples at different concentrations of ZnO analyzed SEM*

Name of analyzed samples	ZnO (mg/L)
SpongeMat/ZnO/17.5 %	1750
SpongeMat/ZnO/10 %	1000
SpongeMat/ZnO/5 %	500
SpongeMat/ZnO/1 %	100

In figure 4.7. the appearance of the sample with the ZnO layer deposited on the surface of the synthesized support material - SpogeMat/ZnO is presented. The material was analyzed morphologically and structurally by SEM electron microscopy.

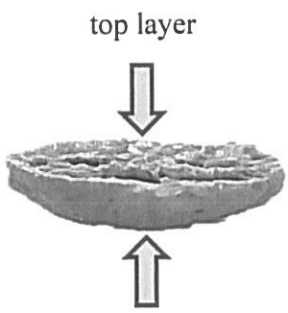


Figure 4.7. Appearance of the oxide material - SpongeMat/ZnO synthesized

The microstructure of all synthesized materials is almost the same and consists of a spongy architecture and can be seen in figure 4.8. a) and b) (red arrows). The amount of gas released (CO_2 and N_2) caused by the decarbonation of the eggshells and the creation of a high temperature (750°C) during the synthesis process it led to the formation of the porous structure.

Due to the irregular distribution of eggshell powder in different regions of the material, the inhomogeneous distribution of pores in size and shape took place. The average particle diameter is between 18.6 - 33.7 μm and is shown in the SEM images in Figure 4.8. c).

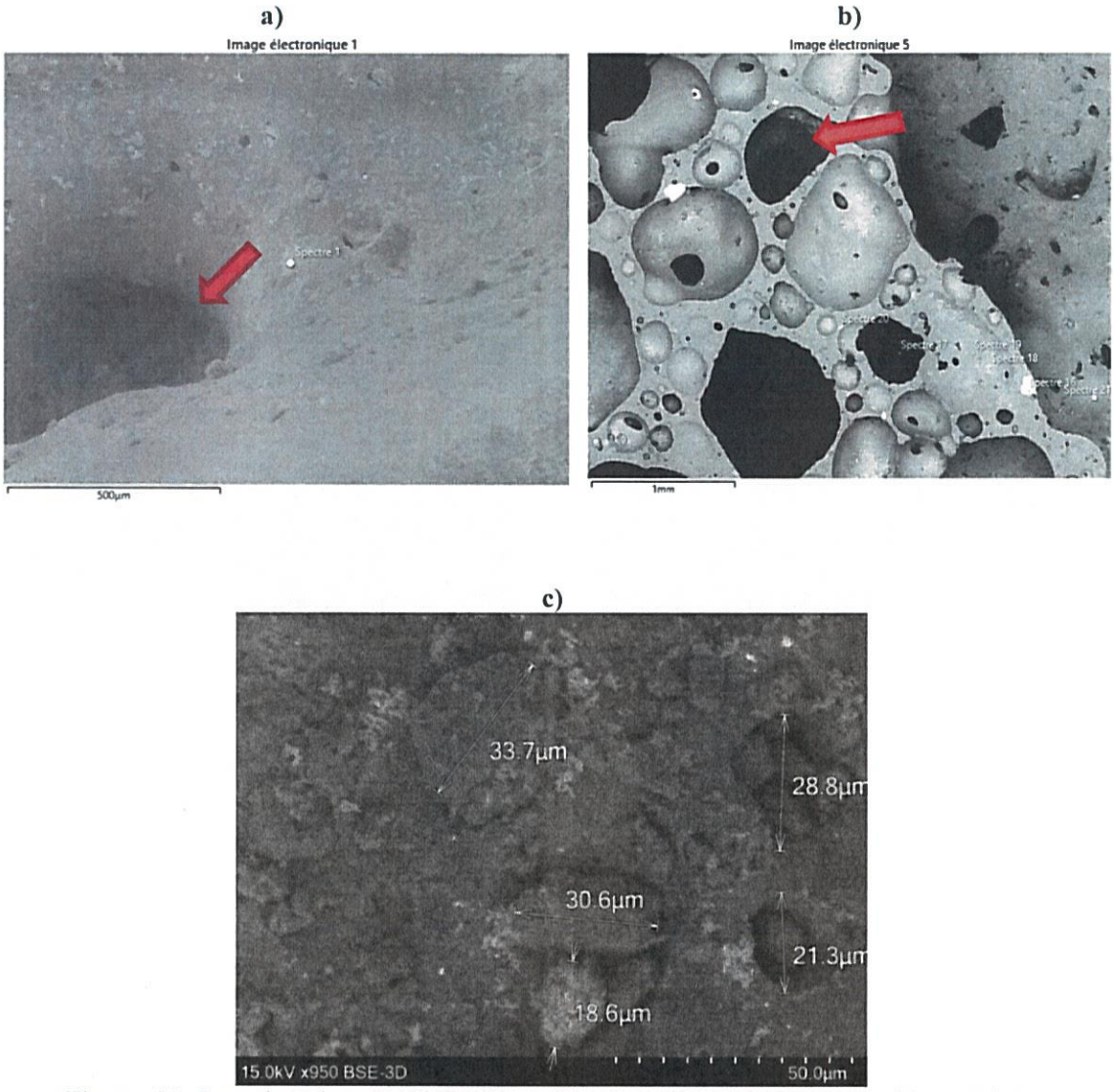


Figure 4.8. Scanning electron microscopy of the spongy structure of the oxide material - SpongeMatZnO synthesized a) lower layer and b) top layer of the sample for SpongeMat/ZnO/17.5% ; c) sample porosity - top layer SpongeMat/ZnO/1%

4.3. SEM-EDX spectrum analysis

The SEM-EDX spectral compositional analyzes were performed in turn for: uncalcined eggshell powder, glass powder from fluorescent lamps and powder from the synthesized oxide material - Sponge Mat/ZnO.

4.3.2. Fluorescent lamp glass powder

SEM-EDX analyzes of the glass powder from the fluorescent lamp residues were performed to analyze the elemental composition of the powder before sintering the oxide-SpongeMat/ZnO material. The SEM-EDX spectra of glass powder are shown in Figure 4.13. and 4.14., all the obtained spectra show the presence of the predominant peaks characteristic of the chemical elements Si, O and Na specific to the glass composition, in addition small traces of other chemical elements are observed such as: Fe, Mo, Na, Cr, Mg and Al.

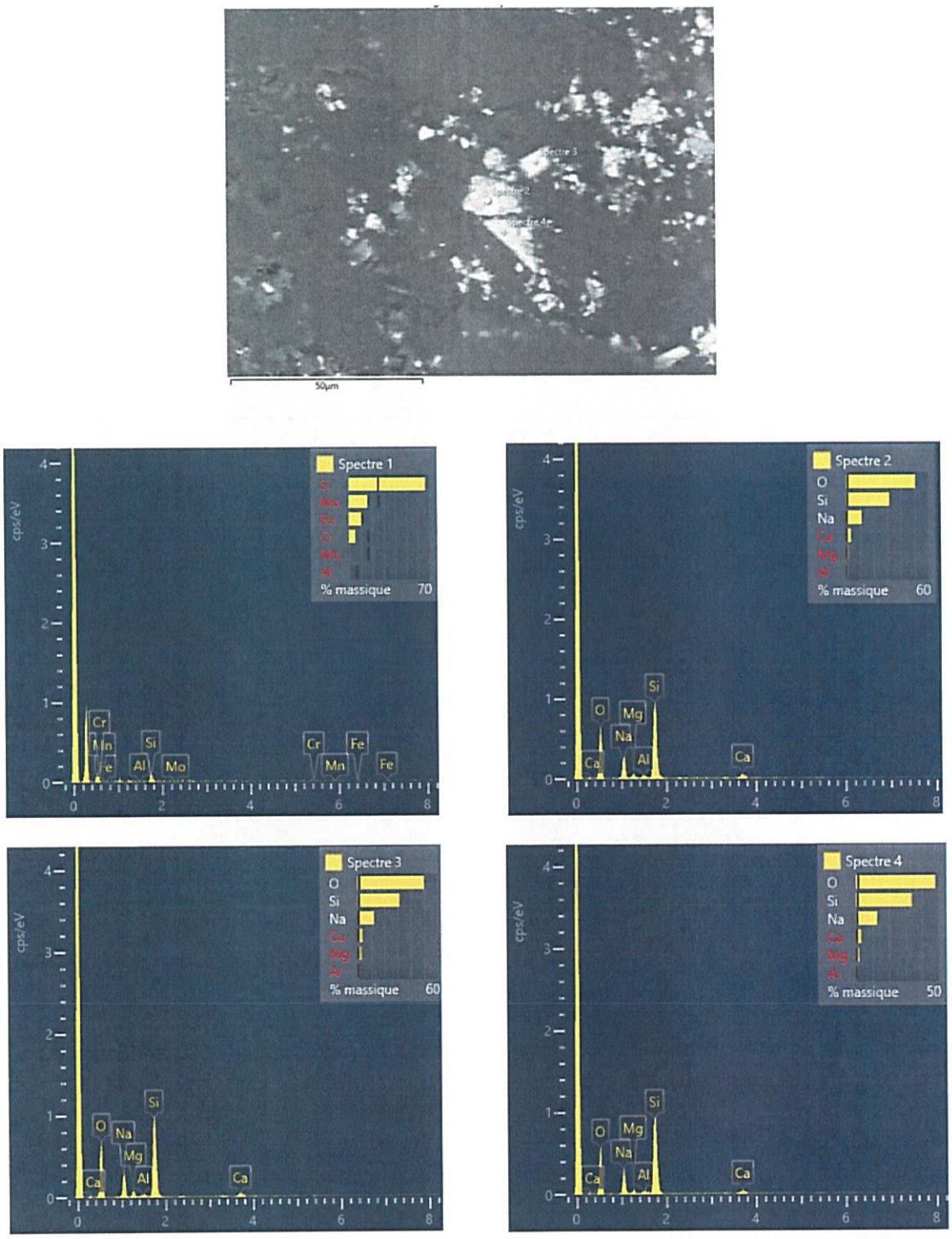


Figure 4.13. SEM-EDX spectra corresponding to glass powder, spectra 1, 2, 3,4

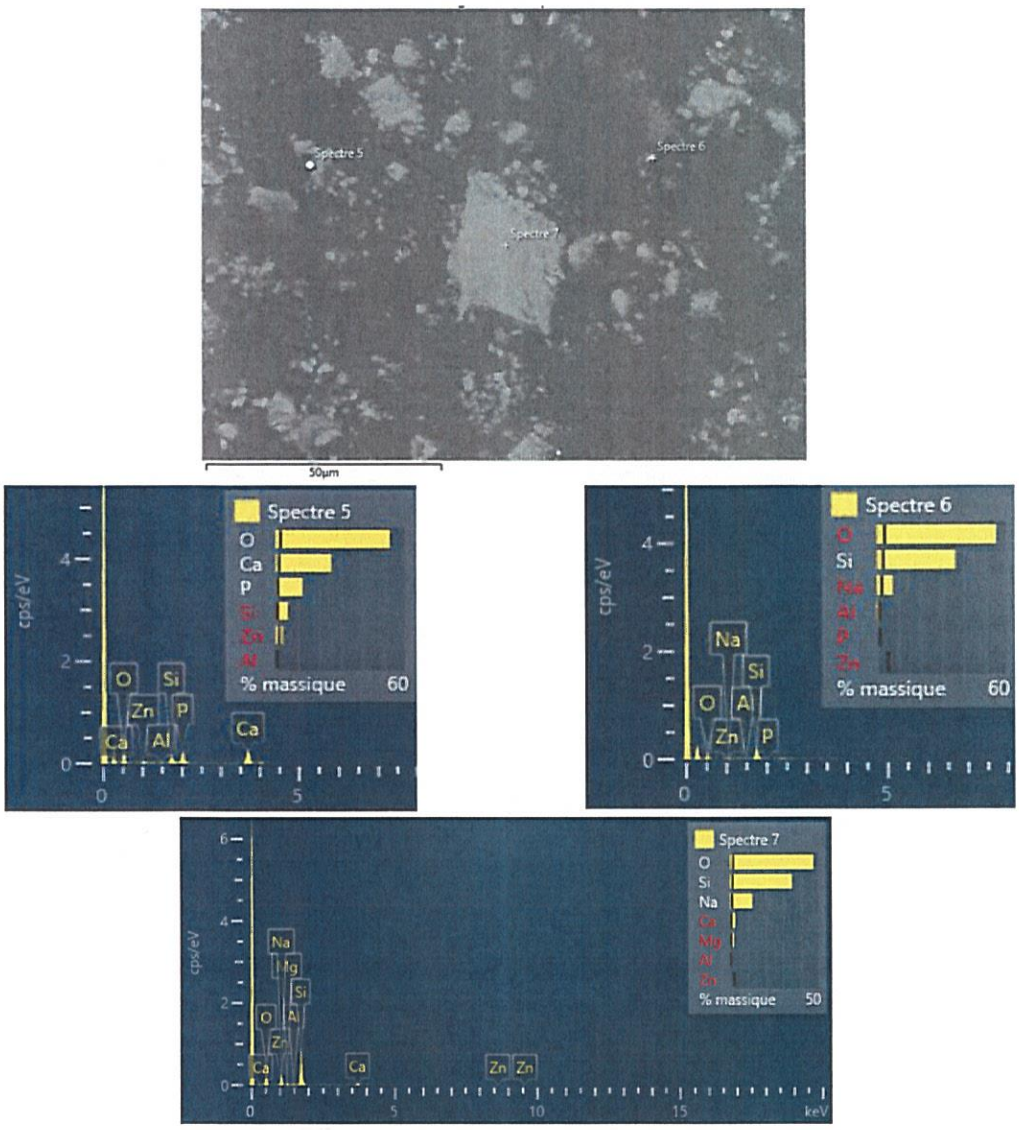


Figure 4.14. SEM-EDX spectra corresponding to glass powder fluorescent lamp, spectra 5, 6, 7

From the SEM-EDX analyzes presented in figures 4.13. and 4.14., images of the spectrum corresponding to fluorescent glass powder, from the SEM-EDX spectra of glass powder from fluorescent lamp residues, the presence of the peaks of the predominant elements Si, O and Na which are characteristic of the glass composition was observed.

4.4. Optical profiling

Optical profilometry and 3D measurements were performed using the Contour GT-K 3D optical microscope.

