POLYTECHNICA UNIVERSITY OF BUCHAREST
FACULTY OF MATERIALS SCIENCE AND ENGINEERING

PhD THESIS

NANOSTRUCTURED MATERIALS WITH A PHOTOCATALYTIC ROLE IN THE WATER TREATMENT PROCESSES

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Summary

Keywords: cavitation nanostructures, nanostructured ternary composite, magnetic core, alkaline chemical treatment, advanced oxidation, photocatalytic processes, scanning electron microscopy, X-ray diffraction

Introduction

In the 21st century, the most important scientific and technical challenges facing the world are related to the protection of the environment, pollution and saving of the energy resources in order to improve the quality of life. One of the consequences of the rapid development of the industry is the production of large quantities of wastewater which is a real danger to both the aquatic environment and the population. The materials engineering is a field that has experienced rapid development, being one of the most promising areas leading to the synthesis of new materials, the development of methods for obtaining new products, the replacement of existing equipment with high energy consumption with some that produce materials with improved performance. Thus, the materials engineering offers solutions to existing problems and measures for future problems. The research in this field has led to the development of materials with special properties, which open opportunities with applicability in materials science, medicine, chemical engineering and environmental engineering.

The nanoscale progress in science and engineering suggests that many of the current problems involving water quality could be solved or improved using nanocatalysts, as an economical and effective alternative for water purification and decontamination. The nanomaterials are globally available and have a remarkable ability to effectively remove organic and inorganic pollutants from water. However, for a successful commercialization of water treatment technology, certain inherent shortcomings need to be adequately addressed. These include the aggregation of nanoparticles in the process of water filtration and their adverse effects on human health and the environment. In order to overcome these problems and simultaneously obtain two or more desired properties, efforts are made for the design and development of nanostructures.

The use of TiO_2 nanoparticles for the photodegradation of dyes from wastewater can be considered a viable alternative, due to the fact that the optical, chemical and electrical properties of photocatalysts are exploited. In practice, however, the efficiency of the photocatalytic process varies quite a lot, depending on the material used, as well as the environmental factors in which the process takes place. The optimization of the photocatalytic process depends on obtaining the materials with characteristic properties, such as: crystalline structure, crystallite size, specific area, reduced operating time and possibility to be used on an industrial scale with a low production price. Starting from these premises, the research carried out in this doctoral thesis aimed to investigate the properties of nanostructures based

on TiO2, synthesized in different forms, in order to develop rapid methods of synthesis and functionalization, with low costs and high efficiency in photodegradation of dyes. The strategy approached in order to improve the recovery efficiency of the photocatalytic material took into account the immobilization of the photocatalyst.

The doctoral thesis is relevant for fundamental and applied research in the field of materials engineering, aiming to obtain nanostructured materials based on TiO_2 that provide photocatalytic efficiency, rapid and controlled removal from aqueous systems after the photocatalytic process and regeneration capacity for reuse. Taking as a reference the literature in the field of materials engineering, two types of TiO_2 nanostructures fixed on the support were obtained, which were subsequently used in photocatalytic processes in order to remove target dyes from the textile industry.

The doctoral thesis is structured on 5 chapters comprising 14 tables, 62 figures and 256 bibliographical references.

Chapter 1 entitled **"The current state of research in the field of obtaining nanostructured materials with photocatalytic properties"** contains general information from the literature on oxide nanomaterials focusing on the TiO_2-based nanostructures and their possible applications in photodegradation processes. Also, based on specialized publications are presented the methods of obtaining nanostructured TiO_2 on a fixed support.

Chapter 2 entitled **'The research objectives and methodology'** contains information on the objectives, the research methodology and experimental design. At the same time, this chapter briefly describes the equipments used and the kinetic mechanisms of photodegradation of dyes using nanostructured TiO_2-based materials obtained.

Chapter 3 entitled "**Obtaining and characterizing TiO_2-based nanostructures**" presents the design and obtaining of two photocatalytic materials based on nanostructured TiO_2, one obtained on Ti support by advanced chemical treatment of its surface, in order to develop nanostructured cavities with specific surface large active and the other obtained in the form of nanostructured ternary composite with magnetic core.

The evaluation of the performances of the obtained materials was performed by performing tests on the investigation of structure and morphology, using X-ray diffraction (XRD) measurements and scanning electron microscopy (SEM). The determination of the specific surface and porosity of the nanostructures were investigated by the Brunauer-Emmett-Teller (BET) method, and the determination of the electric charge of the materials surface, the interactions between the solid/liquid substance and the agglomeration tendency was performed using zeta potential measurements. By comparing the results obtained with TiO_2

nanopowders in suspensions, used as a standard of the classic photocatalysis process, the advantages of using the 2 types of nanostructured materials were demonstrated.

Chapter 4, entitled "**Evaluation of the performance of TiO_2-based nanostructures**" reveals the results obtained for nanostructured TiO_2-type photocatalytic materials fixed on Ti support and TiO_2comp in the photodegradation processes of methylene blue dye (MB). In order to demonstrate the degradation efficiency of the studied dye, the results obtained were compared with the nanostructured TiO_2 powder frequently used in photocatalysis processes. Another dye, naphthol green (NGB) was also tested in the presence of TiO_2 nanoparticles and the magnetic ternary composite $Fe_3O_4/SiO_2/TiO_2$ (TiO_2comp) in powder form.

Chapter 5 entitled "**Final conclusions, original contributions and future perspectives**" highlights the performance of the materials obtained. Therefore, two nanostructured materials based on TiO_2 were designed and tested, one obtained by alkaline treatment, followed by oxidation of the surface of pure Ti, using NaOH and acetone, in order to grow TiO_2 nanostructures on a fixed Ti support, with the advantage of controlled removal of catalytic material from aqueous media and other $Fe_3O_4/SiO_2/TiO_2$ composite catalytic material (TiO_2comp), with magnetic core protected by a silica layer which ensures the maintenance of the photocatalytic properties of the TiO_2 coating and controlled magnetic field removal of the material by the action of the magnetic core.

The two types of materials obtained and tested have the advantage of a large specific surface, due to the structures with nanometric dimensions, the recovery efficiency provided by the fixed support, respectively the magnetic core, while maintaining the photocatalytic efficiency. The characterization of the materials was performed using X-ray diffraction measurements (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller method (BET) and zeta potential measurements. By comparing with the TiO_2 nanopowders used as a standard of the classical photocatalysis process which have limitations, the advantages of using the two types of materials regarding the catalytic capacity have been demonstrated.

Chapter 1

THE CURRENT STATE OF RESEARCH IN THE FIELD OF OBTAINING NANOSTRUCTURED MATERIALS WITH PHOTOCATALYTIC PROPERTIES

1.1. General considerations

The development of efficient wastewater treatment materials capable of improving water quality is undoubtedly one of the main problems facing society today. The unavailability of drinking water is a crucial problem, especially in regions where conventional drinking water treatment systems do not eliminate pathogens, the metal ions and industrial waste. Clean and potable water is needed in a variety of industries, such as the textile, electronics, food and pharmaceutical industries. Different types of nanomaterials can be used in the environmental remediation process and therefore several approaches can be exploited for this purpose [1].

The research in this area has generated new processes called advanced oxidation processes, especially in the form of heterogeneous photocatalysis, which converts photon energy into chemical energy. The application of the concept of materials engineering in heterogeneous catalysis is based on the transformations that take place at the surface of the catalyst at the molecular level [2]. Obtaining materials with nanometric dimensions allows the understanding of reaction mechanisms as well as useful catalytic systems. However, despite several advances in the design of new methods for obtaining nanomaterials, there are still many difficulties to be overcome.

In the last decade, the photocatalytic activities have been reported for many oxide nanomaterials, such as TiO_2, ZnO, graphitic carbon nitride (g-C_3N_4), etc. [4, 5]. For more than three decades, the most studied of these nanomaterials is TiO_2 due to its excellent photocatalytic activity. Moreover, to ensure the magnetic separation of TiO_2, the incorporation of a Fe_3O_4 core has proven to be very useful [6]. Fe_3O_4, being a photocatalyst in itself, has a superparamagnetic behavior for particles with a size below 20 nm [7, 8]. This property together with its photocatalytic capacity has been reported to be promising for water and wastewater treatment technologies [9 - 11]. Similarly, ZnO and g-C3N4 have recently emerged as effective materials for photocatalytic applications [12 - 14]. Another very important material used in photocatalytic processes is graphene, which since its discovery in 2004 [15], together with its derivatives have gained significant attention in many applications.

1.3. General characteristics of nanostructured TiO_2

Among the oxide nanomaterials, nanocrystalline titanium dioxide (TiO_2) is considered as one of the most studied metal oxides in the field of materials science with excellent catalytic, antimicrobial activities and self-cleaning capacity [21].

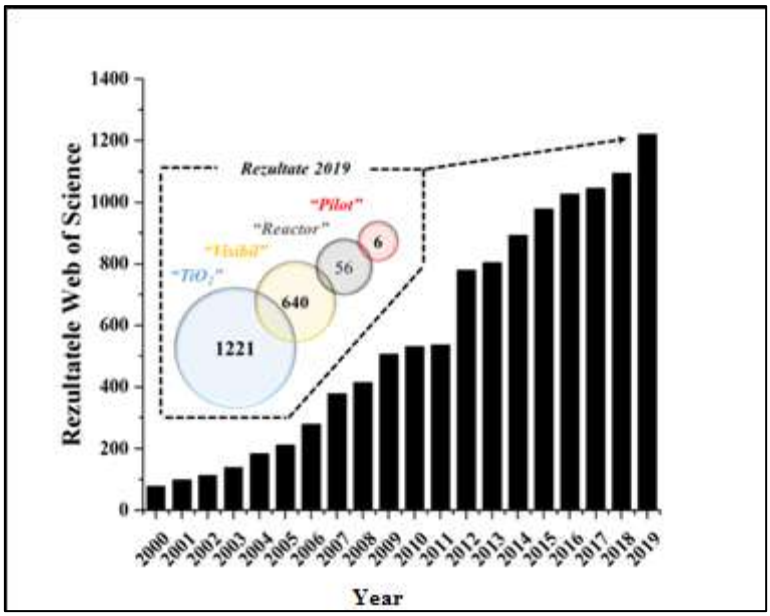

Figure 1.6. Number of publications on the use of TiO_2 in photodegradation processes, from Web of Science from 2000 to 2019. Detailed results from the last year (2019) indicate the search keywords: TiO_2, visible, reactor and pilot

The literature mentions that TiO_2-based photocatalysis has been extensively researched for photodegradation applications with generally positive results, due to the fact that TiO2 compared to other photocatalysts has hydrophilicity, long-term stability and high photoreactivity, along with lower costs and non-toxicity [83]. These properties, together with the photocatalytic capacity of TiO_2 have been reported to be effective for water treatment and wastewater treatment technologies as evidenced by over 8,000 articles published from 2000 to 2019 (Figure 1.1) [9-11 , 84]. The results seen in Figure 1.6 indicate that only a small number of publications consider reactor design or pilot-scale investigations.

1.5.Oxide nanostructured materials based on TiO_2 used in photocatalytic processes

TiO_2-based photocatalysis uses two types of reaction systems, namely suspended and immobilized systems [138]. Although TiO_2 is considered an ideal and reference photocatalyst

among photocatalysts, the literature also presents information on the limitations of photocatalysis using TiO_2 for wastewater treatment with organic compounds.

Thus, in order to implement heterogeneous photocatalysis in practical wastewater treatment applications, the overall cost of the process should be kept to a minimum. One of the ways to reduce the cost is to improve the reuse of the photocatalyst. These difficulties can be overcome and the application of TiO_2 can be extended by using different materials as a substrate [139]. To overcome this problem, the literature proposes three main approaches such as photocatalytic membranes, immobilization of photocatalysts and magnetic photocatalysts. Given that photocatalytic membranes have the disadvantage of easy clogging and magnetic separation involves an additional step, further, the immobilization of the photocatalyst was studied.

1.6.5. Anodization method

Among the many methods of immobilizing TiO_2 on the support, the literature mentions few works in which metallic Ti can be oxidized directly with the help of oxidants such as O_2, H_2O_2 and acetone to form crystalline TiO_2 [218]. Thus, direct oxidation has gained attention and has often been used in biomedical applications by applying an alkaline chemical treatment providing submicron or nano roughness on the Ti surface. In a publication, Kokubo highlighted the use of the treatment with a 5M NaOH solution on the Ti surface at 60°C and a consecutive heating to 600°C in the air, followed by biomimetic coating with hydroxyapatite by SBF solutions (solutions synthetics that simulate fluids in the human body) [219].

Similarly in the paper by Huo and colleagues, acetone was used as an oxidant on Ti to obtain nanowires of TiO_2 at a temperature of 800°C, through the oxidation process. Prior to the reaction, the Ti foil was pretreated to remove the oxide layer from the surface by placing it in a ceramic oven at an oxygen-saturated atmosphere, the oven being heated to 800°C for 1 hour. This was followed by an annealing treatment at 650°C for 30 min to remove amorphous C from the surface, resulting in rutile-shaped TiO_2 nanowires with a diameter of 20–50 nm and a length of several micrometers.

Chapter 2
THE RESEARCH OBJECTIVES AND METHODOLOGY

2.1. The objectives of the doctoral thesis

The main objective of the thesis is the design and realization of oxide nanostructured materials based on TiO_2, with the role of photocatalyst in photocatalytic processes. The results of this research lead to a complex and multidisciplinary study in the field of materials science, which will highlight the importance of fixing TiO_2 nanostructures on a fixed support or on a magnetic core, so that, by using them in water decontamination processes, the risk of discharging pollutants into the natural environment is reduced and some economic advantages are obtained.

The proposed topic contributes to scientific research in the field of photocatalytic materials by:

(i) reducing the risk of environmental pollution with TiO_2 nanoparticles frequently used in the photocatalysis process;

(ii) the possibility of reusing in at least 4 cycles the newly obtained materials, of type TiO_2 on fixed support of Ti (TiO_2/Ti) and TiO_2 with a magnetic core (TiO_2comp), with proven superior efficiency for both materials compared to TiO_2NP which registers a material loss of about 27%.

In order to fulfill the main objective of the doctoral thesis, the following scientific and technical objectives were taken into account:

- Formulation of the concept regarding the design and obtaining of two photocatalytic materials based on nanostructured TiO_2, one obtained on Ti support by advanced chemical treatment of its surface, in order to develop nanostructured cavities with specific active surface and the other obtained in the form of a nanostructured ternary composite with a magnetic core;
- Evaluation of the characteristics of the 2 materials obtained, through structural, morphological and surface investigations, with the establishment of investigation methods and parameters
- Demonstration of the proposed concept regarding the use of nanostructured TiO_2 fixed on a fixed or magnetic support by testing in solutions of different concentrations of dyes with the establishment of the optimal conditions for their degradation process;

- Validation of the photocatalytic performances of the materials used by modeling the kinetic mechanisms of the photodegradation processes and comparison with TiO_2 (TiO_2NP) powders, including the evaluation of the reuse capacity of the 2 designed materials;

Chapter 3
OBTAINING AND CHARACTERIZATION OF TIO2-BASED NANOSTRUCTURES

In this chapter we aimed to obtain and characterize nanostructured materials based on TiO_2 such as TiO_2/Ti type catalytic material obtained chemically by alkaline treatment, followed by oxidation of the surface of pure Ti in the presence of NaOH and acetone, for the purpose of growing TiO_2 nanostructures on a fixed Ti support, with the advantage of controlled removal of catalytic material from aqueous media; $TiO_2/SiO_2/Fe_3O_4$ composite catalytic material (TiO_2comp), with magnetic core protected by a silica layer that ensures the maintenance of the photocatalytic properties of the TiO_2 coating and removal in the magnetic control field by the action of the magnetic coreand TiO_2NP nanoparticles standard in the classic photocatalysis process. The types of photocatalysts obtained are presented in table 3.1.

Tabel 3.1. Characteristics of photocatalysts obtained based on nanostructured TiO_2

Nr. crt.	Photocatalysts	Sample abbreviation	Average size, nm	Synthesis method	Ref.
1.	TiO_2/Ti	P1, P2, P3, P3T, P4	150	Alkaline treatment, followed by oxidation with acetone	[227]
2.	$Fe_3O_4/SiO_2/TiO_2$	TiO_2 comp	90	Hydrothermal method	[228]
3.	TiO_2	TiO_2 NP	45	Sol-gel method	[229]

Next, the results obtained regarding the obtaining and characterization of the structures with photocatalytic role are presented.

3.1. Obtaining nanostructured materials based on TiO_2

3.1.1. Obtaining TiO_2 nanostructures on the Ti surface (TiO_2/Ti)

In order to obtain some TiO_2 nanostructures immobilized on a fixed support, a pure Ti bar was chosen 99.97, which has previously been mechanically processed in order to obtain a homogeneous reaction surface. The samples were prepared by mechanical grinding and

polishing. The samples were then washed in running water for a few seconds and rinsed with distilled water to be dried in an oven at 80°C for 1 hour. After mechanical processing, the samples were chemically treated to obtain a nanostructured TiO_2 layer on the mechanically prepared surface. The chemical treatment consisted in the application of an alkaline treatment, followed by advanced oxidation, using acetone as an oxygen source, in order to obtain dense honeycomb-type nanostructures.

The alkaline precursor used was NaOH, in different concentrations: 10, 20.30 and 40%. The 2.5 cm diameter samples were immersed in NaOH solutions, over which acetone was added and left in the dark for 72 hours. To remove possible traces of impurities, the samples were washed with deionized water and ethanol, and then subjected to heat treatment at 550˚C for 1 hour, with a rate of temperature increase of 2˚C/min. Based on the morpho-structural results recorded by the chemically treated sample with 30% NaOH solution (noted P3) clearly superior to the other samples, it was decided to apply a hot NaOH solution treatment for this sample, in order to reduce the time. reaction.

3.1.2. Obtaining the nanostructured composite type $Fe_3O_4/SiO_2/TiO_2$ (TiO_2comp)

To obtain this material, successive steps of sequential obtaining of each oxide were applied, by known classical chemical methods. The motivation for choosing such a material is given by the need to identify a material that overcomes the obstacle regarding the separation of TiO_2 suspensions used in photocatalytic processes.

Obtaining the $Fe_3O_4/SiO_2/TiO_2$ (TiO_2comp)

To obtain the TiO_2comp nanocomposite, 0.1 g of Fe_3O_4/SiO_2 was dispersed in 30 mL isopropanol and 2-3 drops of diethylenetriamine (DETA) were used as a stabilizing agent. To this mixture, 1.8 mL of titanium tetra-isopropoxide (TTIP) was added with gentle stirring. The entire reaction mixture was transferred to an autoclave where it was kept for 24 hours at 200°C and cooled to room temperature. A gray product was obtained, which was separated by means of an external magnet and then washed with ethyl alcohol and water to pH 7, after which it was dried at 60°C. The obtained powder was ground and heat treated at 550°C for 1 hour, with a temperature rise rate of 2˚C/min.

3.1.3.Obtaining TiO_2 nanoparticles (TiO_2NP)

The 2 types of materials obtained were subsequently compared with TiO_2NP nanoparticles used as a suspension in photocatalytic tests, in order to establish their performance. TiO_2 nanoparticles were obtained in the laboratory by the sol-gel method [236].

The Ti precursor used was Ti tetraisopropoxide (TTIP), which was mixed with 25 mL of ethanol and subjected to magnetic stirring for 1 hour. To this mixture was added 4 mL of acetic acid and stirring was continued for 1 hour, after which concentrated HNO_3 was added until the solution became transparent. The clear solution was then kept in the oven at 50 - 60°C for 48 hours to form pale yellow crystals. The crystals were finely ground and then calcined in the oven at 700°C for 1 hour at a rate of temperature rise of 2°C/min until a white crystalline powder was obtained.

3.2. Characterization of the obtained nanostructures

3.2.1. Characterization of TiO_2 nanostructures obtained on Ti support

The samples obtained by alkaline treatment, followed by advanced oxidation showed different morphology and structures, depending on the NaOH concentrations used.