4.4.1. 2D and 3D optical profiling measurements

The thickness of the zinc oxide layers deposited on the synthesized support material was measured by optical profilometry. In figure 4.15. the profiles of the 4 different samples of the synthesized oxide-SpongeMat/ZnO material coated with different amounts of ZnO are shown as it follows: a) SpongeMat/ZnO/17,5%, b) SpongeMat/ZnO/10%, c) SpongeMat/ZnO/5% and d) SpongeMat/ZnO/1% obtained by an autoclaving process lasting 15 minutes. The morphology of the zinc oxide layer deposited on the surface of the support

material could be observed with the help of profilometry, by observing the presence of cracks, adhesion to the substrate and homogeneity of the layers.

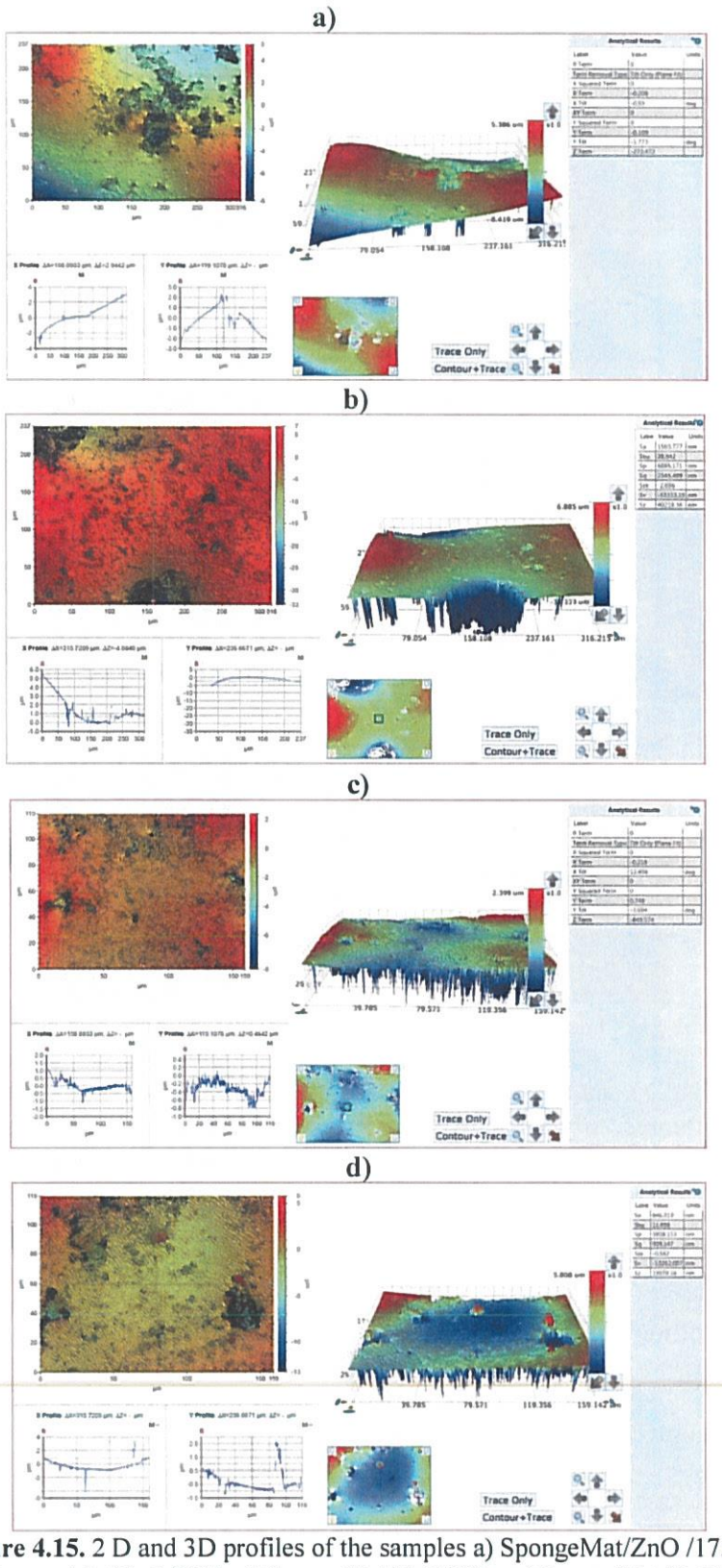


Figure 4.15. 2 D and 3D profiles of the samples a) SpongeMat/ZnO /17.5%, b) SpongeMat/ZnO/10%, c) SpongeMat/ZnO/5% and SpongeMat/ZnO/1%

Table 4.2 shows the thickness of the oxide films obtained:

Table 4.2. *Thickness of oxide films*

Analyzed sample [%]	Catalyst solution concentration, ZnO (mg/L)	Layer thickness of ZnO (nm)
SpongeMat/ZnO/17.5%	1750	5.386
SpongeMat/ZnO/10 %	1000	6.885
SpongeMat/ZnO/5 %	500	5.399
SpongeMat/ZnO/1 %	100	5.808

It has been shown that the layer thickness increases with the number of immersions in the oxide film solution. According to the data obtained we see that the thickness of the oxide film deposited on the surface of the support material does not vary much in the case of the 4 samples analyzed, this may be due to the sinking rate, which in our case was equal to 1, but also the sampling rate but also other variables.

The thickness of a zinc oxide film is strictly dependent on the number of immersion cycles of the support material in the zinc oxide solution. A good quality of oxide films (absence of cracks, good adhesion on the substrate, homogeneity of the layer, etc.) can also be observed with the help of SEM. It has been observed that the coloring phenomenon observed on films strongly depends on the thickness and varies from brown to yellow, blue and pink when the thickness increases. Films produced under the same conditions always show the same interference color, due to their comparable thickness.

4.5. Characterization of surface roughness

Determining the roughness parameters of zinc oxide layers deposited on the surface of oxided materials - SpongeMat/ZnO synthesized, has a significant role in assessing how these catalytically functionalized surfaces have efficiency in the degradation of organic pollutants.

2 D and 3 D surface analysis methods were used to calculate roughness parameters, in order to obtain important information related to the surface topography and its physico-chemical and mechanical performance, there is a close link between the increase of roughness and certain crystallographic processes that take place at the surface of the material.

According to data from the literature, it has been found that a higher surface roughness leads to better adhesion of oxides on the surface of the material, which is why it is so important to study this indicator.

4.5.1. Influence of zinc oxide layers deposited on the surface of the support material

From the analysis of the 2D and 3D roughness profile recorded on the surface of the oxide material - SpongeMat/ZnO/17.5% presented in figure 4.16. a value of 0.082 μm of the average roughness parameter Ra was determined.

a)

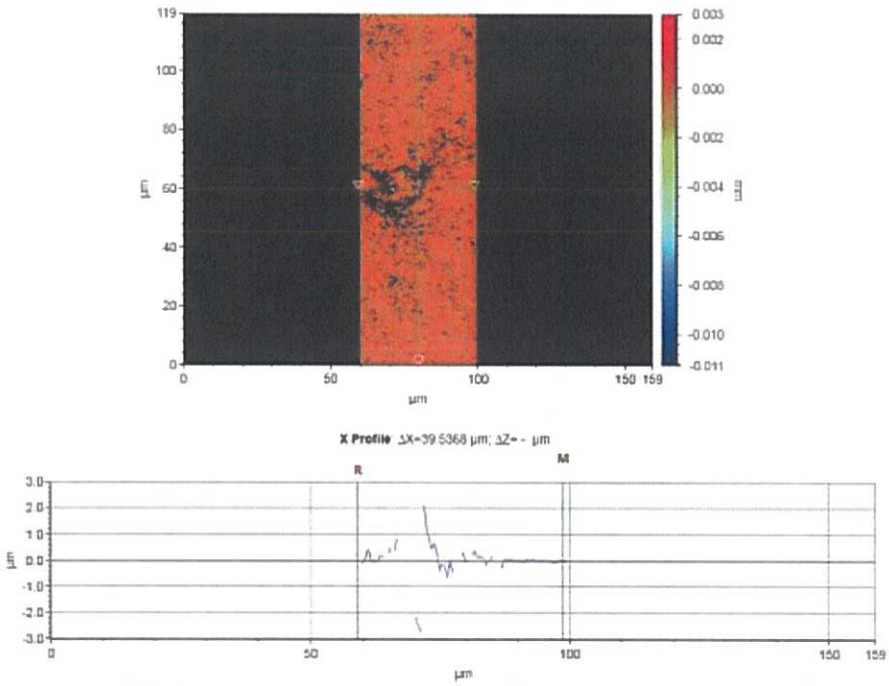


Figure 4.16. Roughness of the oxide sample - SpongeMat/ZnO/17.5 %

From the analysis of the 2D and 3D roughness profile recorded on the surface of the oxide material - SpongeMat/ZnO/17.5% presented in figure 4.16. a value of 0.082 μm of the average roughness parameter Ra was determined.

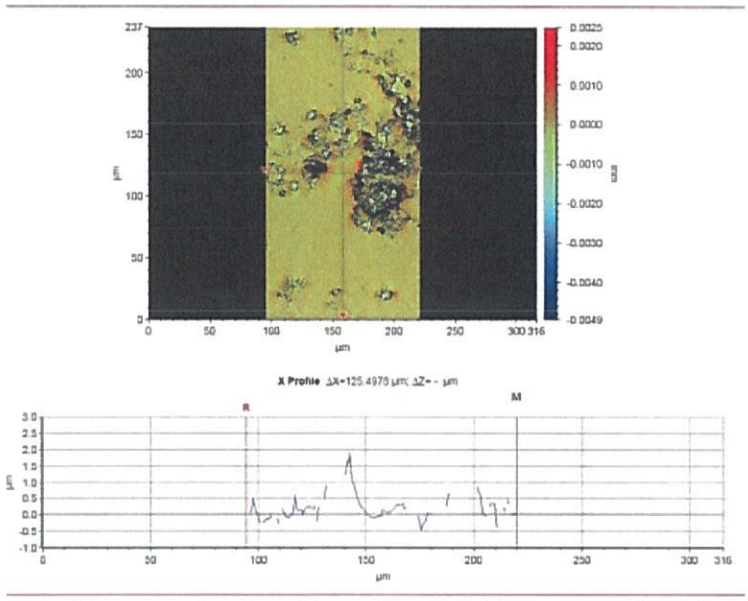


Figure 4.17. Roughness of the oxide sample SpongeMat/ZnO/*10%*

From the analysis of the 2D and 3D roughness profile recorded on the surface of the oxide material - SpongeMat/ZnO/5% presented in figure 4.18. a value of 0.089 μm of the average roughness parameter Ra was determined.

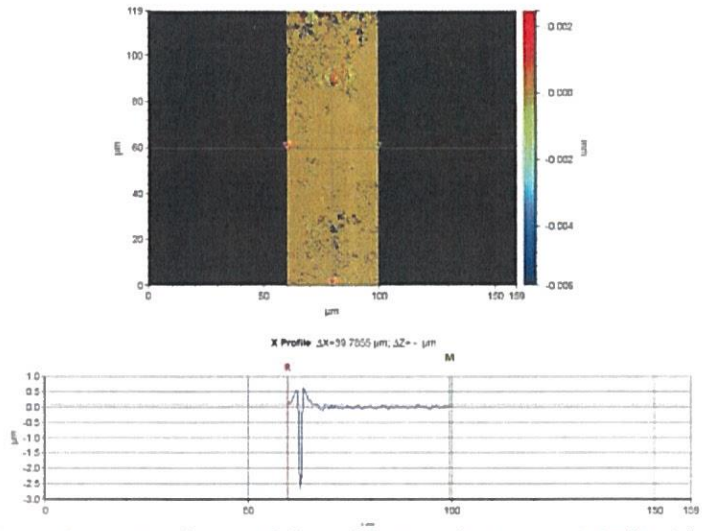


Figure 4.18. Roughness of the oxide sample - SpongeMat/ZnO/5 %

From the analysis of the 2D and 3D roughness profile recorded on the surface of the oxide material - SpongeMat/ZnO/1% presented in figure 4.19. a value of 0.101 µm of the average roughness parameter Ra was determined.

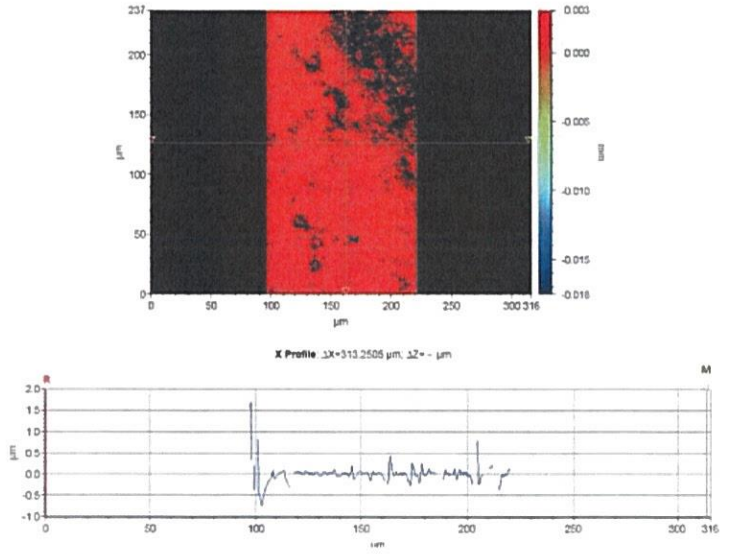


Figure 4.19. Roughness of the oxide sample - SpongeMat/ZnO/*1 %*

The roughness of the 4 samples of oxide materials - SpongeMat/ZnO functionalized photocatalytically at percentages of different concentrations in zinc oxide of 17.5%, 10%, 5% and 1% respectively is different in the case of each analyzed sample, but no significant evolution is observed on the roughness parameter Ra. The roughness between the porosities is low: Ra being mostly lower than 0.1 µm.

This effect may be due to the reproducibility of synthesis of oxide materials under the same operating conditions. We notice on the surface some porosities, with dimensions around 50 µm; we can say that the higher the adhesion of the ZnO layers to the surface, the higher the roughness of the support material, hence a close connection between the photocatalytic efficiency.

4.6. Evaluation of the hardness of the oxide material - SpongeMat/ZnO

4.6.1. Vickers micro-indentation tests

The synthesized oxide material - SpongeMat/ZnO was evaluated in terms of mechanical strength by micro-indentation tests on the surface of the oxide material sample - SpongeMat/Zn/17,5% using the BUEHLER apparatus, the load used was 500 g time of 10 s, as attempts were made to apply higher loads but cracks occurred on the surface of the material. Due to the shape of the surface and the presence of porosity, we measured a very low hardness equal to 16, which corresponds to that of a porous material. Attempts were made to test the hardness and other synthesized samples of ZnO concentrations (10%, 5% and 1%), obtaining approximately the same result as in the first case, this can be explained by the fact that the composition of the support material is unique and the ZnO concentration deposited on its surface does not influence the value of the mechanical strength of the material itself. These results show that the material obtained has a low mechanical strength due to its porosity.