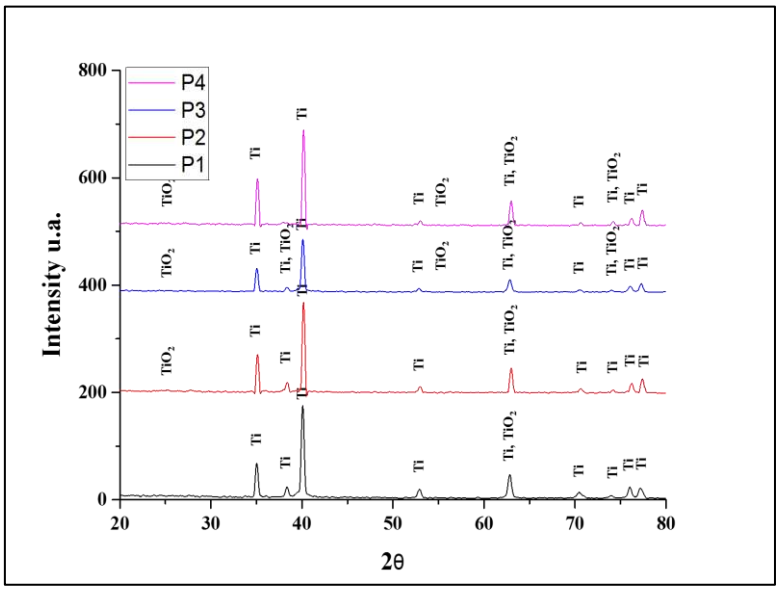

Fig.3.6. *X-ray diffractograms of TiO_2 nanostructures obtained using different concentrations of NaOH*

Further, the results obtained by X-ray diffraction measurements to identify purity and crystalline phases are presented. Regardless of the concentration of NaOH used, the diffractogram highlights the appearance of specific maxima for pure Ti according to PDF no. 01-089-2762, as seen in Figure 3.6. With the increase of NaOH concentration, from the X-ray diffraction analyzes, it can be observed that besides the presence of Ti, in the structure of the samples the crystalline compound of TiO_2 is formed, which according to PDF file no. 01-085-5943 indicates the crystalline phase of the anatas type. The morphological aspect corresponding to the TiO_2 nanostructures developed on the Ti support surface using different

NaOH solution concentrations of 10%, 20%, 30% and 40% respectively are presented in figure 3.7.

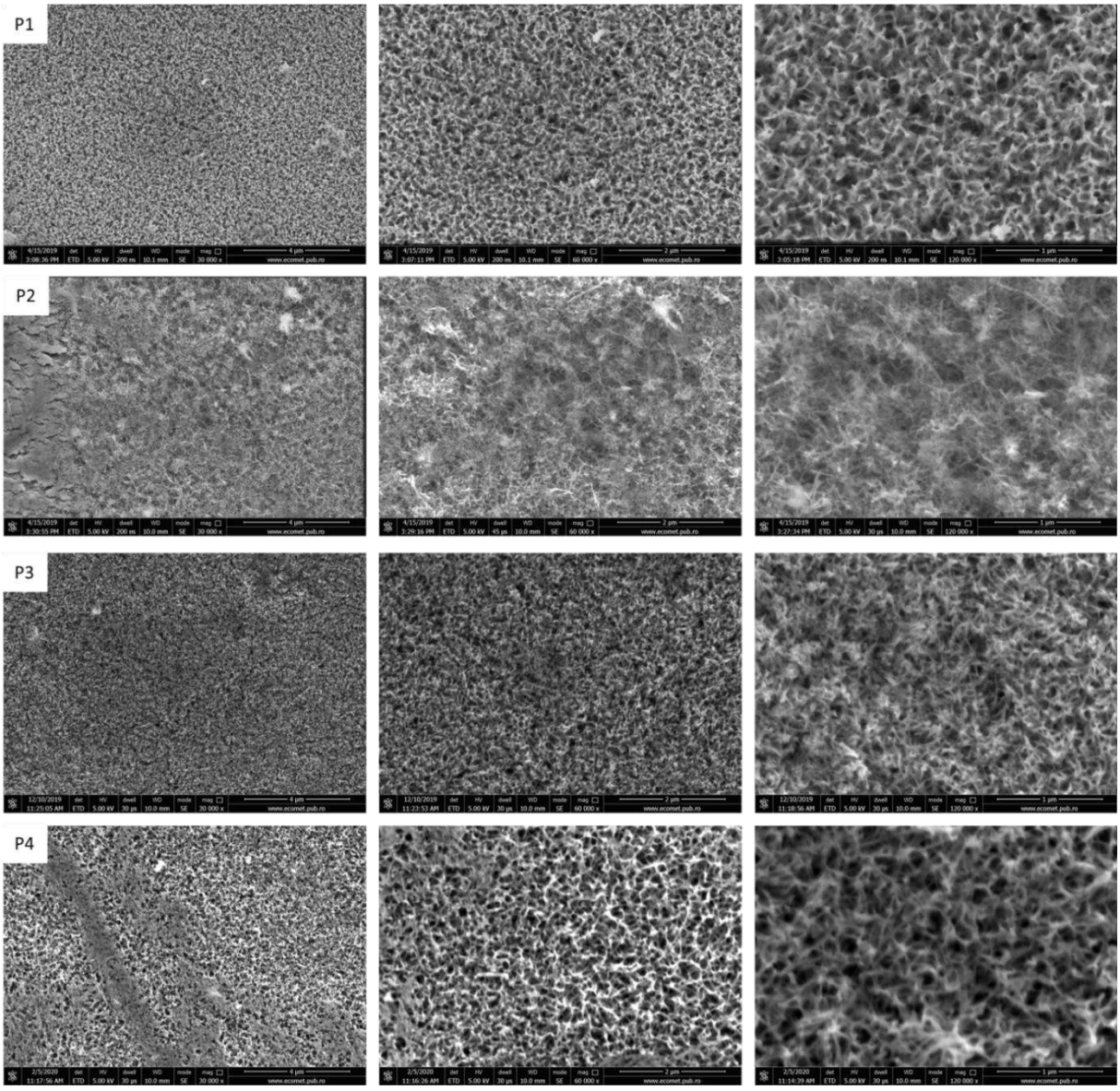

Fig.3.7. *SEM images at different magnifications (M = 30,000x, 60,000x, 120,000x) of samples P1, P2, P3 and P4 obtained on the Ti surface using 10%, 20%, 30% and 40% NaOH solutions*

The analyzes were performed at different magnifications to highlight the uniform and homogeneous structure of the surface as well as to determine the average pore size formed after treatment. It can be observed that for each sample treated with different concentrations of NaOH, nanodimensioned structures in the form of honeycomb were obtained, with a well-defined profile depending on the concentrations used. At a low concentration of 10% NaOH a surface reaction is observed on the surface, while for 20% NaOH the formed structures begin

to show fragility, a tendency that disappears at the concentration of 30% NaOH, in this case appearing on the surface, acicular and spherical nanodimensional structures. If the sample has been treated with 40% NaOH solution, it is found that the destruction of the formed structures begins, the gaps formed in the honeycomb structure begin to increase which leads to an increase in size. Although these structures would favor the photodegradation process, the fact that the structures do not show homogeneity over the entire surface, leads to a decrease in the specific active surface required for the degradation of dyes.

In order to reduce the reaction time for the alkaline chemical treatment, from 72 hours to 12 hours, the P3 sample was treated with warm NaOH solution. Photocatalysis results, in the case of using the hot NaOH solution to obtain TiO_2 nanostructures on a fixed support, indicated higher efficiencies for the 30% concentration sample which also have a well-defined morphological structure, similar to that obtained by treatment with cold NaOH solution. Because in the case of the other samples treated with concentrations of 10, 20 and 40% NaOH hot solution respectively, the morphological and structural aspect, including the photocatalysis results, did not improve, it was decided to present the results comparatively only in the case of conclusive samples, namely for samples treated with 30% cold and hot NaOH solution. Figure 3.9 shows the diffractograms for the 2 samples, observing, according to ICCD PDF sheet no. 01-082-1123 that the diffraction peaks correspond to the plans for TiO_2, and according to ICCD PDF sheet no. 01-089-2762 for titanium.

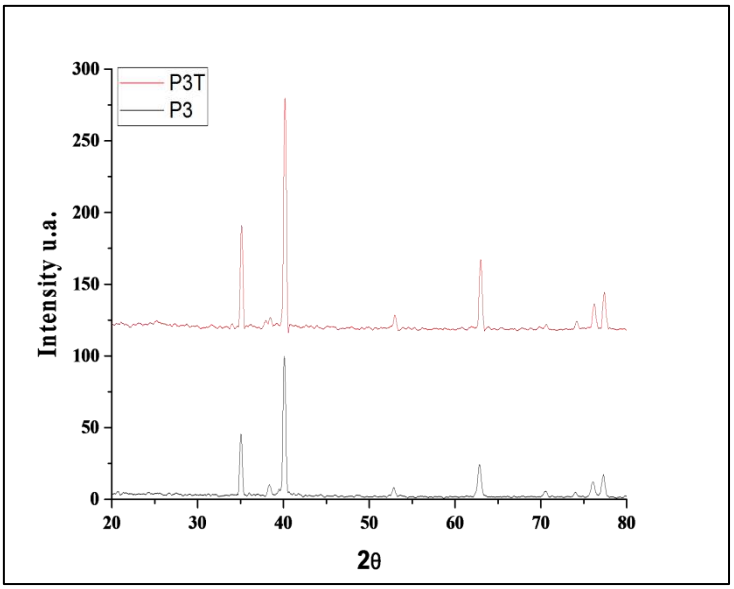

Fig.3.9. *X-ray diffractograms of TiO_2 nanostructures for samples P3 and P3T*

The dissolution of Ti in the NaOH solution was accelerated with the heat treatment, which makes the reaction faster. Therefore, a heat treatment can favor the growth of the network of TiO_2 nanostructures on the surface of the Ti disk, this is visible in the SEM analyzes.

The morphologies of TiO_2 nanostructures obtained by cold alkaline treatment and with hot solution of 30% NaOH are shown in Figure 3.10. It is found that in the case of chemical treatment of the surface of Ti with NaOH solution cooled to 20˚C and respectively with warm NaOH solution of 60°C, both samples maintain their honeycomb structure.

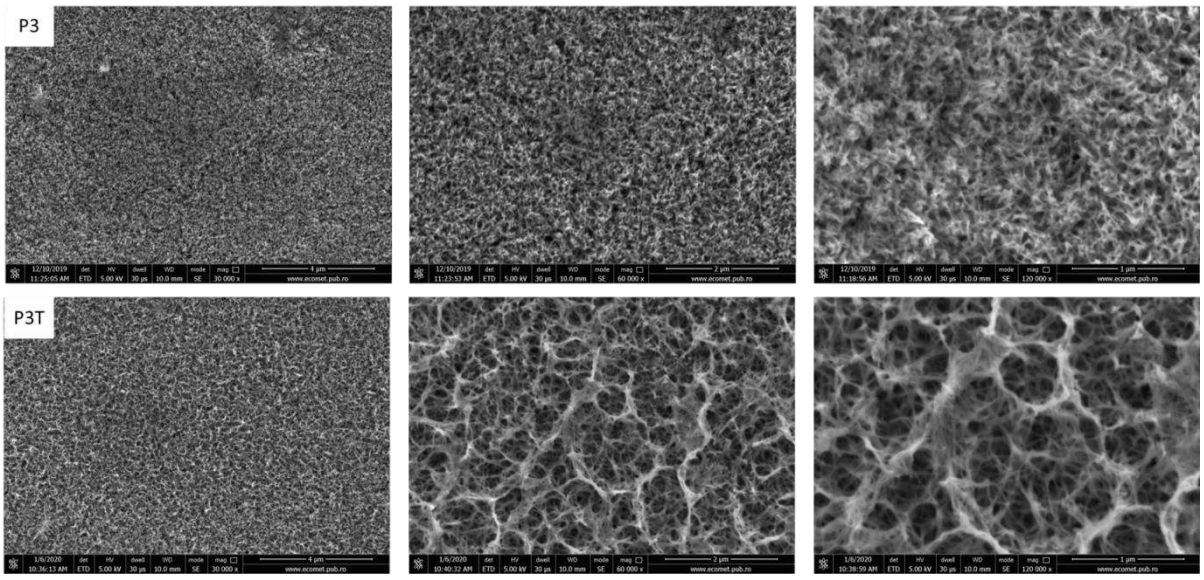

Fig.3.10. *SEM images of TiO_2 nanostructures for P3 and P3T samples at different magnifications (M = 30,000x, 60,000x, 120,000x)*

In the case of sample P3, with solution cooled to 20°C, the attack reaction was on the surface obtaining homogeneous cavities with nanometric dimensions, on the entire surface of the disk, while in the case of the attack with hot solution resulting from the reaction of exothermic dissolution of NaOH, the P3T sample developed a deep cavitational structure, the surface being damaged thus leading to the appearance of larger, inhomogeneous cavities, a mechanism probably favored by the role of oxygen in acetone.

3.2.2. Characterization of the nanostructured composite TiO_2 comp

The crystal structure of the nanostructured ternary composite type TiO_2comp is highlighted by the results of X-ray diffraction, compared to the nanostructured material with magnetic role (Fe_3O_4) and the binary composite (Fe_3O_4/SiO_2), used as precursor materials in obtaining the nanostructured composite. From the analysis of the diffraction spectra it results that the

magnetic nanocomposite TiO_2comp crystallized in the form of TiO_2 anatas according (PDF no. 01-085-5943).

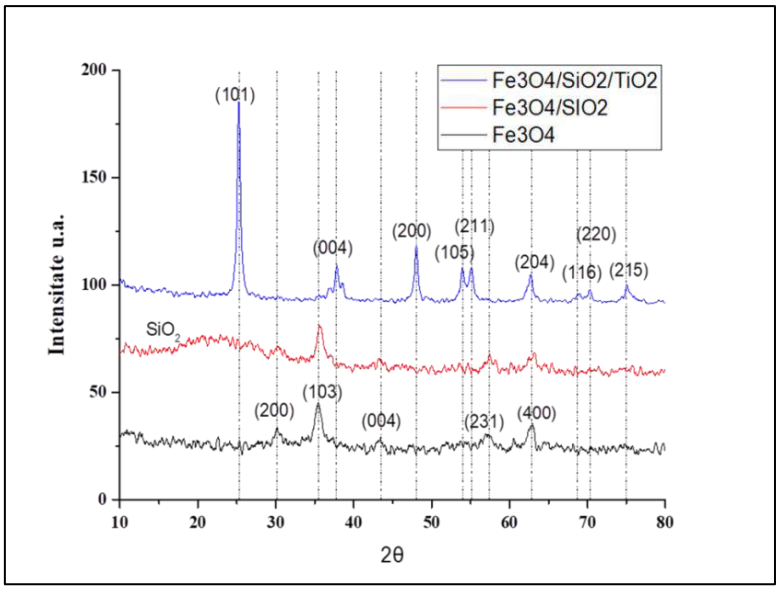

Fig.3.11. *X-ray diffractograms of the ternary nanocomposite TiO_2comp, Fe_3O_4/SiO_2 and Fe_3O_4*

As shown in Figure 3.11, their shape as well as diameters between 15 and 90 nm are highlighted, depending on the materials analyzed. Figure 3.12 (a) shows the irregular crystalline shape of Fe_3O_4 nanoparticles with a marked agglomeration tendency and magnetic character. The SiO_2-coated Fe_3O_4 nanoparticles in Figure 3.12 (b) show the spherical, ordered shape associated with agglomerates with an average size of 40 nm, in which the Fe_3O_4 nanoparticles are integrated into the SiO_2 structures.The synthesized magnetic nanocomposite TiO_2comp has a spherical morphology with homogeneous nanometric dimensions of 90 nm, due to the agglomeration of Fe_3O_4 nanoparticles in the SiO_2 coating (Figure 3.12b).

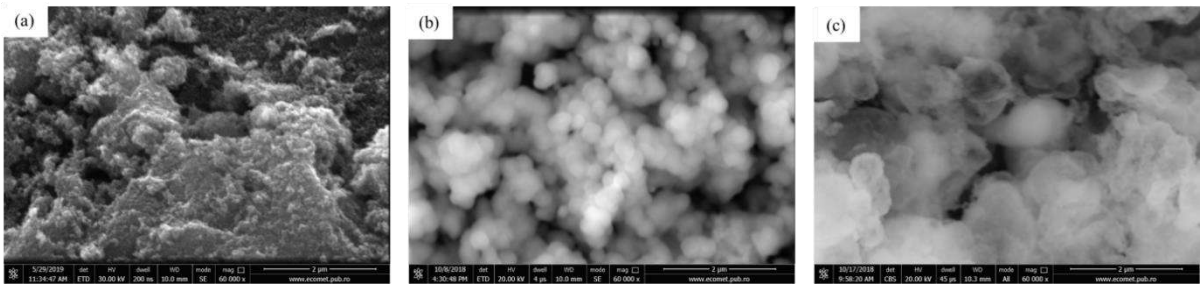

Fig.3.12. *SEM images for Fe_3O_4 nanoparticles, Fe_3O_4/SiO_2 nanocomposite and TiO_2comp magnetic core nanocomposite.*

The specific surface and porosity of the nanostructured composite with magnetic core TiO_2comp was investigated by using the nitrogen adsorption-desorption isotherm at liquid nitrogen temperature 77 K, which indicated a type IV isotherm specific to the mesoporous structure [237]. The specific BET surface of the obtained ternary nanocomposite TiO_2comp is 62.183 cm^2/g with a pore volume of 0.1241 cm^3/g. Also, the value of the isoelectric point is recorded at pH 4.6. Thus, below this value the exposed surface is positively charged, and above this value the surface becomes negatively charged.

3.2.3. Characterization of TiO_2 nanoparticles (TiO_2NP)

The X-ray diffractogram (XRD) of the obtained TiO_2 nanoparticles is shown in Figure 3.16.

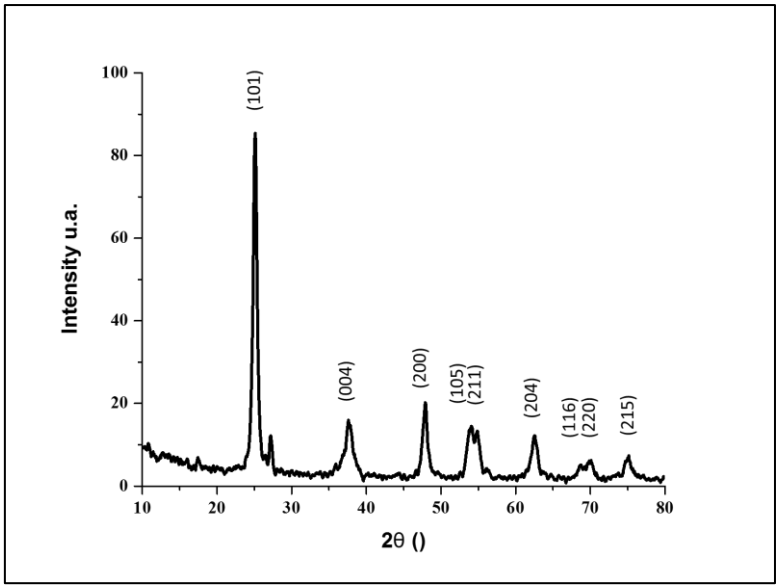

Fig.3.16. *X-ray diffractogram of TiO_2 nanoparticles*

From the analysis of the diffraction spectra it results that the TiO_2 nanoparticles crystallized in the form of a phase mixture, anatase according to PDF no. 01-085-5943 and rutile according to PDF no. 01-088-1175, the predominant phase being anatas. SEM images show the spherical shape of nanoparticles with a nanoparticle diameter of 45 nm. From the nitrogen adsorption-desorption isotherm at liquid nitrogen temperature 77 K, the specific surface of TiO_2 nanoparticles was investigated which is 79.219 cm^2/g with a pore volume of 0.1505 cm^3/g and the average pore size 3.14 nm. Also, the isoelectric point of TiO_2 nanoparticles in different pH solutions was identified as 6.4. In this context, TiO_2 nanoparticles are strongly

positively charged under acidic conditions (below 6.4) compared to the hydroxylated surface where the surface is strongly negatively charged (above 6.4).

Chapter 4
EVALUATION OF PHOTOCATALYTIC PERFORMANCES OF TiO_2-BASED NANOSTRUCTURES

This chapter presents the results obtained in the photodegradation processes of methylene blue dye (MB), using nanostructured TiO_2 photocatalytic materials fixed on Ti and TiO_2comp support. In order to demonstrate the degradation efficiency of the studied dye, the results obtained were compared with nanostructured TiO_2 powder frequently used in photocatalysis processes. Also, another dye, naphthol green (NGB) was tested on TiO_2 nanoparticles and on magnetic ternary composite $Fe_3O_4/SiO_2/TiO_2$ (TiO_2comp) in powder form. Next, the performances recorded at laboratory level by using materials with photocatalytic properties in the photodegradation processes of the dyes mentioned above are presented.