Research on the morphological, compositional and structural characterization of spongy oxide material - SpongeMat/ZnO was carried out in the research laboratories of the University of Lille 1, Unité Matériaux et Transformation, in Lille, France, with the financial support of the Ministry of Foreign Affairs. through the French Romanian Institute as well as within the Polytechnic University of Bucharest, Faculty of Materials Science and Engineering, Romania.

CHAPTER 5. Photocatalytic degradation tests of an organic compound of the pharmaceutical grade using the spongy oxide material obtained

The photocatalytic activity of the synthesized oxide material/SpongeMat/ZnO was tested by photodegradation of the pharmaceutical compound, Clofibric Acid (CA), which was chosen due to its different chemical structure. In addition to the study of the degradation kinetics of the chosen pharmaceutical compound, other experiments were performed in order to test the degradation efficiency of the synthesized material on other types of organic compounds belonging to the class of dyes and phenols.

In the study of the influence of the reaction parameters involved in the photocatalytic degradation process of the degraded organic compound with the help of the synthesized oxide material SpongeMat/ZnO, the following experimental equipment and installations were used:

- Experimental laboratory photocatalytic degradation system, equipped with 1 UV fluorescent lamp F24W/10/4P (Philips) located above, irradiation in the UV-A range, with wavelengths between 270 -340 nm;
- High Perfomance Liquid Cromatograph, HPLC Waters 600
- pH meter Hanna HI 19812-5 pH/C/EC/TDS;
- Ultrapure water system (ultrapurifier), Millipore Direct Q3 UV3.

5.1. Materials

5.1.1. Clofibric acid (4- Chloro-pnenoxy- 2 methylpropionic acid)

Clofibric acid (CA) (2-(p-chlorophenoxy)-2-methylpropionic acid), MW 214.65 g/mol) was purchased from Sigma-Aldrich. The chemical structure of CA is shown in figure 5.1. and the main features in Table 5.1.

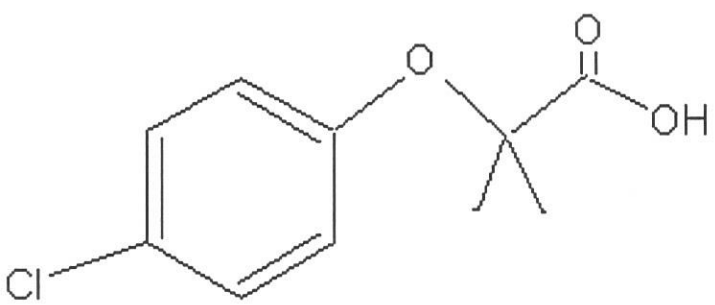


Figure 5.1. Molecular structure of Clofibric Acid (CA)

Table 5.1. *Clofibric Acid characteristics*
Source:https://pubchem.ncbi.nlm.nih.gov/compound/Clofibric-acid#section=3D-Conformer [126]

Therapeutic class	lipid regulator
Chemical formula	$C_{10}H_{11}ClO_3$
CAS number	882 09 7
Aspect	white powder
Molar mass (g/mol)	214.65
pK_a la 295°K	4.2
Solubility in water at 20°C (mg/L)	583
log K_{ow} (coefficient at pH 7.5)	0.76

For all experiments performed, a known mass of the pharmaceutical compound Acid Clofibric is dissolved under stirring for 24 hours in ultrapure water solutions, and then the solution is fed into the experimental system.

5.1.2. Photocatalyst used - SpongeMat/ZnO oxided material synthesized

The synthesized spongy composite material was obtained from glass waste from fluorescent tubes, eggshells and agricultural fertilizer Epsom salt ($MgSO_4$), was coated with a layer of ZnO which gives it photocatalytic properties. The synthesized composite material was obtained in two steps, *Step 1. Obtaining the support material* and *Step 2. Coating with zinc oxide layers the surfaces of the obtained support materials, for catalytic functionalization.* The process of obtaining the material was described in detail in *Chapter 2* - Own contributions of this thesis.

5.2. Experimental installation used in testing the photocatalytic degradation efficiency of the synthesized material - SpongeMat/ZnO

5.2.1. Laboratory installation for photocatalytic degradation and working method

For the testing of oxide materials - SpongeMat/ZnO synthesized, a laboratory installation designed and realized within the doctoral program was used. The experimental set-up used and the way of working is represented in figure 5.2. and consists of:

- a Quartz crystallizer, volume 200 mL in which the clofibric acid solution is placed
- 200 mL of CA solution is prepared in a volumetric flask by dilution in ultrapure water, then the reaction mixture of the CA solution is stirred using a magnetic bar for 24 h before being transferred to the experimental set-up, when the photodegradation process is initiated, it is subjected to a compressed air tube
- SpongeMat/ZnO oxide material synthesized at different ZnO concentrations (17.5%, 10%, 5%, 2.5% and 1%)
- Philips PL-L 24W/10/4P UV lamp with a maximum emission at 365 nm (illuminates for one hour before handling) and is placed above the crystallizer after one hour
- Magnetic stirrer
- Chronometer, which is turned on when the reactor is placed in the dark with a cardboard box for t = 0 min adsorption and then up to 8 h respectively 24 h hours of photocatalysis.

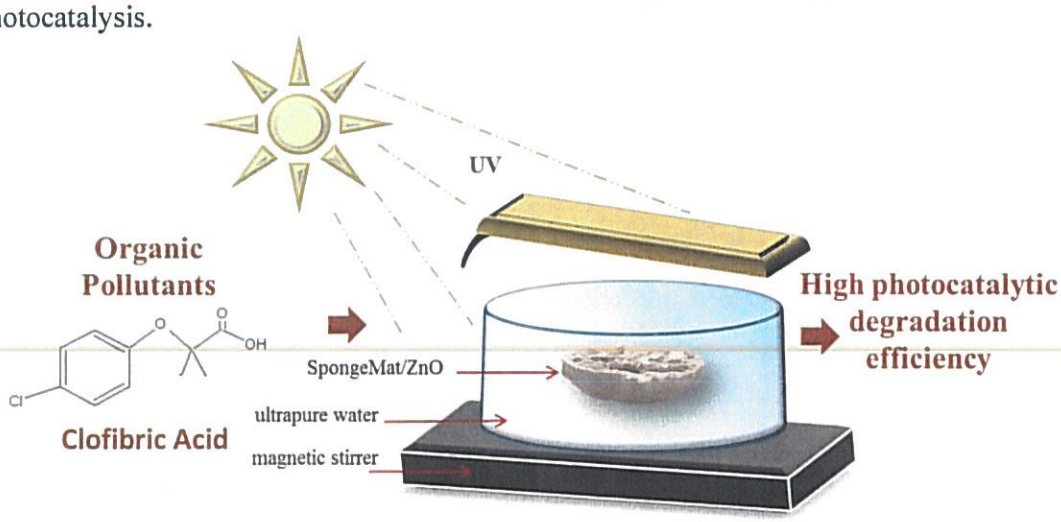


Figure 5.2. Experimental set-up used in the photocatalytic degradation process

5.3. Study of the kinetics of photocatalytic degradation

5.3.1. Work experience protocol

200 ml of ultrapure water solution containing CA at established concentrations were put in contact with each SpongeMat/ZnO synthesized catalytic material chosen for testing in the experimental set-up presented at the beginning of this chapter. Clofibric acid is weighed using a precision balance (10-2g +/- 0.005 g). At room temperature, the solution had a temperature between 25 and 27 ° C, it was continuously aerated and left for 1 hour in the dark to establish an adsorption/desorption equilibrium of the studied compound. Subsequently, the lamp was lit to initiate the photoreaction, the maximum irradiation intensity of the lamp was 8.17 mW/cm^2 and the wavelength was 227 nm.

Two tubes were immersed in the photo-reactor assembly, one for sampling (samples were taken with a syringe at regular and predefined intervals) and another for bubbling with compressed air with a pressure between 0.4 - 0.6 bar. Stirring and bubbling with compressed air were maintained during the reaction to maintain the homogeneous suspension. Samples of 5 mL of AC-containing solution were taken at regular intervals, filtered using 0.45 mm pore diameter membrane syringe filters, PET 45/25 and subsequently analyzed for residual AC concentrations. The reactor walls were covered with aluminum foil to minimize interference from external radiation.

In table 5.2. the synthesized oxide materials and the codings corresponding to the zinc oxide concentration are centralized, which have been photocatalytically tested.

Table 5.2. *Sample labeling for oxide materials (SpongeMat/ZnO) synthesized and photocatalytically tested*

Samples labeling for SpongeMat/ZnO at different concentrations of ZnO used in photocatalytic tests	Concentration of the solution in ZnO (mg/L)
SpongeMat/ZnO/17.5%	1750
SpongeMat/ZnO/10 %	1000
SpongeMat/ZnO/5 %	500
SpongeMat/ZnO/2.5 %	250
SpongeMat/ZnO/1 %	100

In each experiment, a number of 9 samples were taken, as follows, a sample was taken at the start of the experiment and then every hour for 8 hours, and in some cases an additional sample was taken 24 hours after the experiment starts.

In order to evaluate the efficiency of the synthesized spongy oxide material in the study of the kinetics of heterogeneous photocatalytic degradation, the effect of six parameters was followed:

- initial concentration of CA, the concentration values in CA for the experiments performed varying in the range: 1.5 mg/L, 5 mg/L, 10 mg/L, 20 mg/L;
- ZnO concentration deposited on the surface of the support material, the ZnO concentration values for the experiments performed varying in the range: 100 mg/L, 250 mg/L, 500 mg/L, 1000 mg/L, 1750 mg/L;
- the supply of dissolved oxygen by compressed air bubbling;
- light flux intensity: minimum, average and maximum light flux;
- cycles of reuse of the synthesized oxide composite material;

• the influence of anions.

To compare the differences between the studies, we varied one parameter at a time. We will determine the percentage reduction of CA to see the efficiency at eight hours of irradiation.

To calculate the percentage reduction/degradation of the studied compound, the following formula given by relation 13 was used:

$$(\%)elimination = \frac{[CA]f-[CA]i}{[CA]f} \times 100 \qquad (13)$$

$[CA]_{60}$ corresponds to the concentration of CA obtained by HPLC at t = 60 minutes (with the lamp on).

$[CA]_{f}$ corresponds to the concentration of CA obtained by HPLC at t = 8 hours (end of the study period of eight/twenty-four hours of irradiation

For the calculation of the ZnO adsorption capacity deposited on the surface of the support material we used the following formula, given by relation 14:

$$Absorption\ capacity = \frac{[CA]init - [CA]60}{m} \qquad (14)$$

$[CA]_{60}$ represents the concentration of Clofibric Acid obtained using HPLC at t = 60 minutes (when the lamp is on).

$[CA]_{inițial}$ corresponds to the concentration of Clofibric Acid obtained using HPLC at t = 0 minutes (basic).

m = mass of zinc oxide on the surface of the support material (in grams)

Monitoring the evolution of the pollutant concentration as a function of time provides access to the initial rate of degradation of this pollutant, from where a direct relationship can be observed between the inverse of the initial concentration and the inverse of the degradation rate.

5.3.2. Influence of the pollutant concentration variation at constant concentration of immobilized ZnO catalyst on MS (SpongeMat/ZnO/0,1%)

The influence of the initial concentration of the pollutant solution on the photocatalytic degradation is an important aspect to study, because this parameter could influence the photodegradation efficiency of the synthesized material. In the study of the influence of this parameter, photocatalytic experiments were performed for different initial concentrations of pollutants in the range of 1.5 mg/L, 5 mg/L, 10 mg/L and 20 mg/L and the amount of immobilized ZnO on the surface of the synthesized support material was kept constant, being chosen the oxide material SpongeMat/ZnO/10%, covered with zinc oxide film of concentration 1000 mg/L. Working parameters: UV –A irradiation, maximum flux 8.17 mW/cm^2 and natural pH of the solution.

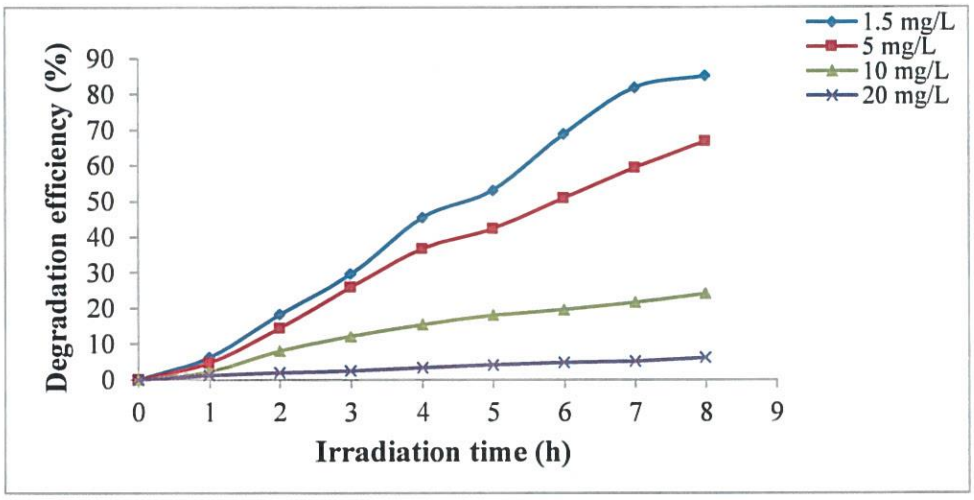


Figure 5.5. Influence of initial pollutant concentration on the photocatalytic degradation efficiency of clofibric acid, catalyst concentration =1000 mg/L, maximum irradiation = 8.17 mW/cm^2, ambient temperature, pH 7.4

From the results presented in Figure 5.5., it can be seen that the photocatalytic degradation of CA is strongly affected by the initial pollutant concentration. Indeed, an elimination yield of about 50% was obtained after 4 hours of reaction and 90% after 8 hours of reaction for an initial pollutant concentration of 1.5 mg/L and 5 mg/L, respectively. However, at higher levels of the pollutant concentration of 10 mg/L and 20 mg/L, respectively, a slower degradation can be observed, after 4 hours of reaction not even 10% was removed, while the interval of 8 hours was not enough for a complete degradation.

This can be explained by the fact that when the initial pollutant concentration increases and the irradiation and catalyst loading remain constant, the available sites on the ZnO surface are reduced due to the adsorption of pollutants on the catalyst surface and only fewer active sites remain available for formation of hydroxyl radicals, reactive species that are generally involved in organic oxidation compounds. Thus, this leads to a decrease in the elimination of pollutants.