4.1. Experimental conditions for the application of the photocatalysis process for the degradation of pollutants in the form of dyes using nanostructured materials based on TiO_2

4.1.1. Materials used and their characteristics

The reagents used in the photocatalytic testing process are common dyes with different structure used in the textile industry. Methylene blue (MB) is a thiazine cationic dye and green naphthol B (NGB) dye belongs to the nitroso category, being a Fe (III) complex of 1-nitroso-2-naphthol-6-sulfonic acid. The presence of the two dyes in water causes high toxicity for aquatic flora and fauna, the sources of pollution being generally the finishing sections of the textile industry [247].

4.1.2. Procedure

The photodegradation tests in the presence of photocatalysts obtained in the laboratory were performed based on stock solutions of 1g/L MB and NGB respectively. From these stock solutions were prepared standard working solutions, with initial concentrations between 1 - 15 mg/L MB. In the case of NGB dye, the concentrations of 1 mg/L and 2 mg/L showed instability and a variable response to the UV-vis absorbance reading, respectively. Therefore, it was considered useful to continue the experiments with values of NGB concentrations

between 4 and 15 mg/L. In the process of photodegradation under UV-A light, samples were taken from the reaction systems at regular intervals, every 15 minutes. The absorbances were measured using a CINTRA 202 UV-Vis spectrometer at wavelengths specific to each dye, respectively 665 nm (MB) and 714 nm (NGB). The results were obtained as absorbance values, being subsequently transformed, according to the Lambert - Beer law (Ec.2.5), into concentration values, expressed in mg/L. The adsorption and photodegradation experiments were performed on a laboratory scale, at room temperature, reaction volume of 50 mL and pH 5 conditions, as close as possible to that of most solutions in the textile industry, without any corrections. In order to ensure a good reaction and to improve the concentration of dissolved oxygen in the solution, the whole system was connected to a compressed air filter. The systems were subjected in parallel to the following stages:

-UV irradiation of the solutions for 120 minutes for the study of the photolysis process;

- direct contact with the photocatalytic material for 120 minutes, without irradiation for the study of the adsorption phenomenon;

- direct contact with photocatalytic material and UV irradiation, for 120 minutes for the study of photodegradation. These tests were necessary to properly design the experiments and to minimize errors due to non-photocatalytic degradation.

For the photocatalysis experiments, a UV-A lamp equipped with 4 tubes of 15W each Philips ($\lambda max = 365$ nm).

4.2. The photocatalytic efficiency of nanostructured TiO_2 on fixed Ti support

4.2.1. Correlations between the active surface of the nanostructured fixed support and the powder-type nanostructure

To evaluate the useful amount of nanocatalyst on a fixed support in order to compare the technical and economic performance with the usual TiO2 catalysts in the form of nanostructured powder, it was necessary to elaborate a mathematical calculation program regarding the correlation between the active surfaces of the nanostructured fixed support with powder-type nanostructures. Thus, it was determined that 0.005 g (5 mg) of TiO2NP and 0.01 g (10 mg) of TiO2comp ternary nanocomposite were required for covering a 2.5 cm Ti support on the surface of which TiO2 nanostructures were obtained.

4.2.2. The influence of the parameters on the efficiency of the photodegradation process

For photocatalytic testing, 50 mL of solutions of concentrations between 1 and 15 mg/L MB (1, 2, 4, 8, 10 and 15 mg/L) were brought into contact with nanostructured TiO_2 on

a fixed Ti support, obtained after alkaline treatment with NaOH. The samples thus obtained are noted P1 (10% NaOH), P2 (20% NaOH), P3 (30% NaOH), P4 (40% NaOH). The P3 sample was subsequently treated with 30% hot NaOH solution and used as a catalytic material in the photodegradation process. This is noted by P3T.

The influence of UV radiation on the photodegradation process has been studied in photolysis, adsorption and photodegradation processes. The three processes were expressed as a function of the optimal concentration of 1 mg/L MB dye for the experimentally established P3T sample. Also, all values expressed as a function of time are considered to have the moment t = 0 minutes, after the 30 minutes, considered as the optimal duration both in the case of the photolysis and adsorption process, the values obtained after this period, up to 120 minutes remaining unchanged. The degradation efficiency of the dye on contact with the material used and in the presence of UV light, reaches a maximum efficiency of 96% after 60 minutes of irradiation. After this period, the efficiency remains unchanged at 120 minutes. It can be stated that for the degradation of MB, the intensity of UV radiation contributes about 79% (from 17% in the absence of light to 96% with UV light).

The evolution of the photocatalytic degradation efficiency for 60 minutes for the five samples, using a concentration of 1 mg/L MB optimal concentration, recorded the maximum value for the P3T sample and decreasing values in the following order: 96% (P3T)> 83% (P3) > 60% (P4)> 49% (P2)> 40% (P1).

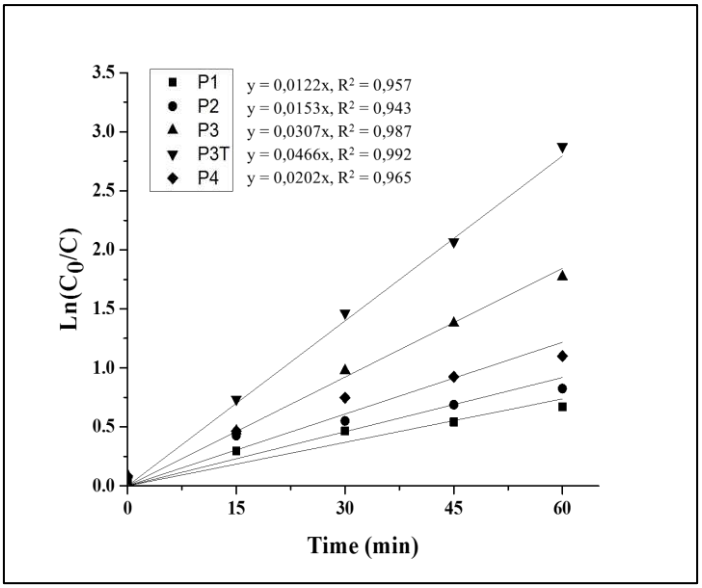

Fig.4.9. *First order kinetics of MB photocatalytic degradation for photocatalysts obtained on fixed Ti support*

Trend that is also validated by first order kinetics, according to the values of the correlation coefficients obtained. It can also be observed the change of the value of the regression coefficient (R^2) with the increase of the NaOH concentration used to treat the Ti surfaces according to figure.4.9.

The results obtained from the slope of the lines represent the first order constants (kobs) associated with the photodegradation efficiencies in the case of MB in contact with samples P1, P2, P3, P3T, P4. The variation of the NaOH concentration from 10 to 40%, used in obtaining TiO_2 nanostructures on a fixed Ti support influences the performance of the photodegradation process, observing an increase of the first order constant from 0.0122 (10% NaOH) to 0.0307 (30% NaOH) and 0.0466 (P3T), respectively. Due to the morpho-structural and catalytic performances observed in the case of the P3T sample, below are presented the results obtained for this sample, using MB dye concentrations in the range l - 15 mg/L.

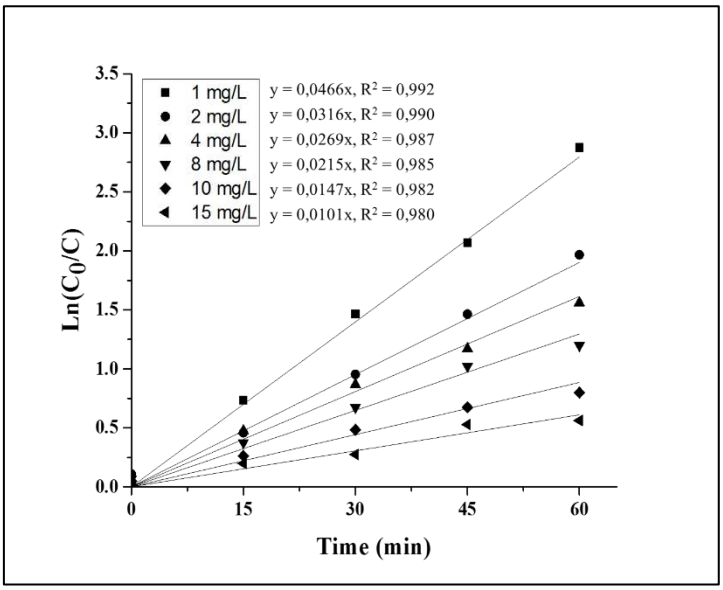

Fig.4.10. *First order kinetics of photocatalytic degradation of MB using P3T*

The results shown in Figure 4.10 indicate a linear relationship between ln C_0/C and the irradiation time t, from the slope the kobs values can be determined, while the values of the correlation coefficients (R^2) obtained for the concentrations in the range 1 - 15 mg/L means a good correlation of experimental data. As can be seen, the photocatalytic degradation of MB in the presence of nanostructured TiO_2 on a fixed Ti support, for the P3T sample is subjected to first order kinetics for the studied experimental conditions. The maximum value of the constant of the first order kinetics (k_{obs}) obtained was 0.0466 with the value R^2 being 0.992. The results presented according to the first order kinetics, show that for the time interval of 60

minutes, k_{obs} decreases with the decrease of the dye concentration used. This can be explained by considering that at low MB concentrations, the molecules adsorb on the active surface of the catalyst and react with the photogenerated voids and hydroxyl radicals on the surface of TiO_2 nanostructures. Instead, at high concentrations, the dye molecules will occupy the active places, the penetration of UV light being achieved at low speed and the interaction with the catalyst being impossible, finally, generating an insufficient amount of electron-empty pairs. This causes a decrease in the number of hydroxyl radicals required in the process of photodegradation of MB. The photocatalytic activity due to the TiO_2 nanostructures in the P3T sample can also be explained by their morphology, the nanostructures becoming longer and denser on the Ti surface forming a well-defined network structure.

Given that the product $k_{obs}C$ is less than 1, the L-H model expressed by the linear variation between $1/k_{obs}$ and the initial MB concentrations according to equation 2.10 [254] is shown in Figure 4.11.