Photocatalytic experiments were developed under the following operational conditions: C_0 = 1.5 mg/L, 5 mg/L, 10 mg/L and 20 mg/L - initial concentration in pollutant and SpongeMat/ZnO/10%, at natural pH, contact time 8 hours.

In figure 5.6. we can see the diagrams of ln (C/C_0) as a function of time.

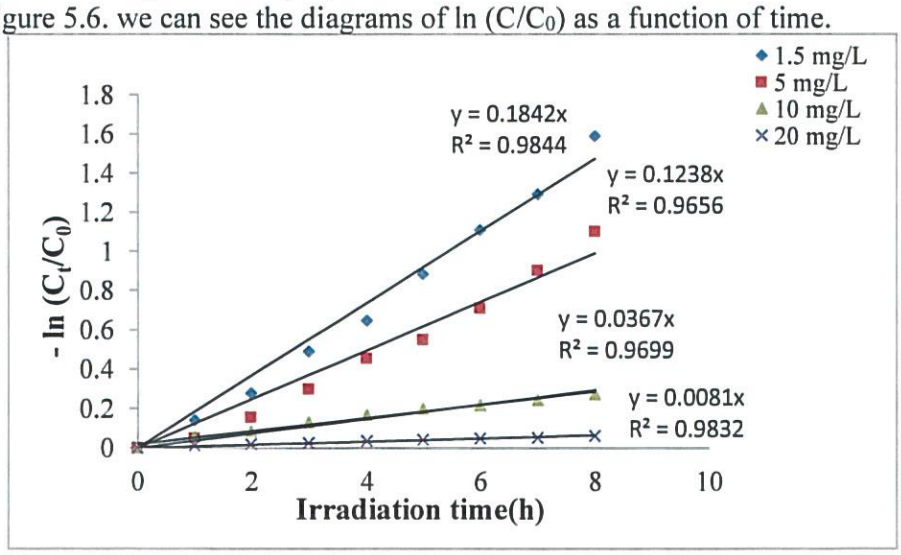


Figure 5.7. First- order kinetics plots for different initial pollutant concentrations, SpongeMat/ZnO/10%, maximum irradiation 8.17 mW/cm^2, ambient temperature, pH 7.4

As can be seen from these plots, the photocatalytic degradation of CA by the SpongeMat/ZnO oxide material follows the kinetics of first-order according to relation 15:

$$-ln\ (C/\ C_0) = k_{app}\ t \qquad (15)$$

where C_0 is the initial concentration of pollutant in aqueous solution and C is the residual concentration of pollutant at time t. The first-order rate constant, k is determined by integrating the experimental data using this model. The k_{app} rate constants and the correlation coefficient R^2 are shown in Table 5.3.

The values obtained for k_{app} are between 0.81 and 18.42 for the synthesized oxide material SpongeMat/ZnO/10%, ZnO concentration = 1000 mg/L.

Table 5.3. *Calculated values of the rate of apparent photodegradation constant (k_{app}) and R^2 as a function of initial pollutant concentration C_0 = 1.5 mg/L, 5 mg/L, 10 m/L, 20 mg/L, synthesized oxide material, SpongeMat/ZnO/10%, value kept constant, maximum irradiation 8.17 mW/cm², ambient temperature, pH 7.4*

[AC] mg/ L	$K_{(app)}$ (10^{-2} h^{-1})	R^2
1.5	18.42	0.09844
5	12.38	0.9656
10	3.67	0.9699
20	0.81	0.9832

In figure 5.7. the evolution of the apparent constant is presented as a function of the initial pollutant concentration, we can observe a decrease of the rate with the increase of the pollutant concentration.

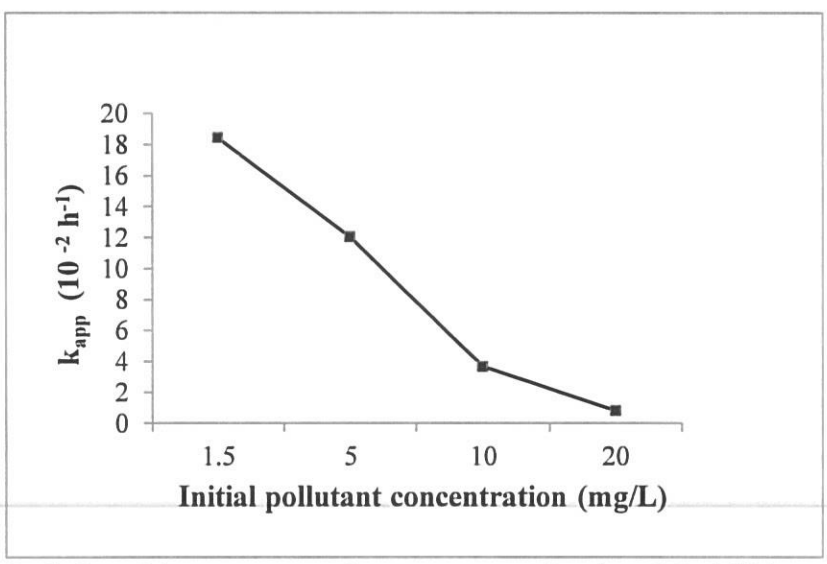


Figure 5.7. Evolution of the apparent reaction constant as a function of the initial concentration of pollutant, synthesized oxide material, SpongeMat/ZnO/10%, maximum irradiation 8.17 mW/cm², ambient temperature, pH 7.4

5.3.3. Influence of variation of immobilized ZnO catalyst concentration on MS

Various papers [127-129] have reported a relationship of strong dependence of catalyst concentration on the rate of removal of organic pollutants. Data from the literature reported the existence of an optimal catalyst charge below which the degradation rate increases linearly with the catalyst concentration. However, above this value and assuming that the initial solute concentration remains constant, the elimination rate decreases drastically due to the light scattering effect. On the other hand, it was found that this threshold value depends on the process conditions and the geometry of the experimental installation.

In this study, the ZnO concentration was varied from 100 to 1000 mg/L to test the effect of the catalyst concentration on CA degradation. For these analyzes, an initial pollutant concentration of 5 mg/L was used. Figure 5.8. presents the time-efficiency profiles of CA degradation for the investigated conditions. The obtained results confirmed that the efficiency of CA degradation increases with increasing photocatalyst concentration. The CA elimination yield increased from 10% to 60% for an irradiation time of 6 hours when the ZnO content increased from 100 mg/L to 1000 mg/L.

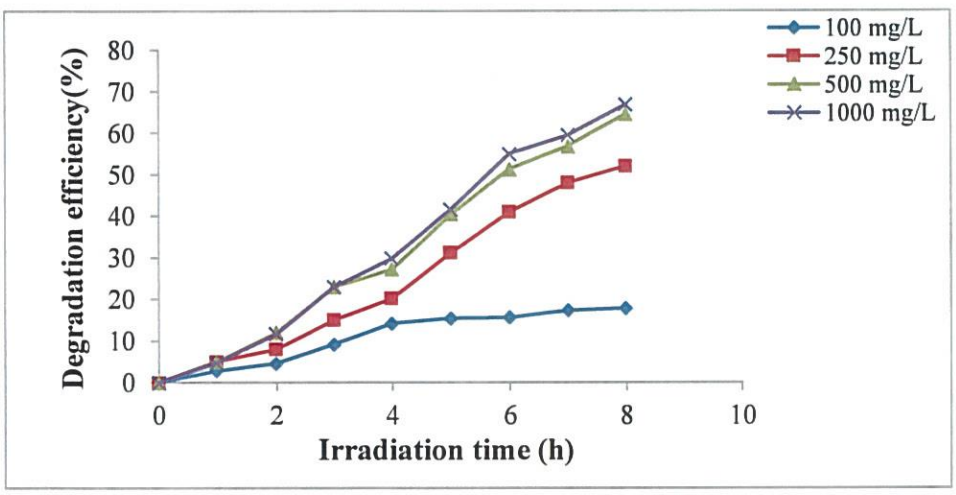


Figure 5. 8. Influence of catalyst concentration on the photocatalytic degradation efficiency of clofibric acid as a function of irradiation time, pollutant concentration = 5 mg/L, maximum irradiation = 8.17 mW/cm^2, ambient temperature, pH 7.4

These results could be explained by the fact that the total active surface increases with increasing catalyst dosing, and the light scattering phenomena leading to a loss of photocatalytic degradation efficiency is insignificant for the investigated conditions. Similar results have been previously reported for other organic water pollutants [10, 12].

The effect of the amount of ZnO catalytic material on CA degradation is shown in figure 5.9. Experiments performed with different ZnO concentrations showed that the photodegradation efficiency increases with increasing ZnO concentration up to 1000 mg/L. This observation may be due to the higher number of active sites on the surface of the catalytic material and the efficiency of UV light penetration, the total active surface increases as the dosage of catalyst material increases.

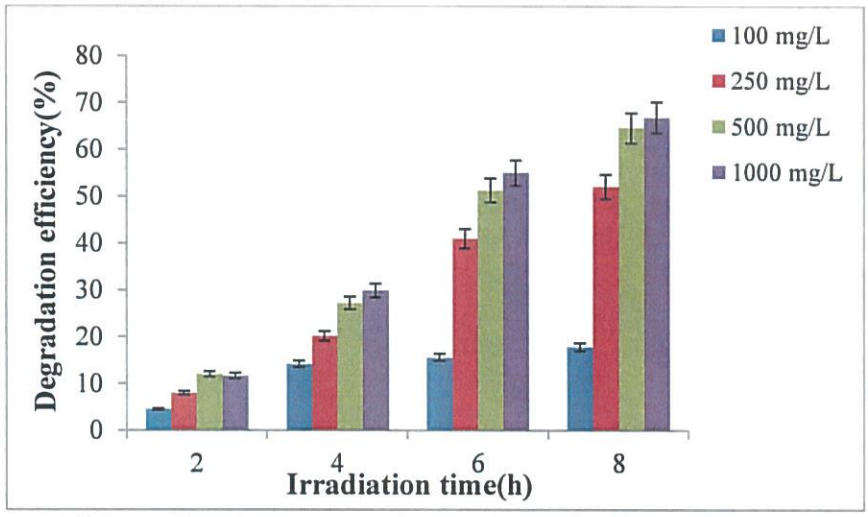


Figure 5.9. Influence of catalyst concentration on the photocatalytic degradation efficiency of clofibric acid as a function of irradiation time, pollutant concentration =5 mg/L, maximum irradiation = 8.17 mW/cm^2, ambient temperature, pH 7.4

In figure 5.10. the degradation kinetics of CA is presented, at a constant concentration of pollutants (5 mg/L) and different amounts of ZnO (100 mg/L, 250 mg/L, 500 mg/L, 1000 mg/L) after 8 h of UV-A irradiation. From figure 5.11., where Ct is the concentration of CA at the end of the process and C_0 is the initial concentration, it is observed that for the amount of 1000 mg/L more than 30% of the CA degradation is obtained after 4 hours and more than 70% after 8 hours. Thus, it can be seen that increasing the amount of catalyst leads to a higher rate of degradation.

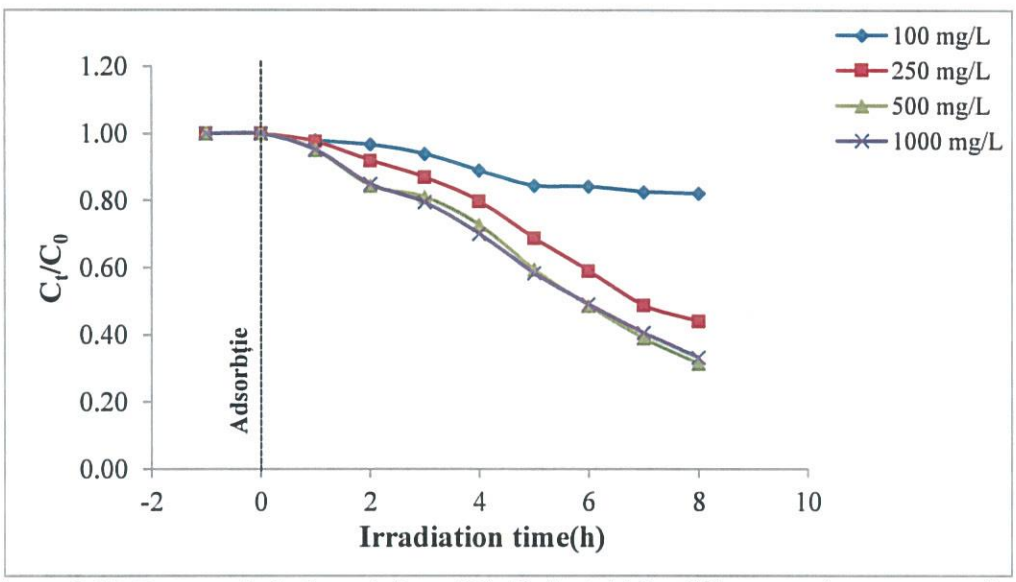


Figure 5.10. Photocatalytic degradation of Clofibric Acid for different catalyst concentrations depending on irradiation time, pollutant concentration = 5 mg/L, maximum irradiation 8,17 mW/cm^2, ambient temperature, pH 7,4

Photocatalytic experiments were developed under the following operational conditions: C_0 CA = 1.5 mg/L 5mg/L, 10mg/L and 20 mg/L as initial concentration in the pollutant and SpongeMat/ZnO/10%, at natural pH, contact time 8 hours.

In figure 5.11. we can see the diagrams of ln (C/C_0) as a function of time.