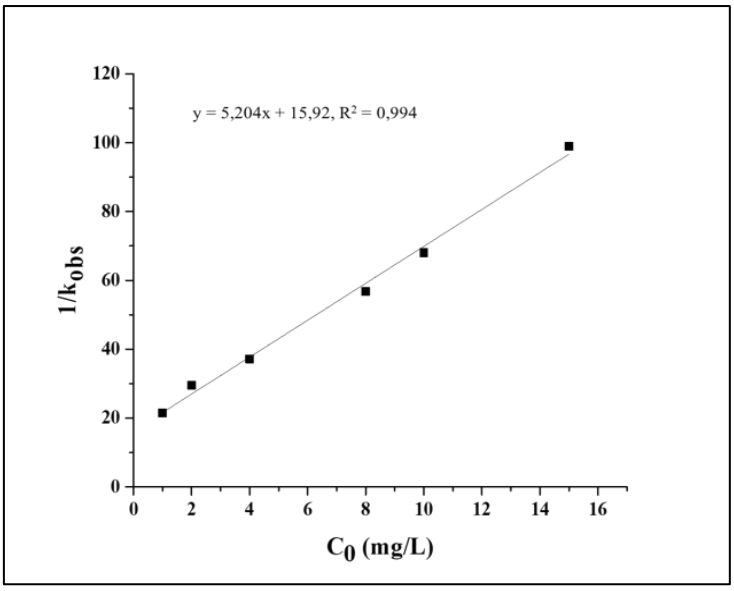

Fig.4.11. *Linearization of the Langmuir Hinshelwood equation for the photocatalytic degradation of MB*

According to figure 4.5, from the slope of the line results 1/k, and the reaction rate constant k = 0.19 mmol · L^{-1} · min^{-1}, while from the intersection of the line obtained with the ordinate at the origin the equilibrium constant of adsorption (K_{LH} = 0.32 L · $mmol^{-1}$).

4.3. The photocatalytic efficiency of TiO_2comp

4.3.1.The influence of the parameters on the photodegradation efficiency

It is important to establish the optimal parameters used in the process, in order to optimize the experimental conditions of the photodegradation process. The photocatalytic performance of TiO_2comp was studied on two types of dyes, MB (methylene blue) and NGB (naphthol green B), on a laboratory scale, under the following conditions: volume 50 mL, bubbling and stirring, pH 5, dose of catalyst (5 - 150 mg), concentrations MB (1-15 mg/L) and NGB (4-15 mg/L).

The processes of photolysis, adsorption and photodegradation of the dyes chosen in the presence of the nanostructured composite TiO_2comp were carried out using the same concentration of dye respectively 4 mg/L in the presence of 50 mg TiO_2comp. The obtained results suggest that both dyes are subjected to the photolysis process and the photodegradation efficiency is insignificant, demonstrating that the decomposition of the dyes has a low and slow efficiency. Instead, for both dyes a maximum of 30 min was observed, which corresponds to an adsorption efficiency in the dark of 25% MB and 12% NGB, respectively. These values obtained suggesting that the removal of dyes from the aqueous system may also be due to the physical adsorption of dye molecules on the surface of the TiO_2comp nanocomposite. Moreover, the photodegradation process carried out in the presence of UV radiation registers an efficiency of 89% for MB and 83% for NGB, respectively, at 60 minutes. Under these conditions, it can be established that the equilibrium time is 30 min and the photodegradation process takes place at 60 min, after this period there is a stagnation of the photodegradation efficiency for the two processes.

The amount of TiO_2comp nanocomposite influences the photodegradation, by the number of active sites on the catalyst surface with the dye molecules to be degraded. The effect of increasing the amount of TiO_2comp on the photodegradation process was studied experimentally in order to establish an optimal amount of TiO_2comp, by varying the amount of catalyst from 5 mg to 150 mg for the same concentration of 4 mg/L for both MB and NGB. Increasing the amount of TiO_2comp from 5 mg to 50 mg ensures the improvement of the photodegradation process from 49% to 89% for MB while for NGB, the photodegradation efficiency increases from 32% to 83%. This result is due to the increase in the specific surface area available for the adsorption of dyes with a positive effect on the photodegradation process. Increasing the amount of TiO_2comp over 50 mg causes a decrease in the photodegradation process in both cases, so for the amount of 150 mg there is a photodegradation efficiency of 64% for MB and 62% for NGB, respectively. The negative

effect of excessive use of TiO_2comp is due to the increase in turbidity which reduces the efficiency of the photodegradation process. Thus, it was determined that 50 mg is the optimal amount of TiO_2comp. The determination of the optimal dye concentration had a maximum photodegradation efficiency of MB dye (at a concentration of 1 mg/L) of about 97% and a maximum photodegradation efficiency of NGB dye (at a concentration of 4 mg/L) of about 83%. In both dye cases as the dye concentration increases, the values of photodegradation efficiencies obtained for the two dyes decrease from 97% to 66% for MB and from 83% to 63% for NGB. This trend can be explained by considering that at low concentrations, the molecules are adsorbed on the active surface of TiO_2comp, while at high concentrations, the penetration of light through solutions would lead to poor interaction with the catalyst. Under these conditions, it was established that 1 mg/L is the optimal concentration for MB and 4 mg/L for NGB. This trend was validated by the trend of constant values (k_{obs}) that decrease with increasing initial dye concentration, the photodegradation process being described by first order kinetics [255].

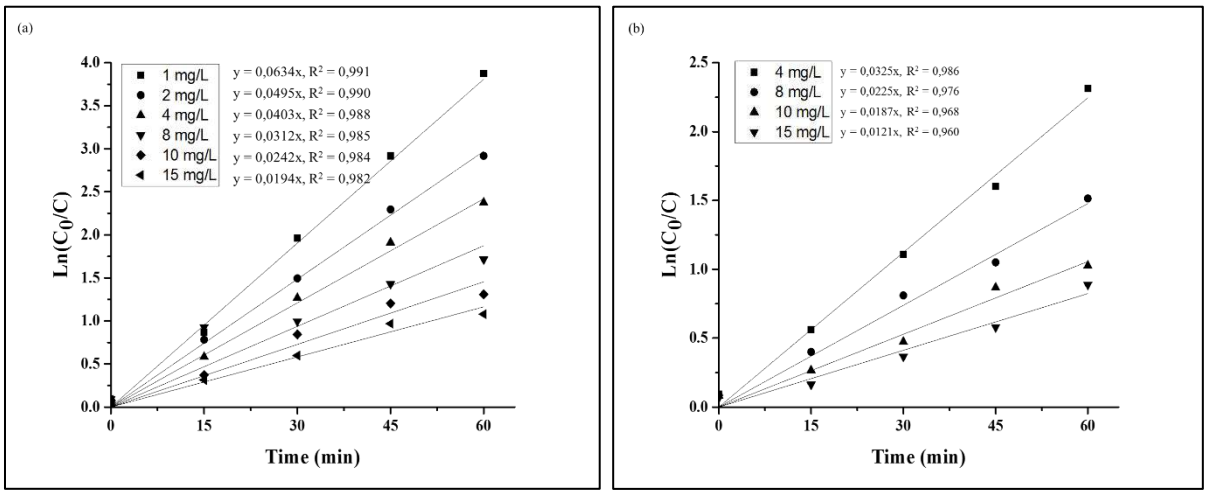

Fig.4.16. *First order kinetics of photocatalytic degradation using 50 mg TiO_2comp for (a) MB and (b) NGB*

Given that the product $k_{obs}C$ is less than 1, the L-H model can be expressed by the linear variation between $1/k_{obs}$ and the initial concentrations of the dyes. Therefore, the velocity constant k is obtained from the slope of the linear regression line while the adsorption equilibrium constant K_{LH} is obtained from the intersection of the line with the ordinate at origin, according to Figure 4.17.

The linearization of the graphs in figure 4.7 on the concentration range chosen for each dye describes a linear behavior especially for the dye MB having the regression coefficient R^2 = 0.993.

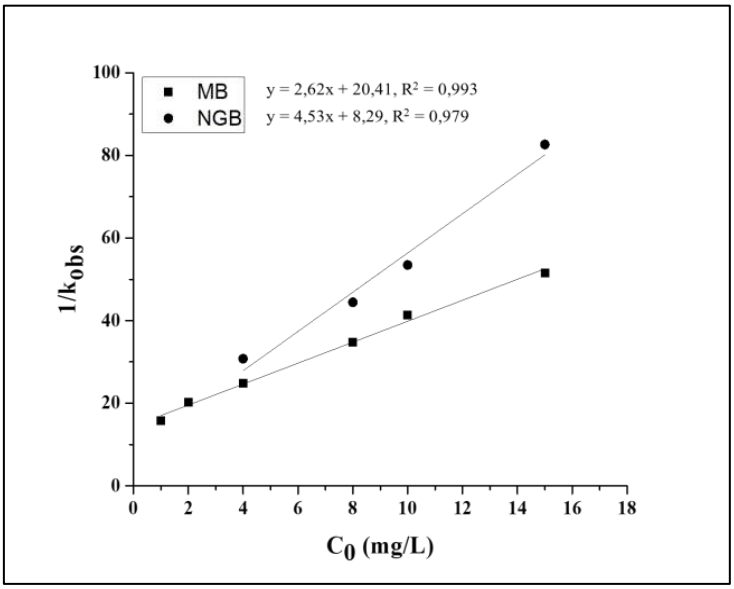

Fig.4.17. *Variation $1/k_{obs}$ from initial concentrations*

The kinetic parameters for the two dyes are: for the dye MB, the value of the reaction rate constant on the surface of the catalyst (k) is 0.38 (mmol · L^{-1} · min^{-1}), and the adsorption equilibrium constant K_{LH} is 0.12 (L · mmol-1), while for the NGB dye these values are 0.22 (mmol · L^{-1} · $min^{-1)}$ respectively 0.29 (L · $mmol^{-1}$).

4.4. The photocatalytic efficiency of TiO2 nanoparticles (TiO_2NP)

4.4.1. The influence of the parameters on the photodegradation efficiency

The determination of the photocatalytic performance of TiO_2 nanoparticles was tested by photodegrading dye solutions such as methylene blue (MB) and naphthol green B (NGB). The purpose of the TiO_2NP test was to compare with the new materials obtained in order to evaluate the photocatalytic performances. The factors influencing the photodegradation process were studied: the concentration of the dye, the amount of TiO_2 nanoparticles and the interaction between the surface of the TiO_2 nanoparticles and the dyes.