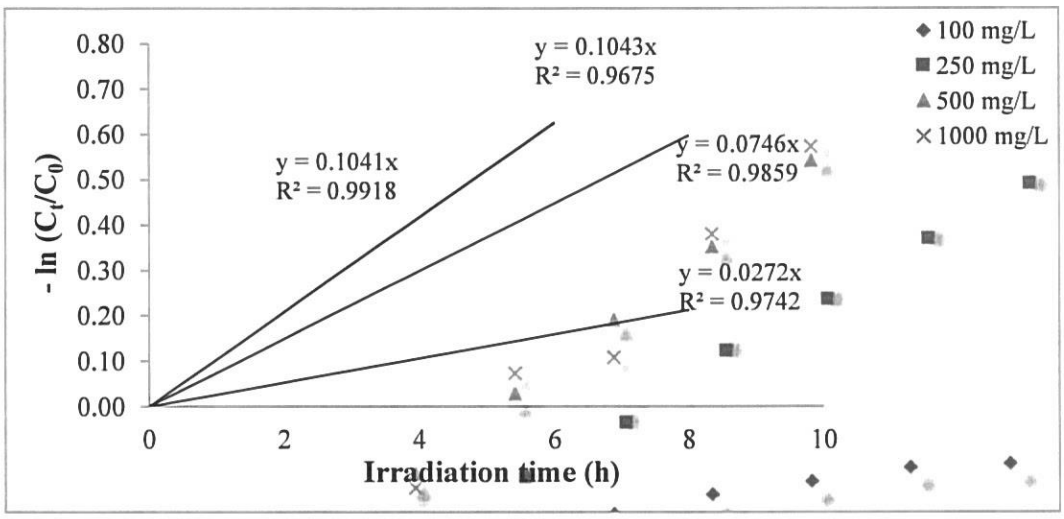


Figure 5.11. Plots of first order kinetics for different catalyst concentrations, pollutant concentration = 5 mg/L, maximum irradiation 8.17 mW/cm^2, ambient temperature, pH 7.4

The k_{app} rate constants and the resulting correlation coefficient R^2 are presented in Table 5.4. The values obtained for k_{app} are between 2.72 and 10.43 for the synthesized oxide material SpongeMat/ZnO, O1, ZnO concentration = 1000 mg/L.

Table 5.4. *Calculated values of the apparent rate constant (k_{app}) of photodegradation and R^2 as a function of catalyst concentration, initial pollutant concentration = 5mg/L, maximum irradiation 8.17 mW/cm^2, ambient temperature, pH 7.4*

[ZnO] mg/ L	$K_{(app)}$ (10^{-2} h^{-1})	R^2
100	2.72	0.9675
250	7.4	0,9859
500	10.41	0,9675
1000	10.43	0.9918

In figure 5.12. the evolution of the apparent constant in relation to the catalyst concentration is represented:

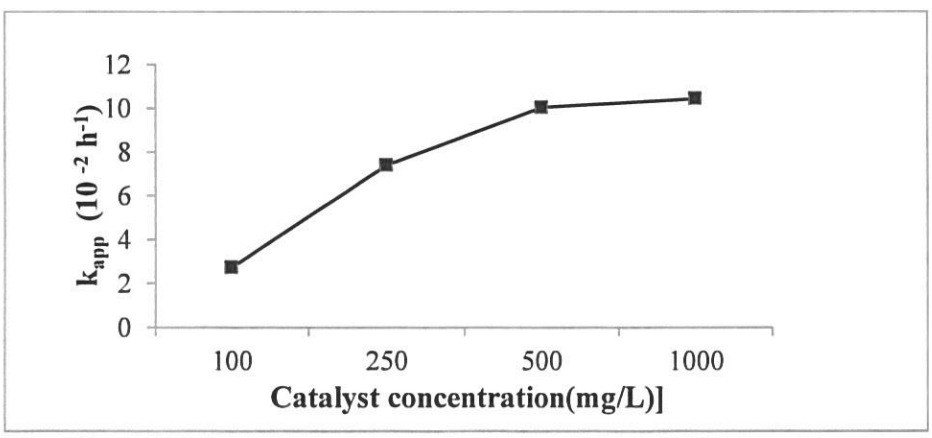


Figure 5. 12. Evolution of the apparent rate constant as a function of catalyst concentration, pollutant concentration = 5 mg/L, maximum irradiation 8.17 mW/cm^2, ambient temperature, pH 7.4

A stabilization of the degradation kinetics is observed as the amount of catalyst increases. A higher amount of catalyst could even lead to a decrease in kinetics according to some studies [130].

This phenomenon can be explained by the fact that when we increase the concentration of the catalyst and it forms aggregates. Thus, this phenomenon results in a decrease in the specific surface area of the catalyst and therefore reduces its effectiveness. Moreover, the excessive increase in the amount of zinc oxide leads to a greater dispersion of light.

5.3.4. The influence of compressed air bubbling on the efficiency of the photocatalytic degradation process

The presence of dissolved oxygen is not a mandatory factor for the photodegradation of pollutants, but nevertheless it can be observed from figure 5.13. the influence of compressed air, so that compressed air bubbling in solution increases the efficiency of degradation.

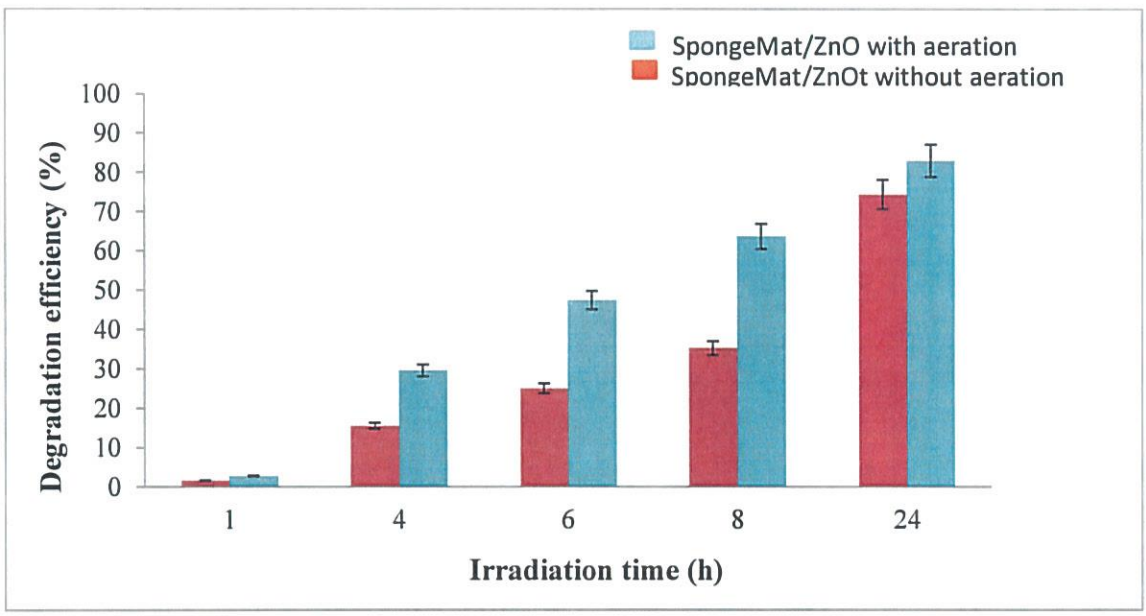


Figure 5.13. Degradation efficiency of Clofibric Acid (10 mg/L) using ZnO = 1750 mg/L immobilized on a fixed support, SpongeMat/ZnO/17.5%, with/without aeration at maximum irradiation flow 8.17 mW/cm^2, ambient temperature, pH 7.4

This phenomenon can be explained by the fact that oxygen molecules are adsorbed on the surface of the catalytic oxide material and contribute to a better capture of electrons from its conduction band. Therefore, a constant supply of air in the solution to be treated leads to an improvement in the efficiency of the photocatalytic degradation, in *table 5.5.* the elimination percentage with/without air bubbling is compared.

Table 5.5. *Degradation efficiency depending on the amount of dissociated oxygen*

Compressed air bubbling	Elimination percentage after 8 hours of irradiation
No	70%
Yes	85%

5.3.5. The influence of the variation of the light flux intensity in the photocatalytic degradation process

Luminous flux intensity is another process parameter that can affect the kinetics of the photodegradation reaction. Since the energy of photons is related to the energy input, so it depends on the intensity of the incident light. Thus, this section is dedicated to investigating the influence of this parameter by performing a series of experiments at an initial pollutant concentration of 1.5 mg/L and 1000 mg/L of catalyst at different light intensities.

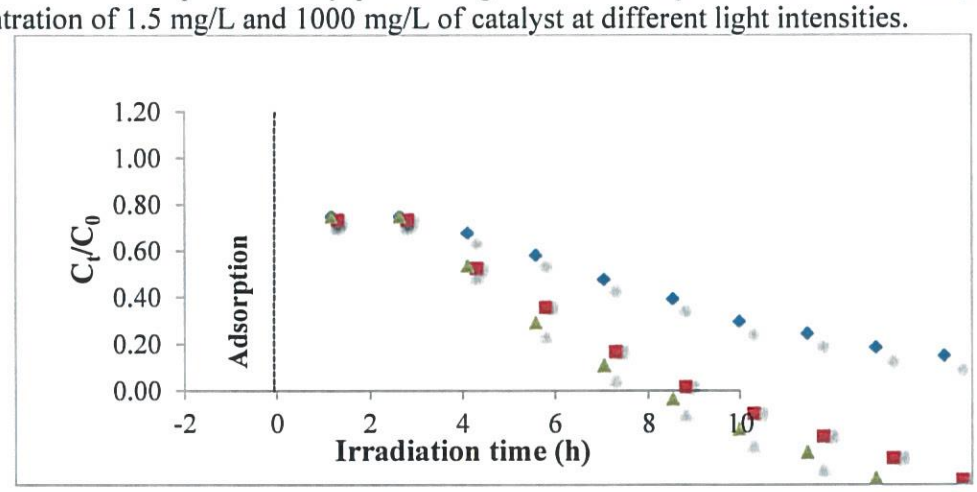


Figure 5.14. Photocatalytic degradation of Clofibric Acid at different light intensities as a function of irradiation time, pollutant concentration =1.5 mg/L, SpongeMat/ZnO/10%, ambient temperature, pH 7.4 (blue- 0.280 mW/cm^2, red colour- 1,867 mW/cm^2, green- 8.170 mW/cm^2)

From figure 5.14. it can be seen from the experiment that the intensity of the incident light flux has a direct influence on the degradation of clofibric acid. Indeed, the photocatalytic degradation method requires a photon input flux during the species activation step in solution. It can be seen that for a low photon flux 0.280 mW/cm^2, there is a direct link between the reaction rate and the flux, resulting in a lower degradation after 8 hours compared to a maximum flux. This result is in line with theoretical expectations.

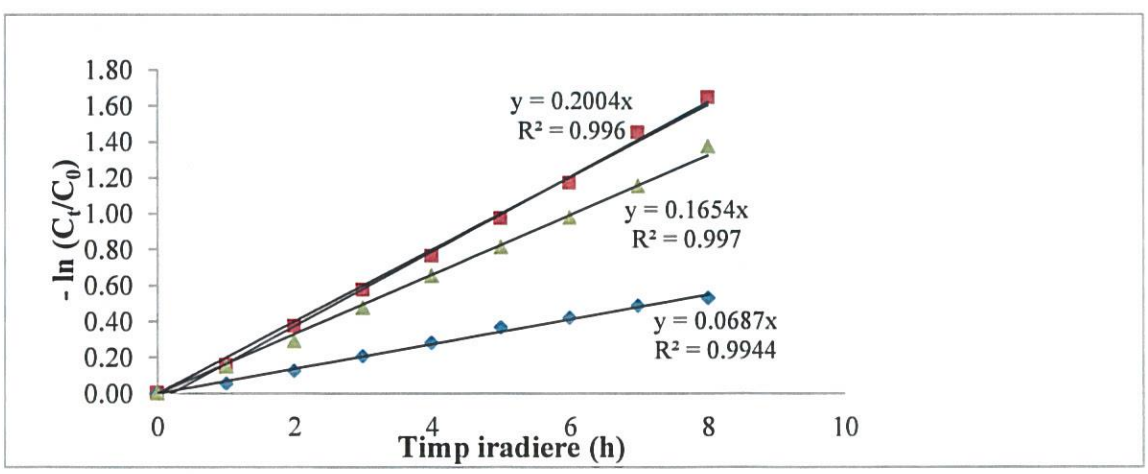


Figure 5. 15. First order kinetics, SpongeMat/ZnO/10%, pollutant concentration 1.5 mg/L, ambient temperature, pH 7.4
(blue- 0.280 mW/cm^2, red colour- 1,867 mW/cm^2, green- 8.170 mW/cm^2)

Ln plots (C_t/C_o) shown in figure 5.15. reveals that with increasing light intensity increases the rate of decomposition of CA. At a maximum irradiation intensity of 8,1770 mW/cm^2, the pollutant was removed by 50% in 4 hours of reaction, while at 1,867 mW/cm^2 corresponding to the minimum irradiation intensity only 20% of clofibric acid was removed for the same irradiation period. A possible explanation for these results is that at a high light intensity, more photons are absorbed on the surface of the catalyst. Thus, more pairs of electron holes will be generated on the catalyst surface increasing the degradation rate of pollutants [131].

In figure 5.16. the relationship between the luminous flux intensity and the apparent reaction speed is represented graphically, and in *table 5.7.* the values for k_{app} and R^2 calculated are presented. The values of k_{app} are as follows 6.87, 16.54 and 20.04, corresponding in turn to the minimum to maximum light flux, progressively showing that the higher the intensity of the luminous flux, the higher the reaction rate is.

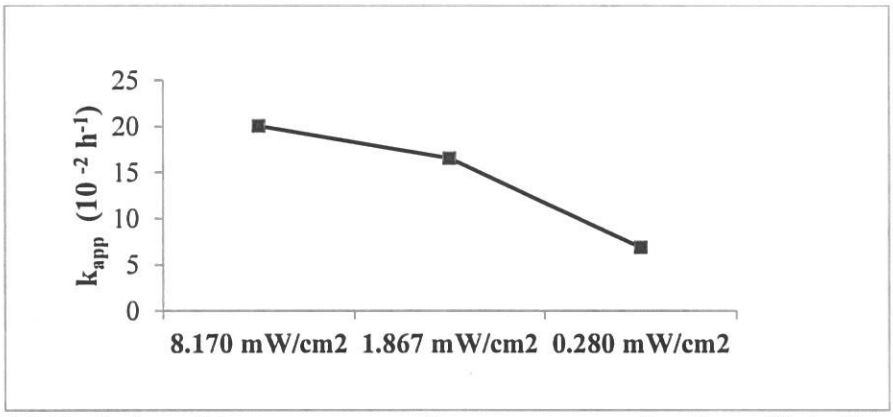


Figure 5.16. Evolution of the apparent reaction constant as a function of light flux intensity, pollutant concentration = 1.5 mg/L, SpongeMat/ZnO/10%, ambient temperature, pH 7.4

Table 5.6. *Calculated values of the rate of apparent photodegradation constant (kapp) and R^2 as a function of catalyst concentration, initial pollutant concentration = 1.5 mg/L, ambient temperature,* pH 7.4

Luminous flux intensity (mW/cm^2)	$K_{(app)}$ (10^{-2} h^{-1})	R^2
0.280	6.87	0.9944
1.867	16.54	0.9970
8.170	20.04	0.9960

In addition to studies of the kinetics of photocatalytic degradation, the ability to reuse the synthesized oxide material, the efficiency in the VISIBLE spectrum and the degradation of other types of organic compounds that are presented below have been investigated.

5.3.6. Reuse of SpongeMat/ZnO oxide material in the degradation of pollutants

In the catalytic efficiency experiments, the stability of the ZnO film deposited on the surface of the synthesized support material was investigated in 5 consecutive experiments using CA solution of concentration 5 mg/L in a volume of ultrapure water of 200 mL, pH of the solution being the natural one, measured at the beginning of the experiments as 7.4 and ZnO deposited on the support material having a concentration of 1750 mg/L (arbitrarily

chosen concentration) related to the sample P. Samples were taken at time t_0 and 24 h. After each experiment, the oxide material, SpongeMat/ZnO was washed with distilled water several times and dried at 110 ° C for 12 h.

The degradation efficiency of Clofibric Acid by SpongeMat/ZnO remained high at over 92% even after being used in 3 consecutive cycles. The efficiency of photocatalytic degradation remained over 98% after the first 2 cycles (figure 5.17). The activity of the photocatalyst began to decrease very little in cycles 4 and 5, resulting in an efficiency of 93% and 92%, respectively. Deactivation of the catalyst may be related to contamination during reuse of the material surface, with certain intermediate by-products occureance.

We can say that it turns out that the synthesized oxide material - SpongeMat/ZnO has a good stability of the fixation of the oxide film on its surface, showing only small gaps in the degradation yield on reuse.

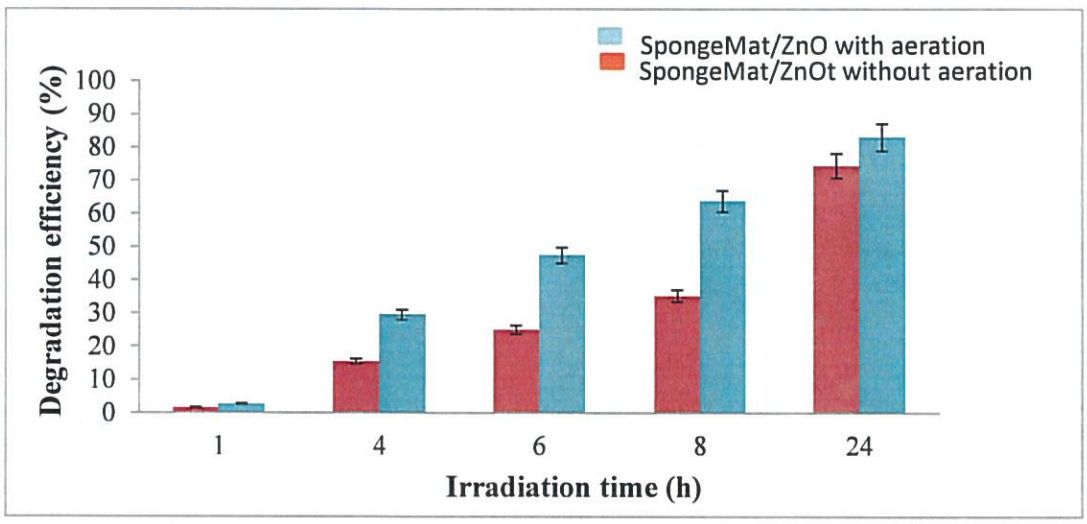


Figure 5. 17. Photocatalytic degradation efficiency of Clofibric Acid = 5 mg/L depending on 5 cycles of reuse of the synthesized catalytic oxide material (24h). SpongeMat/ZnO/17.5%, maximum irradiation flux 8.17 mW/cm2, ambient temperature, pH 7.4

As shown in figure 5.17., the first degradation cycle of CA is 98%, and subsequently at the 5th cycle of reuse, the degradation efficiency is 92%, indicating that the synthesized oxide material SpongeMat/ZnO, shows good stability and can be successfully reused several times.

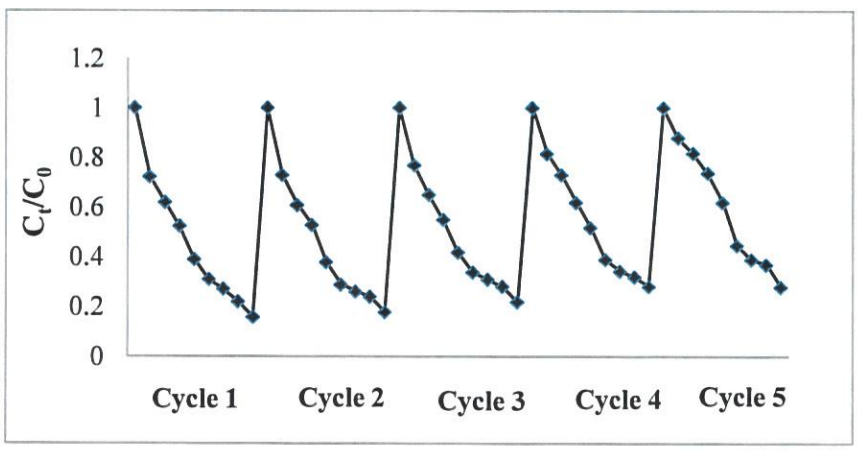


Figure 5.18. Reusability of the synthesized oxide material, SpongeMat/ZnO, after 24 hours of UV-A irradiation. SpongeMat/ZnO/17.5%, maximum irradiation 8.17 mW/cm^2, ambient temperature, pH 7.4

Figure 5.19. shows the variation of ln (C_t/C_0) after repeating the experiments under the same conditions, it is obvious that the synthesized oxide material, SpongeMat/ZnO, can efficiently degrade CA.

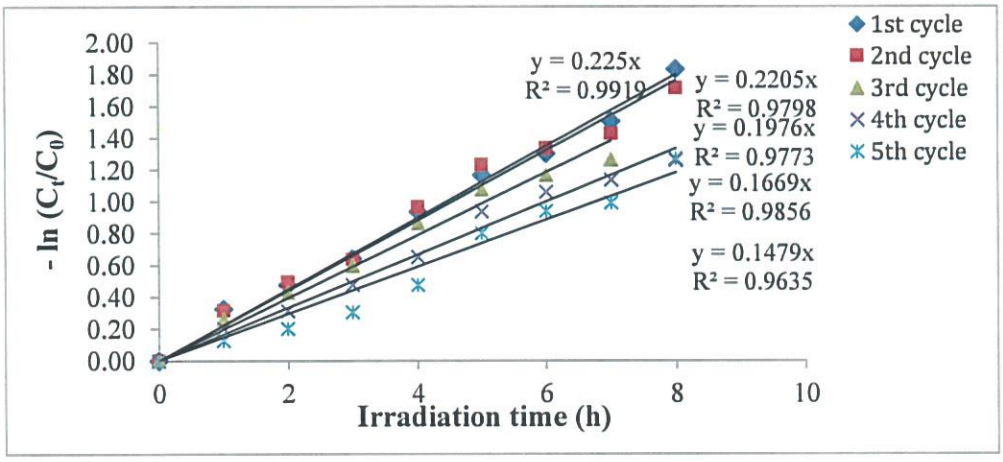


Figure 5.19. First order kinetics, SpongeMat/ZnO, SpongeMat/ZnO/17.5%, pollutant concentration 1.5 mg/L, ambient temperature, pH 7.4

Figure 5.20. shows the evolution of the apparent constant rate as a function of the reuse cycles of the synthesized material. The apparent rate constant k_{app} for each reuse cycle is 22.5 x 10^{-2} h, 22.05 x 10^{-2} h, 19.76 x 10^{-2} h, 16.69 x 10^{-2} h and 14.79 x 10^{-2} h, these values are also presented in the table 5.7.

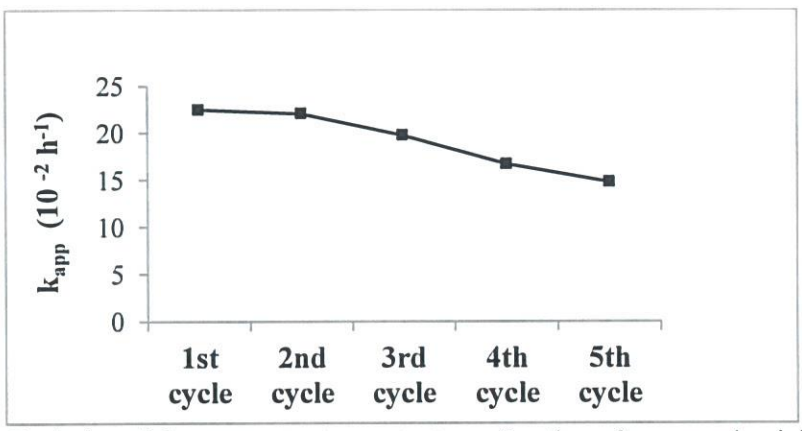


Figure 5.20. Evolution of the apparent rate constant as a function of reuse cycles, initial pollutant concentration 1.5 mg/L, SpongeMat/ZnO/17.5%, ambient temperature, pH 7.4

Table 5.7. *Calculated values of the apparent rate constant k_{app} and R^2 as a function of catalyst concentration, initial pollutant concentration = 1.5 mg/L, ambient temperature, pH 7.4*

Reuse cycles	$K_{(app)}$ (10^{-2} h^{-1})	R^2
Cycle 1	22.5	0.9919
Cycle 2	22.05	0.9798
Cycle 3	19.76	0.9773
Cycle 4	16.69	0.9856
Cycle 5	14.79	0.9653

In any catalytic process, the life of the catalyst is an important factor that directly affects the process costs, concluding, it can be said that after reuse tests, the synthesized oxide material, SpongeMat/ZnO, showed a good stability of the catalyst on its surface and kinetics tests have shown that the process of photocatalytic degradation follows first-order kinetics.

5.3.7. Capacity of SpongeMat/ZnO oxide material for photocatalytic degradation of the studied organic compound in the VISIBLE spectrum

The latest research in the field of heterogeneous photocatalysis in the advanced oxidation processes used in water treatment focuses on the convergence to the visible light spectrum, in order to be able to transpose the process on a real scale. In this context, the SpongeMat/ZnO oxide material obtained was tested in terms of the degradation efficiency of organic compounds and in the VISIBLE light spectrum. Figure 5.21 shows the degradation percentage as a function of irradiation time in terms of SpongeMat/ZnO efficiency of Clofibric Acid degradation in the VISIBLE spectrum.

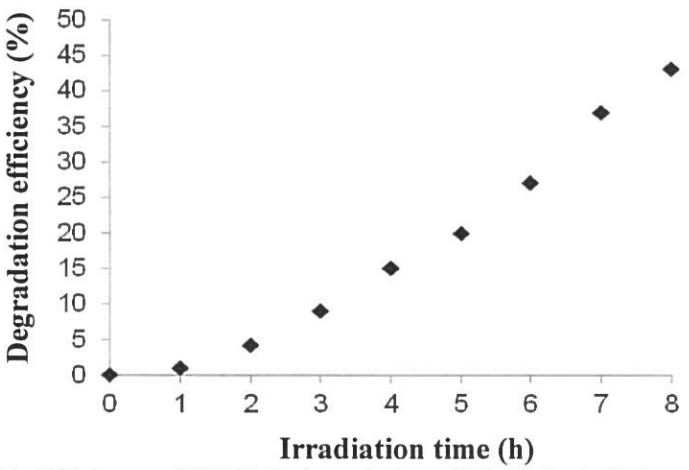


Figure 5.21. Efficiency of MS/ZnO degradation of Clofibric Acid (concentration of 5mg/L in ultrapure water), SpongeMat/ZnO/17.5%, in the VISIBLE spectrum

From the analysis of the data in figure 5.21, we can see that, after 8 hours of irradiation in the UV light spectrum, the degradation percentage of Clofibric Acid follows an ascending slope reaching the end of the 8 hours of irradiation at over 43%.

5.3.8. Evaluation of the capacity of SpongeMat/ZnO oxide material for photocatalytic degradation and other types of organic compounds

The photocatalytic activity of the oxide material obtained (SpongeMat/ZnO) was also tested for the degradation of other types of organic compounds belonging to the class of dyes and phenols, methylene blue dye (MB) and phenol 4-nitrophenol (4-NP). Methylene blue and 4-nitrophenol have different molecular structures and different functional groups. 4-NP was chosen as one of the two organic compounds due to its high use, however, there are not many studies regarding its photocatalytic degradation. MB is an organic dye often used as a model molecule in photocatalytic degradation assays.

The results of the photodegradation of methylene blue dye and phenol 4-nitrophenol are presented in figure 5.22., The experiments were performed under the following operating conditions: initial concentration of the two pollutants was 5 mg/L, SpongeMat/ZnO/10%, in UV-A irradiation for maximum light flux and natural pH of the solutions, the experiments were carried on in ultrapure water solution.

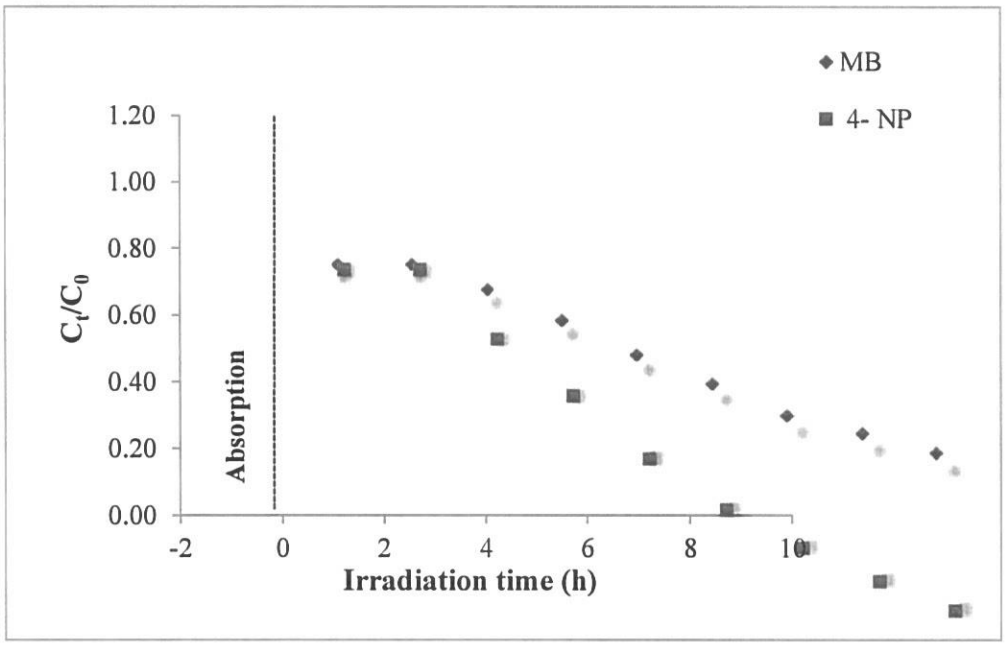


Figure 5.22. Photocatalytic degradation and other groups of organic compounds, maximum luminous flux, as a function of irradiation time, pollutant concentration = 5 mg/L, SpongeMat/ZnO/10%, maximum irradiation 8.17 mW/cm^2, ambient temperature

From figure 5.22. it can be seen from the experiments that more than 70% of the pollutant was removed, both for the dye and for the phenol after 8 hours of irradiation, thus proving that the degradation efficiency of the synthesized material remains high for other groups of organic compounds.