The results of preliminary studies to determine the effect of UV radiation on the photodegradation process indicated that in both cases, the degradation efficiency in the case of direct photolysis of dyes was negligible, while adsorption in the dark led to dye degradation by approx. 13-44 %. The photodegradation efficiency was significantly improved

when the TiO_2 nanoparticles were used in the presence of UV light, obtaining efficiencies of 83% MB and 96% NGB.

In suspended photocatalytic processes, the amount of catalyst is a very important parameter that can affect the photodegradation process. The evolution of the catalyst amounts in the range of 5 - 150 mg TiO_2NP over time for a concentration of 4 mg/L dye showed a constant increase in the range of 5 - 50 mg TiO2, followed by a decrease in the range of 75 - 150 mg. Therefore, up to a certain ratio between catalyst and dye, the photocatalytic efficiency can reach a maximum of saturation, after which the photodegradation process decreases, thus, the optimal amount being 50 mg TiO_2NP.

The effect of the initial concentration of the two MB and NGB dyes under irradiation with UV light was investigated by varying the initial concentrations between 1 - 15 mg/L MB dye and 4 - 15 mg/L NGB dye at the optimal amount of TiO_2NP of 50 mg. After irradiation with UV light for 60 minutes, the photodegradation efficiencies reached the following values for MB dye: 92% (1mg / L)> 90% (2mg / L)> 85% (4mg / L)> 80% (8mg / L) L)> 65% (10mg / L)> 57% (15mg / L) and 97% (4mg / L), respectively> 85% (8mg / L)> 82% (10mg / L)> 76% (15mg / L)) for the NGB dye.

To investigate the kinetics of the photocatalytic reaction of MB and NGB in the presence of TiO_2NP, the mechanism of first order kinetics was studied (Ec.2.8.). The values of the first-order constants are consistent with the values expressing the photodegradation efficiency, decreasing with increasing initial dye concentrations as seen in Figure 4.24.

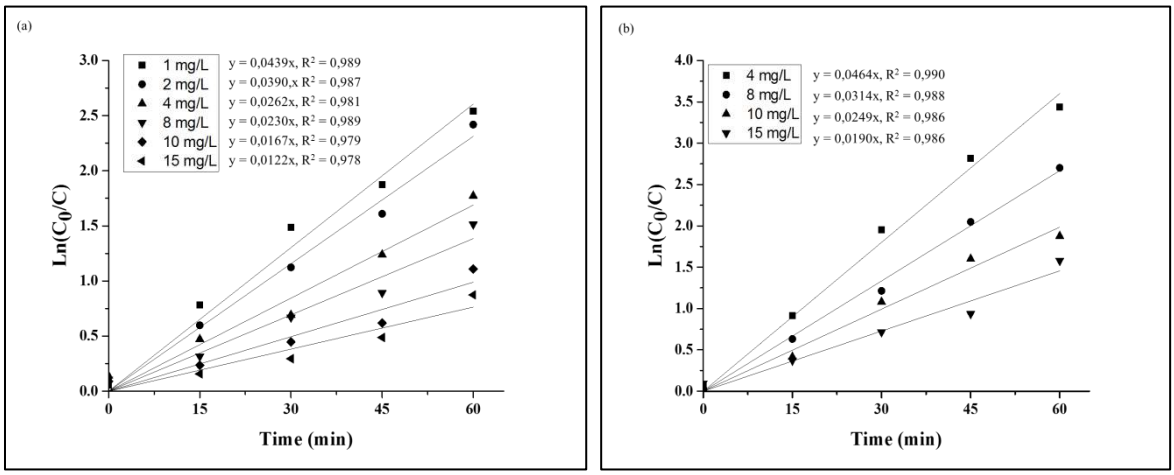

Fig.4.24. *Linear variation of Ln (C_0/C) over time for degradation of (a) MB and (b) NGB, varying the initial catalyst concentrations*

Given that the product $k_{obs}C$ is less than 1, the L-H model proposes the linear variation between $1/k_{obs}$ and the initial dye concentrations according to equation Ec.2.10. Therefore, the rate constant k is obtained from the slope of the linear regression, while the adsorption constant K_{LH} from the ordinate at the origin, for each dye separately. The linearization of the equations in Figure 4.25 on the concentration range chosen for each dye describes a linear behavior especially for the NGB dye having the regression coefficient $R^2 = 0.993$.

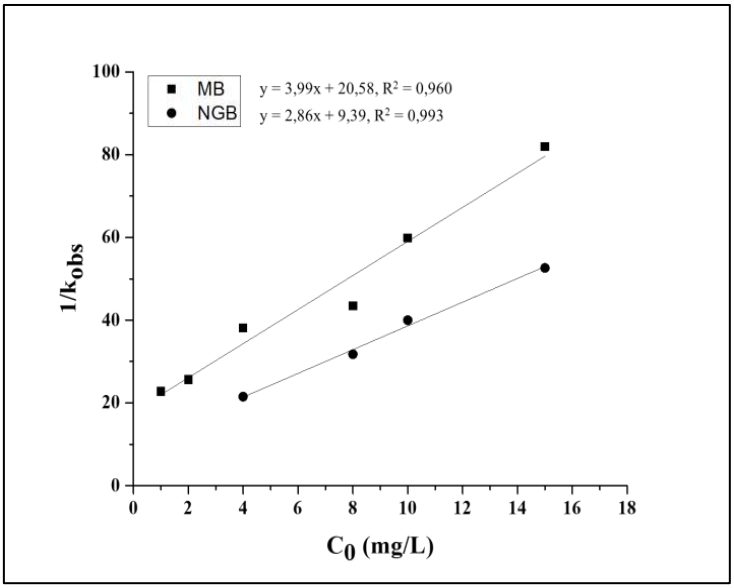

Fig.4.25. *Variation $1/k_{obs}$ from initial concentrations*

In the case of MB, the value of the reaction rate constant on the surface of the catalyst (k) using the LH psuedo first order model is 0.25 (mmol · L^{-1} · min^{-1}) and the adsorption equilibrium constant K_{LH} obtained from the intercept is 0.19 (L · $mmol^{-1}$) while for NGB these values are 0.34 (mmol · L^{-1} · min^{-1}) respectively 0.54 (L · $mmol^{-1}$). During the experiments it was observed that the adsorption activity on TiO_2 nanoparticles depends on the photocatalytic activity.

4.5. Comparative photocatalytic performance of TiO_2-based nanostructures in suspension and immobilized on a fixed support for the degradation of methylene blue (MB)

The photocatalytic performance of some TiO_2 nanostructures developed by advanced chemical treatment, followed by oxidation on the titanium surface (TiO_2/Ti, P3T sample) was compared with the powdered materials: $Fe_3O_4/SiO_2/TiO_2$ ternary hybrid nanocomposite (TiO_2comp) in suspension and nanostructured TiO_2(TiO_2NP) in suspension, in order to

photodegrade the MB type dye. The performance of these materials was evaluated using the optimum dye concentration of 1 mg/L, for which the highest efficiency was recorded, at the optimum irradiation time of 60 minutes and equivalent amount of catalyst for the surface of a TiO_2/Ti disc. Thus a 96% MB removal efficiency from the aqueous system was recorded using a 2.5 cm TiO_2/Ti disk, equivalent to 10 mg TiO_2comp and 5 g TiO_2NP, respectively. The fact that the photodegradation efficiency of MB is the highest in the case of TiO_2/Ti, registering the value of 96%, confirms that the chemical treatment of the Ti surface in order to form nanostructured TiO_2 is an advantage in terms of controlled development of nanostructures, integrated in fixed systems so as to prevent their agglomeration and uncontrolled evacuation due to the size of the nanoparticles. Also, in the case of the catalyst obtained with magnetic core, TiO_2comp, due to the specific structure of ternary composite, the material has a more pronounced photodegradation capacity, due to the TiO_2 structures integrated in the silica mass as a support layer, which provides stability and a much more efficient dispersion on the composite surface, compared to TiO_2NP where an agglomeration probably takes place, decreasing the photocatalytic performance.

The experimental data were modeled using 4 kinetic models, which indicated the existence, based on the constants specific to each model, of four mechanisms: Langmuir-Hinshelwood, first-order kinetics, second-order pseudo-kinetics and interparticle diffusion. The parameters to kinetically model the evolution of the photodegradation process were as follows: 1 disk with a diameter of 2.5 cm TiO_2/Ti, optimal amount of TiO_2comp and TiO_2NP 50 mg, 60 minutes irradiation time, air bubbling, normal temperature conditions and pressure (25°C and 1 atm).

Table 4.6. presents the kinetic parameters specific to the 4 mechanisms in the case of photodegradation of the MB dye.

Tabel 4.6. *Kinetic parameters specific to the 4 mechanisms in the case of MB photodegradation*

	C_o	Cinetica pseudo-ordin II			Difuzia inter-particule		Cinetica pseudo-ordin I		Langmuir-Hinshelwood		
	mg/L	k_2	q_e	R^2	K_p	R^2	k_{obs}	R^2	k	K_{LH}	R^2
TiO_2/Ti 2,5 cm	1	0,239	4,988	0,995	0,221	0,931	0,046	0,992	0,19	0,32	0,994
	2	0,016	8,703	0,994	0,459	0,901	0,031	0,990			
	4	0,009	16,26	0,984	0,873	0,902	0,026	0,987			
	8	0,005	28,82	0,983	1,581	0,876	0,021	0,985			
	10	0,003	30,67	0,972	1,687	0,921	0,014	0,982			
	15	0,001	36,76	0,971	2,064	0,954	0,010	0,980			
TiO_2comp 50 mg	1	0,352	1	0,990	0,018	0,842	0,063	0,991	0,38	0,12	0,993
	2	0,186	1,9	0,991	0,036	0,828	0,049	0,990			

	4	0,051	3,74	0,985	0,084	0,900	0,040	0,988			
	8	0,037	6,6	0,982	0,149	0,827	0,031	0,985			
	10	0,010	8,3	0,980	0,204	0,938	0,024	0,984			
	15	0,006	11,3	0,980	0,290	0,968	0,019	0,982			
TiO_2NP 50 mg	1	0,064	1,089	0,962	0,0209	0,839	0,043	0,989	0,25	0,19	0,960
	2	0,088	1,864	0,954	0,0506	0,878	0,039	0,987			
	4	0,017	3,61	0,934	0,092	0,856	0,026	0,981			
	8	0,008	6,87	0,924	0,1787	0,864	0,023	0,989			
	10	0,006	7,4	0,921	0,191	0,862	0,016	0,979			
	15	0,005	9,09	0,910	0,240	0,851	0,012	0,978			

From the values presented in table 4.5 can be seen the tendency of photodegradation of MB according to the LH kinetic model, based on the comparison of correlation coefficients (R^2), noting that in the studied concentration range, R^2 value is 0.994 for TiO_2/Ti and 0.993 for TiO_2comp. The different rate (k) and adsorption (K_{LH}) constants imply the affinity of the MB dye to the two materials TiO_2/Ti and TiO_2comp. It can be seen that at high dye concentrations, MB is favored by the adsorption phenomenon, a phenomenon explained by the size of the dye molecules that block the active photodegradation centers on the catalyst surface, which prevents radiation from penetrating the substrate.