5.3.9. Influence of anions in the process of photocatalytic degradation, using synthesized oxide material, SpongeMat/ZnO

In addition to pollutants, industrial effluents also contain different salts in different concentrations. The salts are generally ionized under the conditions of the photocatalytic degradation process. Anions or cations have a certain influence on the process of photocatalytic degradation; the presence of anions such as chlorides, sulfates, carbonates and bicarbonates is quite common in the effluent industry. These ions affect the adsorption of degrading species, and act as traps for hydroxyl radicals and can absorb UV light as well. In this section we studied the influence of anions in the process of photocatalytic degradation, taking into account the following operational parameters, the concentration of CA pollutant 1.5 mg/L and using the synthesized oxide material corresponding to the concentration of ZnO = 1000 mg/L at a solution volume of 200 mL.

In figure 5.23. the influence of anions in the catalytic photodegradation process is presented, we can see that after 4 hours of irradiation, we have 30% degradation for NaCl addition and 40% for $NaHCO_3$ and 60% for $NaNO_3$, respectively, but in case of Na_3PO_4 and Na_2SO_4 addition the photocatalytic degradation process it was significantly slowed down by a degradation of only 10%.

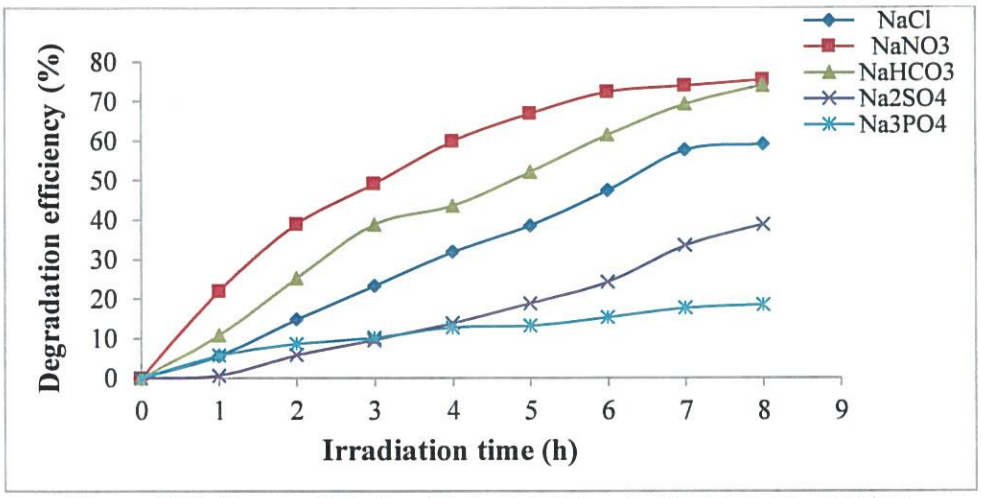


Figure 5.23. Curves of photocatalytic activity under the influence of anions

For the studied cations, following the experiments we notice that the order in which the photocatalytic degradation process is less efficient is the following Na_3PO_4, Na_2SO_4, NaCl, $NaHCO_3$ followed by $NaNO_3$, which has the weakest influence on the catalytic photodegradation process. According to data from the literature, which notes that the presence of $NaNO_3$ has a negligible effect, while Na_2SO_4 ions have been found to slow down the rate of degradation due to their effect on the adsorption substrate. While with the introduction of phosphates the inhibition of hydroxyl radicals increases remarkably leading to a slowdown in the process of photocatalytic degradation.

In figure 5.24. we can see the diagrams of ln (C/C_0) as a function of time.

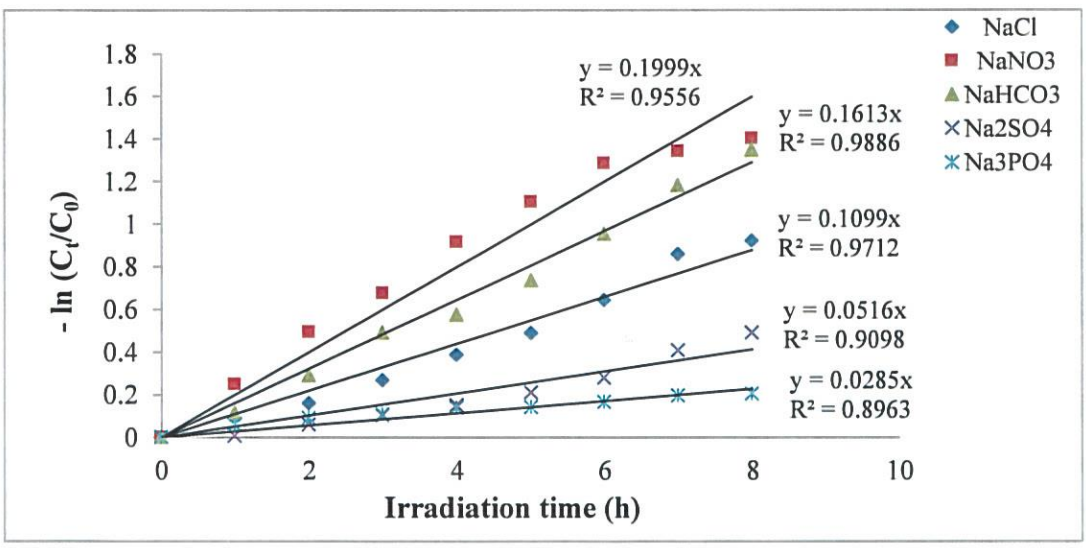


Figure 5.24. Plots of first order kinetics under the influence of different anions for CA solutions under the influence of anions in the presence of immobilized ZnO

As can be seen from these plots, the photocatalytic degradation of CA by the SpongeMat/ZnO oxide material follows the first-order kinetics. The resulting k_{app} velocity constants and the correlation coefficient R^2 are shown in *table 5.8.*

The values obtained for k_{app} are between 2.85 and 19.9 for the SpongeMat/ZnO/17.5% synthesized oxide material.

Table 5.8. *Calculated values of the apparent rate constant (k_{app}) and R^2 under the influence of anions, for a fixed concentration of pollutant = 1.5 mg/L, maximum irradiation 8.17 mW/cm², ambient temperature,p H 7.4*

Anions	$K_{(app)}$ (10^{-2} h^{-1})	R^2
NaCl	10.99	0.9712
$NaNO_3$	19.9	0.9556
$NaHCO_3$	16.13	0.9886
Na_2SO_3	5.16	0.9098
Na_3PO_4	2.85	0.8963

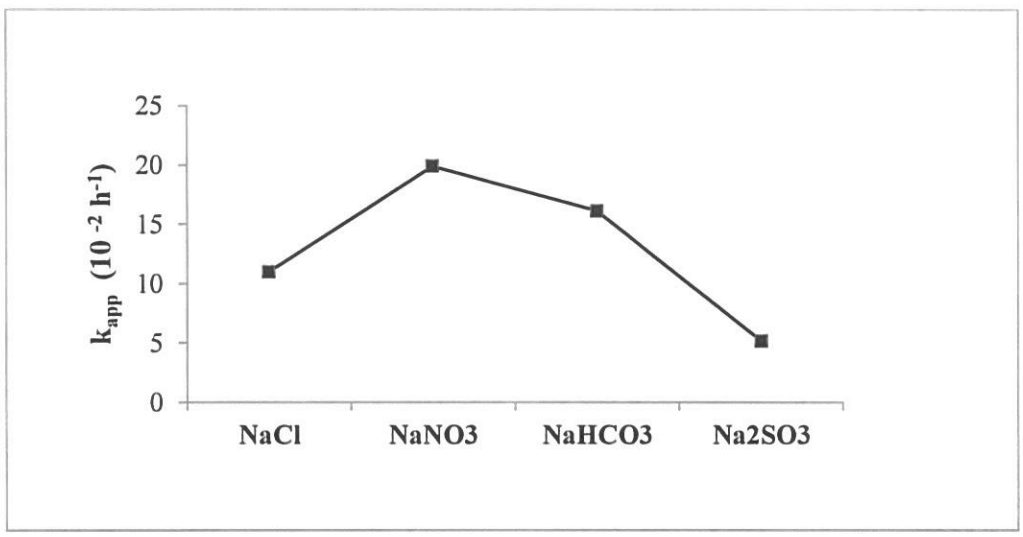


Figure 5.25. Evolution of the apparent reaction constant as a function of anion influence at pollutant concentration = 1.5 mg/L, ZnO = 1750 mg/L

In figure 5.25. the apparent rate constant can be seen as a function of the influence of the anions, from where we can observe that the lowest value for k_{app} is obtained in the case of Na_2SO_3, followed by NaCl, $NaHCO_3$ and $NaNO_3$.

CHAPTER 6. General Conclusions, Original Contributions and Future Research Directions

6.1. General conclusions

The purpose of the research activity was the synthesis of new materials by capitalizing on some wastes and their functionalization for applications in environmental protection. These new materials are important in the context of the continuing need to develop new environmentally friendly technologies for treating water contaminated with emerging organic compounds, thus helping to conserve one of the most important resources - water, but also contributing to efficient waste management through reintegration in the economic circuit.

The synthesis process used to obtain the supporting spongy material coated with zinc oxide does not generate secondary components and involves the recovery of waste thus helping to reduce the impact on the environment generated by the volume of waste stored improperly.

The obtaining of the material was carried out in two stages; the first stage is represented by the obtaining of the support material from glass waste from fluorescent lamps, eggshells and Epsom salt agricultural fertilizer. Following a second stage in which the photocatalytic functionalization took place by depositing on the surface of the support material a zinc oxide film, this gives the material photocatalytic properties. The technique used consisted in depositing the oxide film on the surface of the support material by immersion in solution and orbital stirring and then applying an autoclaving and drying process to immobilize it on the substrate.

The specific objectives proposed by the doctoral topic were as follows:

- Study of semiconductor immobilization techniques on fixed supports;
- Obtaining a new support material for environmental applications by waste recovery;
- ZnO immobilization on the porous surface of the support material obtained by hydrothermal method;
- Catalytic functionalization of the new material obtained by developing a simple process of autoclaving on the surface of the support material of the zinc oxide layer giving it photocatalytic properties in both VISIBLE and UV spectrum applicable to the treatment of contaminated water;
- Morphological and structural characterization of the synthesized SpongeMat/ZnO oxide spongy material;
- Testing the applicability of the oxide material in the degradation of organic compounds from the class of pharmaceuticals, dyes and phenols present in wastewater through advanced oxidation processes - heterogeneous photocatalysis.

We consider that the set objectives have been achieved both in terms of the synthesis section and the photocatalytic testing part.

Following morphological, compositional and structural analyzes of oxide materials synthesized at different concentrations of zinc oxide, as follows SpongeMat/ZnO/17.5%, SpongeMat/ZnO/10%, SpongeMat/ZnO/5% and SpongeMat/ZnO/1% as well as the study of the components of the support material that are part of the synthesized material (namely eggshell, Epsom salt and glass from fluorescent lamp, we can say that: the surface SEM micrographs of the analyzed samples confirmed a fairly homogeneous distribution of components in the microstructure of the synthesized material, which is an important factor, as homogeneity is particularly important for stabilizing the ZnO oxide layers that were deposited on the surface of the support material. Besides the elements we expected to identified in the structure of the material, the occureance of Yttrium element in the cross section of the specimen of oxide material - SpongeMat/ZnO/17.5% appeared.

From the SEM-EDX compositional analyzes of the eggshell powder, the elements Ca, O, C specific to calcium carbon were identified, and in the case of the glass powder from the

fluorescent lamp residues, the presence of the peaks of the predominant elements Si O and Na which are characteristic of the composition of the glass were observed.

From the analysis of the 2 D and 3 D profilometry measurements and of the obtained data we can observe that the thickness of the oxide film deposited on the surface of the support material does not very much in the case of the 4 analyzed samples (17.5% ZnO, 10% ZnO, 5% ZnO, 1% ZnO), this may be due to the sinking rate, which in our case was equal to 1, but also to the speed of withdrawal of the sample but also to other variables.

The roughness of the 4 samples of oxide materials - SpongeMat/ZnO functionalized photocatalytically at percentages of different concentrations in zinc oxide of 17.5%, 10%, 5% and 1% respectively is different in the case of each analyzed sample, but no significant evolution is observed on the roughness parameter Ra. The roughness between the porosities is low: Ra being mostly lower than 0.1 μm. This effect may be due to the reproducibility of synthesis of oxide materials under the same operating conditions.

Vickers micro-indentation tests indicated at a force of 500 g, a very low hardness equal to 16, which corresponds to that of a porous material.

From the XRD diffractogram for the powder of the synthesized SpongeMat/ZnO oxide material, we observe that the intensity band is the same as in the case of fluorescent lamp residue analyzes, respectively between 20° and 40° which is characteristic for an amorphous material and is normal due to the presence of more 90% of the fluorescent lamp residues in the composition of the synthesized oxide material. We also notice some peaks at 29° and 39°, which could be associated with the eggshell diffractograms, present in small quantities and in the composition of the synthesized SpongeMat/ZnO material. In addition, we can observe the appearance of small peaks at 24°, 31°, 32° and 33° due to the presence of the Yttrium element and a corresponding peak at 36.5° due to the ZnO coating of the support material.

The obtained materials have been tested for applications in the field of environmental protection in wastewater treatment. They have been used successfully for degradation by heterogeneous photocatalysis from aqueous solutions of contaminated organic compounds in the class of pharmaceutical compounds, phenols and dyes.

In the photocatalytic degradation tests, a series of parameters were varied as follows: initial pollutant concentration, CA concentration values for the experiments performed varying in the range of 1.5 mg/L, 5 mg/L, 10 mg/L and 20 mg/L ; the concentration of ZnO deposited on the surface of the support material, the values of ZnO concentration for the experiments performed varying in the range: 1%, 2.5%, 5%, 10%, 17.5%; dissolved oxygen supply with bubbling compressed air; light flux intensity: minimum, medium and maximum light flux; the reuse cycles of the synthesized oxide composite material and the influence of anions but also the degradation capacity of other types of organic compounds in the class of phenols and dyes. The material showing degradation efficiencies of over 70% in all 3 classes of organic compounds tested, proving its effectiveness.