Thus, the photodegradation phenomenon occurs at low concentrations of the reactant, for the catalyst quantities presented. It is noteworthy that using a fixed TiO_2/Ti system the amount of nanostructured TiO_2 applied with photocatalytic role in the photodegradation process of MB is about 5 times lower than the conventional use of TiO_2 nanostructure TiO_2NP powder and about 10 times smaller than the structures that are part of the TiO_2comp type ternary nanocomposite, considerably reducing the need for material used in the photocatalytic process, without affecting the process performance.

4.6. Regeneration and reuse studies

The deactivation and regeneration of catalyst are relevant aspects that must be considered when expanding heterogeneous photocatalysis due to the economic implications. The strong adsorption and interaction between the active sites on the catalyst surface and the oxygen-containing intermediates leads to a sudden decrease in the number of active sites during the catalyst reaction. In order to evaluate the performance of the TiO_2-based nanostructures used, their stability tests were also performed in case of reuse in several photocatalytic cycles. Reuse tests were performed under the following conditions: 1 mg / L MB, pH 5 solution volume 50 mL, bubbling with air and irradiation time 60 min, 1 TiO_2/Ti disc and 50 mg TiO_2comp and TiO_2NP.

To evaluate the performance of TiO_2/Ti nanostructures, the P3T sample, material reuse tests were performed in 4 cycles. After each test, the nanostructures were washed with alcohol and distilled water and dried in an oven at 60°C. From the data presented in Figure 4.10a it can be seen that in the first cycles of reuse the photodegradation efficiency of MB did not decrease significantly, registering values from 96% to 72%, the difference appearing in the 3th cycle when the efficiency of photodegradation is 46%.

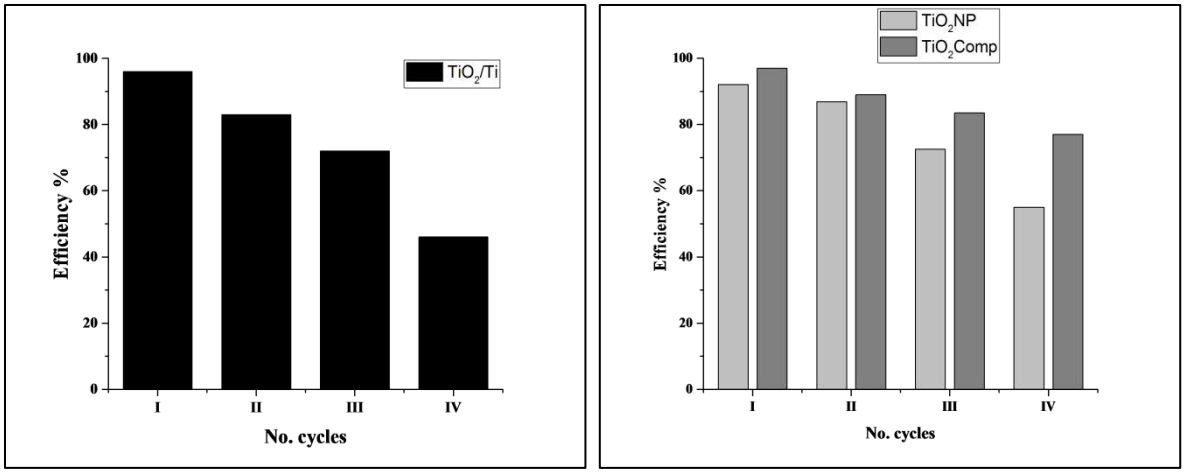

Fig.4.31. *Ability to reuse TiO_2-based nanostructures for MB degradation processes*

In order to test the reuse capacity of the studied catalysts, the optimal amount of 50 mg powder catalyst and 1 TiO_2/Ti disk was chosen in the experiments. In the case of TiO_2NP and TiO_2comp catalysts, the nanoparticles in the aqueous solutions were recovered by means of a magnet, in the case of TiO_2comp and respectively by filtration in the case of TiO_2NP, after which they were washed and dried in an oven at 60°C. In Figure 4.31b, after the 4 reuse cycles, a different behavior is observed regarding the reuse capacity of the catalysts, in the case of TiO_2comp, the photodegradation efficiency varies between 97% and 77%, while in the case of TiO_2NP, the photodegradation efficiency is is in the range of 92% - 54%, probably due to the risk of material loss through filtration, as opposed to the magnetic field that contributed to the proper separation of TiO_2comp type nanostructures from the system. In all 3 systems this decreasing tendency can be explained by the occupation of the organic molecules of the active sites on the surface of the photocatalysts. According to these data, the TiO_2/Ti type photocatalyst has the best regeneration capacity, preserving the photocatalytic properties after 3 cycles of reuse.

Chapter 5

FINAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE PERSPECTIVES

Final conclusions

In the doctoral thesis on "Nanostructured materials with photocatalytic role in water treatment processes", photocatalytic systems based on nanostructured TiO_2 developed on fixed Ti support and integrated in a ternary composite with magnetic core were designed and obtained. The role of these fixed systems is to control the photocatalytically active nanostructures, avoiding their uncontrolled evacuation, together with the purified water. In the current context of rapid industry development, the production of large quantities of wastewater requires the adaptation of advanced materials by characteristics and properties so that their use does not lead to environmental risk after use in decontamination processes.

Based on an extensive study in the literature, it was found that:

- oxide nanomaterials used in photocatalytic processes have a number of characteristic properties such as particle size, specific surface area or the space between electronic levels;
- among the oxide nanomaterials, TiO_2 used in powder form proved to be the most studied, obtaining positive results in photodegradation processes due to its specific properties;
-although it has a high efficiency in photocatalytic processes, the limitations of TiO_2 regarding its use in the form of particles are highlighted, when the removal from the system leads to material losses or when its aggregation takes place;
- it is possible to overcome these limitations by immobilizing TiO_2 on different substrates,
- the ideal substrate must be chosen and designed to meet requirements such as: strong adhesion to the catalyst, stability and strength, such as glass-based materials, activated carbon, silica-based materials and other substrates (stainless steel, etc.);
- known methods for obtaining TiO_2 on a fixed support are: sol-gel method, heat treatment, chemical vapor deposition (CVD), electrodeposition;
- there is an alternative to well-known methods of nanostructured TiO_2 synthesis, especially in the field of biomedical applications, where it is used to obtain nanostructures and direct treatment of metallic Ti with oxidizing agents such as O_2, H_2O_2 and acetone, to form crystalline TiO_2, followed by application of an alkaline chemical treatment that provides roughness and crystalline forms of nanostructured TiO_2 on the Ti surface.

Based on this information, the objectives, the research methodology and the experimental plan were formulated. In order to fulfill the main objective of the doctoral thesis, the following were taken into account:

- obtaining two photocatalytic materials based on nanostructured TiO_2, on a fixed support and respectively by integrating nanostructured TiO_2 in a ternary composite with magnetic core.
- characterization in order to validate the structure, morphology, identify the photocatalytic capacity and establish specific surface properties.
- validation of the photocatalytic performances of the materials used by establishing the photodegradation mechanisms and comparing the photodegradation performances with nanostructured TiO_2 powders.

Original contributions

In order to highlight the original contributions, it was considered the development of many research activities that helped to obtain, characterize and test the materials obtained. Of these, the following are mentioned:

conducting a complex study in the literature focusing on oxide nanomaterials in order to identify some elements of originality in the scientific approach to obtaining nanostructured TiO_2 used in water decontamination;

 carrying out preliminary experiments in order to identify the optimal parameters for obtaining nanostructured TiO_2 on a fixed support;

 designing and obtaining nanostructured photocatalytic materials on fixed metallic Ti support, with honeycomb type structure and with dimensions of 120 nm of the formed cavitation structures;

 designing and obtaining nanostructured materials integrated in a magnetic ternary composite;

 obtaining nanostructured TiO_2 powders for later use as a standard in comparing photocatalytic performance with fixed sports materials;

 selection and testing of a method of chemical treatment of metallic Ti surfaces, known from biomedical applications, using cheap and accessible reagents, with high performance in the formation of stable and controlled honeycomb nanostructures and deep cavitation structures;

 development of honeycomb-type morpho-structures, with anatase phase, by using two synthetic variants: treatment with cold NaOH (0 ℃) and hot NaOH (60 ℃), followed by

advanced oxidation using acetone precursor, with the highlighting in the second case of deep cavitational structures responsible for the high efficiency of the photodegradation process;

 elaboration of a mathematical calculation program regarding the correlation between the active surface of the nanostructured support with powder-type nanostructures;

 selection of dyes specific to the textile industry, such as methylene blue and naphthol green B and characterization by UV-Vis and FTIR spectrometer;

 elaboration of a work plan regarding the laboratory experiments in order to establish the optimal working parameters specific to the photocatalysis process;

 validation of the photocatalytic performances of TiO_2 nanostructures through tests and comparative analyzes between TiO_2NP and TiO_2/Ti and TiO_2comp and establishing the Langmuir-Hinshelwood mechanism responsible for the photograding process.

Future perspectives

 the development of improved materials with the potential for degradation of emerging organic compounds in the visible field, by creating structures doped with metals responsible for this process;

 development of HPLC methods specific to emerging contaminants such as pharmaceuticals, cosmetics, etc .;

 the transfer of the laboratory model regarding the concept and the photodegradation process at pilot level in order to demonstrate the maturity of the technology.

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