All these parameters were evaluated in detail, and the results obtained indicated that they could effectively influence the kinetics of pollutant degradation. Almost complete elimination of the target molecule, after selecting the optimal operating conditions, was obtained in a range for approx. 8 hours, for a maximum irradiation intensity of 8.1770 mW/cm^2, 1.5 mg/L of pollutant and SpongeMat/ZnO/10%.

SpongeMat/ZnO synthesized oxide material has potential for applicability in the field of environmental protection, resulting from tests that it has a high capacity for photocatalytic degradation of organic compounds from wastewater, with over 97% UV efficiency and over 43% efficiency in the VISIBLE field. At the same time, presenting the advantage of the fact that, being a catalyst immobilized on a fixed support, it is no longer necessary to perform an additional step of recovery of particles from the post-experiment suspension. The results obtained indicate that the oxide material - SpongeMat/ZnO synthesized could be used effectively for the degradation of organic compounds from wastewater.

6.2. Original contributions

Elaboration of a bibliographic study based on articles from specialized journals on oxide materials with photocatalytic properties applicable to wastewater treatment and methods of structural characterization of oxide materials.

Identification of the optimal method for the synthesis of a waste support material for use as a support for the deposition of a zinc oxide film, making it functional for environmental applications.

Obtaining a spongy support material by capitalizing on some waste and photocatalytic functionalization with a zinc oxide film, identifying the optimal synthesis parameters.

Elaboration of a process for obtaining the functionalized spongy material and its patenting, by submitting a patent application at the National Office of Inventions and Trademarks (OSIM).

Testing the photocatalytic degradation capacity of some organic compounds in wastewater in the presence of UV and VISIBLE light spectrum using the synthesized material.

Structural, morphological and compositional characterization of spongy support material coated with zinc oxide. Ensuring the sustainability of the doctoral research topic, by submitting a funding application, registration no. PN-III-P2-2.1-PED-2019-3964, project proposal title: *From advanced functionalized materials to demonstrator and environmentally friendly technology for the treatment of drinking water and wastewater by heterogeneous photocatalysis (TechUVCleanWWater)*, within *Subprogram 2.1 - Competitiveness through research, development and innovation - Experimental - demonstration project.* The proposed project proposes the integration of the spongy support material coated with zinc oxide in a dedicated reactor and extrapolation on a pilot scale.

Holding a Seminar on the doctoral thesis topic, *New advanced oxidic material functionalized for applications in wastewater treatment*, at the University of Lille 1, Unité Matériaux et Transformations (UMET), Faculty of Sciences and Technologies, France, in November, 2019.

Interpretation of experimental data obtained from the synthesis process and testing its practical applicability and dissemination of results obtained through the publication of scientific articles and participation in national and international conferences in the field of thesis.

6.3. Future research directions

- Extension of the experimental researches in order to coat on the surface of the spongy support material other types of catalytic oxides;
- Extending the experimental research to obtain other types of support materials and their functionalization;
- Carrying out additional research/tests regarding the time stability of the material, the surface chemistry and the ecotoxicity of the leachate;
- Optimizing the parameters for obtaining the spongy composite material for degradation performances of organic compounds up to 100% both in the UV spectrum and in VISIBLE;
- Testing the efficiency of the material on complex solutions consisting of real wastewater matrices;
- Functionalization of the material for increasing the photocatalytic activity for applications in real processes using as a source of irradiation - solar source (UV VISIBLE light spectrum);
- Integration of the spongy support material coated with zinc oxide synthesized in the doctoral thesis in a larger dedicated reactor and extrapolation of the pilot scale system.

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DISSEMINATION OF THE RESEARCH RESULTS

A. Articles published in Web of Science journals

1. **Burlacu Iasmina- Florina,** Lidia Favier, Ecaterina Matei, Cristian Predescu, György Deák, *Succesful elimination of a refractory emergent organic compound from aqueous system using different catalytic materials*, Scientific Bulletin UPB, Scientific Bulletin, University Politehnica of Bucharest, nr.4, seria B- Chimie and Ştiinţa Materialelor, Vol. 81, Issue 4, pag. 217- 226, 2019, ISSN 1454- 2331
2. **Burlacu Iasmina - Florina**, Gyorgy Deak, Raischi Marius, Marius Olteanu, *Greening Solutions Applicable in the tailing ponds Tăusani and Bosneag from Moldova Nouă*, IOP Conference Series: Materials Science and Engineering, Sci. Eng. 209 012097, 2017, DOI: 10.1088/1757-899X/209/1/012097
3. **Burlacu Iasmina- Florina,** Lidia Favier, Ecaterina Matei, Cristian Predescu, György Deák *Photocatalytic degradation of a refractory water pollutant using nanosized catalysts,* Journal of Environmental Protection and Ecology *(JEPE), vol. 21, 2: 571-578 (2020), ISSN 1311-5065*

B. Papers published in the Web of Science indexed Proceedings in the field of doctoral thesis

1. **Burlacu Iasmina- Florina,** Gyorgy Deak, Marcu Ecaterina, Cimpoieru Cristina, Panait Ana Maria, *Spongy composite material covered with zinc oxide with photocatalytic activity in the UV and VISIBLE spectrum, for environmental protection applications (SpongeMat/ZnO),* Proceedings of the 12th Edition of EUROINVENT European Exhibition of Creativity and Innovation, pag. 401, 2020, ISSN Print: 2601- 4564, online: 2601- 4572
2. **Burlacu Iasmina- Florina,** Cimpoieru Cristina, Daescu Andreea, Voiculet Catalin, *Contributions to the improvement of wastewater quality using modern technologies with the purpose to eliminate hazardous organic compounds,* Proceedings of the 11th Edition of EUROINVENT European Exhibition of Creativity and Innovation, pag. 471, 2019, ISSN Print: 2601- 4564, online: 2601- 4572
3. Daescu Andreea, Holban Elena, Mincu Mariana, **Burlacu Iasmina- Florina,** *Research on the reduction of hazardous substances from urban wastewater through the use of natural products* Proceedings of the 10th Edition of EUROINVENT European Exhibition of Creativity and Innovation, pag. 460, 2018, ISSN Print: 2601- 4564, online: 2601- 4572

C. Articles published in BDI indexed journals in the field of doctoral thesis and related fields

1. A-F Nicolae, G. Poteraş, Gy. Deak, A-I Dăescu, **Burlacu Iasmina- Florina,** *Innovative complex installations for the eco- electricity production in coastal areas,* European Journal of Materials Science and Engineering, EJEMSE, Vol. 3, Issue 4, 173- 183, 2018, ISSN: 2537-4338
2. Ciobotaru I.-E., Marcu E., Deák Gy., Ivanov A.A., Maria C., Tociu C., Ionescu P., **Burlacu Iasmina- Florina,** Zamfir Şt.I., Radu V.M., Cimpoeru C., Vlăduţ N.V. *Assessment of the status of the Arges river near Bucharest-Ilfov* ISB INMA- TEH *Agricultural and mechanical engineering- International Symposium*, pag.647-650 ref.15, volum Symposium 2018, online ISSN-L 2537- 3773, ISSN 2344 – 4118

D. Papers presented at international and national conferences

1. **Burlacu Iasmina- Florina**, DEÁK György, Marcu Ecaterina, Cimpoieru Cristina, Panait Ana- Maria, *Spongy composite material covered with zinc oxide with photocatalytic activity in the UV and VISIBLE spectrum for environmental protection application*, PERLIS INTERNATIONAL ENGINEERING INVENTION & INNOVATION EXHIBITION, MALAYSIA, PERLIS PI- ENVEX Exhibition- online, 2020
2. **Burlacu Iasmina- Florina**, DEÁK György, Marcu Ecaterina, Cimpoieru Cristina, Panait Ana- Maria, *Spongy composite material covered with zinc oxide with photocatalytic activity in the UV and VISIBLE spectrum for environmental protection application*, the 12-th Edition of EUROINVENT 2020- INVENTIONS & INNOVATIONS POSTERS, Catalogue of Posters, Vol. 2, pag. 175, National Exhibitors, Iaşi- online (poster), 2020
3. **Burlacu Iasmina- Florina**, Lidia Favier, Ecaterina Matei, Cristian Predescu, DEÁK György, *Photocatalytic degradation of a refractory water pollutant using nanosized catalysts*, International Workshop on "Environmental Engineering and Sustainable Development, University of Alba Iulia and Balkan Environmental Association (BENA), Alba- Iulia, (poster), 2019
4. **Burlacu Iasmina- Florina**, Daescu Andreea Ioana, Elena Holban, Madalin Silion et al, *Research on the reduction of hazardous substances from urban wastewaters through the use of natural products*, International Conference EUROINVENT, Iaşi, 2018
5. **Burlacu Iasmina- Florina,** Lidia Favier, Ecaterina Matei, Andra Predescu, Cristian Predescu, *Succesful elimination of a refractory pharmaceutic compound from aqueous system using nanosized catalysts*, XXXV-th Romanian chemistry conference, Căciulata, 2018
6. P. Ionescu, V.-M. Radu, I. E. Ciobotaru, **Burlacu Iasmina- Florina**, E. Marcu, *Assessment of heavy metal levels in water, sediment and fish from Plumbuita Lake, Romania*, 1st International Conference on Ecology and Protection of Marine and Freshwater Environments, EcoProWater, October 1-3, 2015, p. 58, ISBN 9788890755361, Viterbo, Italy
7. **Burlacu Iasmina- Florina**, Daescu Andreea Ioana, Elena Holban, Madalin Silion et al, *Electrochemical method for diagnosis of alkali-aggregate reactions in the laboratory*, International Conference EUROINVENT, Iaşi, 2018
8. **Burlacu Iasmina – Florina,** Gyorgy Deak, Raischi Marius, Marius Olteanu, *Greening Solutions Applicable in the Tailing Ponds Tăusani and Bosneag from Moldova Nouă*, International Conference EUROINVENT, Iaşi, 2017
9. **Burlacu Iasmina-Florina,** Ecaterina Matei, Mihaela Ilie, Gina Ghiţă, F. Marinescu, Gy. Deák, *The retention of Zn and Pb using the activated carbon adsorbent of different size*, 8th International Symposium on Cement Based Materials for a Sustainable Agriculture, BENA, Iaşi, 22-25 October 2015
10. Iuliana Marcus, F.D Dumitru, Mihaela Andreea Mocnea, Gyorgy Deak, **Burlacu Iasmina- Florina**, *Presentation of the development of prefabricated elements from binder materials obtained by using waste, with/without hazardous substances*, International Conference EUROINVENT, Iaşi, 2018
11. F.D Dumitru, Mihaela Andreea Mocnea, Gyorgy Deak, Andreea Baraitaru, **Burlacu Iasmina- Florina**, et al, *Presentation of microstructural particularities of the complex ecological composite materials highlighted by scanning electron microscopy*, International Conference EUROINVENT, Iaşi, 2018
12. Iuliana Marcus, F.D Dumitru, Mihaela Andreea Mocnea, Gyorgy Deak, Andreea Baraitaru, **Burlacu Iasmina- Florina,** et al, *Presentation of the assessment of stability and durability over time in different storage conditions of the ash-based compositions resulted from sludge co-incineration*, International Conference EUROINVENT, Iaşi, 2018

E. Patent applications

1. **Burlacu Iasmina- Florina**, Deák György, Marcu Ecaterina, Manea Cristina and Panait Ana-Maria, *Composite material covered with Zinc Oxide and methode of obtaining it*- SpongeMat/ZnO, patent application no. A/2019/00386
2. Poteraș George, Deák György, Nicolae Alina Florina, Dăescu Andreea Ioana and **Burlacu Iasmina- Florina**, *Electrochemical method for diagnosis of alkali-aggregate reactions in the laboratory*, patent application no. A/2018/0099

F. Awards, distinctions

1. **Gold Medal,** *Spongy composite material covered with zinc oxide with photocatalytic activity in the UV and VISIBLE spectrum, for environmental protection application*, **Burlacu Iasmina- Florina**, DEÁK György, Marcu Ecaterina, Cimpoieru Cristina, Panait Ana- Maria, PERLIS INTERNATIONAL ENGINEERING INVENTION & INNOVATION EXHIBITION, MALAYSIA, PERLIS PI- ENVEX Exhibition, online, 2020
2. **Gold Medal,** Spongy composite material covered with zinc oxide with photocatalytic activity in the UV and VISIBLE spectrum, for environmental protection application, **Burlacu Iasmina- Florina**, DEÁK György, Marcu Ecaterina, Cimpoieru Cristina, Panait Ana- Maria, the 12-th Edition of EUROINVENT 2020- INVENTIONS & INNOVATIONS, Iași, online, 2020
3. **Gold Medal,** *Research on the reduction of hazardous substances from urban wastewater through the use of natural products*, Daescu Andreea, Holban Elena, Mincu Mariana, **Burlacu Iasmina- Florina**, la EUROINVENT 2018, X Edition European Exhibition of Creativity and Innovation
4. **Silver Medal,** *Electrochemical method for diagnosis of alkali- aggregate reactions in the laboratory*, authors: George Poteras, Gyorgy Deak, Alina Nicolae, Andrea Daescu, **Burlacu Iasmina- Florina** at EUROINVENT 2018, X Edition European Exhibition of Creativity and Innovation
5. **Silver Medal**, *Researches regarding the possibility of using various types of wastes with/without hazardous substances, in inorganic binders- Development of prefabricated elements from biner materials obtained by using waste, with/without dangerous substances* Marcus Iuliana, Dumitru Florina- Diana, Moncea Andreea, Baraitaru Andreea, **Burlacu Iasmina- Florina**, Gyorgy Deak at EUROINVENT 2018, X Edition European Exhibition of Creativity and Innovation
6. **Bronze Medal,** *Developing of various ecological composite material by using secondary raw materials- Assessment of stability and durability over time in different storage conditions of the ash- based compositions resulted from sludge co-incinaration*, Dumitru Florina- Diana, Moncea Andreea, Baraitaru Andreea, **Burlacu Iasmina- Florina,** Deak Gyorgy at EUROINVENT 2018, X Edition European Exhibition of Creativity and Innovation
7. **Bronze Medal,** *Developing of various ecological composite material by using secondary raw materials- Microstructural particularities of the complex ecological composite materials highlighted by scanning electron microscopy*, Dumitru Florina- Diana, Moncea Andreea, Baraitaru Andreea, **Burlacu Iasmina- Florina**, Deak Gyorgy at EUROINVENT 2018, X Edition European Exhibition of Creativity and Innovation