A WAY TO REDUCE THE EMERGING POLLUTANTS IMPACT ON ENVIRONMENT USING NANO-TiO_2 AS PHOTOCATALYST

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There are different types of emerging pollutants from organic to inorganic substances, also including nanoparticles an microplastics. Often, the use of photocatalytic methods applied for organic contaminants generate low molecular organic compounds less toxic for the environment. The most common and efficient nanomaterial used for photodegradation is TiO_2. This paper presents the main steps of obtaining and characterization of nanostructured TiO_2 (obtained as anatase phase), with emphasizing the main structural and morphological properties responsible for photodegradation process. To assess the effectiveness of nanostructured TiO_2 as photocatalyst, a dye (methylene blue, MB) was degraded under UV light, in the presence of nano-TiO_2.

Keywords: nanotechnology, environmental, materials, water quality.

1. Introduction

Emerging pollutants represents a global threatens for aquatic environment. They are chemicals or natural substances, which are not naturally found in the environment, but have the potential to enter and cause adverse effects on the environment. Emerging pollutants that result from diffuse and punctual pollution are frequently present in the aquatic environment [1]. There are many categories for emerging pollutants appearance in the environment and the most important fact is that surface water, soil, and ground waters are receptors for these types of pollutants. Finding innovative tools in monitoring and remediation is an emergency [2]. Thus, nanomaterials could be a solution for emerging pollutants. In recent years, interest in pollutants emerging from water has increased. For example, a search using the term "emerging pollutants in water" on the ScienceDirect database showed that in 2015, 3,611 research papers were published, and in 2020 11,157 [3].

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Aquatic ecosystems are frequently contaminated by various conventional pollutants, such as dyes, but also heavy metals and microorganisms responsible for various diseases. In terms of colorants, the presence of color is the main impact they can have on water. [4].

Nano-photocatalysts are frequent used to cleanse wastewater, as they help to improve the reactivity of the catalyst, since it has a higher ratio between surface area and shape-dependent characteristics [5]. Oxidic nanomaterials play an important role as catalysts in various oxidation reactions. They have a strong catalytic reactivity on pollutants and turn them into environmentally friendly products. Some properties of these nanomaterials are due to the nano size, high reactivity, and large surface area. [6,7]. In special, photocatalysis with TiO_2 is strong and important in removing various impurities from surface waters [5].

Photocatalytic degradation of pollutants using photocatalysts formed by the TiO_2-based sol-gel method is an effective alternative for uses in environmental protection compared to conventional water treatment technologies [8].

Titanium dioxide has a photocatalytic activity, which comes from its electronic structure and photoelectric characteristics. Band theory can be used to explain the principle of the photocatalytic reaction. TiO_2 has a bandwidth consisting of a valence band and the driving band, and the band energy is 3.2 eV [9].

These researches were focused on preparation and characterization of nano-TiO_2 (as anatase phase) and preliminary tests for methylene blue (MB) degradation. Thus, based on these results future nano-TiO2 materials will be developed in order to increase efficiency and degradation time, including visible conditions.

2. Materials and methods

To obtain titanium dioxide, the sol-gel method was applied, using the following reagents: PVP (polyvinylpyrrolidone), MW 1,300,000, Ethyl alcohol purity 99.5% and Titanium chloride ($TiCl_4$) M = 189.68 g / mol. 0.45 grams of PVP (polyvinylpyrrolidone) was dissolved in 10 ml of ethyl alcohol to form a gel. 1 ml of $TiCl_4$ was added dropwise. The reaction was carried out at room temperature for 30 minutes to form a homogeneous solution. In a porcelain crucible this solution was heat treated at 550 °C to evaporate water, remove PVP and form TiO_2. For the characterization of nanostructured TiO_2, with emphasis on the main structural and morphological properties responsible for the photodegradation process, were used scanning electron microscopy (SEM) techniques, X-ray diffraction spectrometry and atomic force microscopy (AFM). The evaluation of the efficiency of the nanostructured material was performed in the presence of a dye that was degraded to UV light.

3. Results and discussion

Material formation

Applying the sol-gel method, titanium dioxide was made (Fig.1), which was subsequently heat treated.

Fig. 1. Titanium dioxide solution

Material characterization

To identify the structure and purity of the product synthesized in the form of TiO_2, X-ray diffraction (XRD) investigations were performed. Thus, the X-ray diffraction identified as a single phase TiO_2 in the form of anatase according to Fig. 2, due to the thermal process that took place at 550 °C.

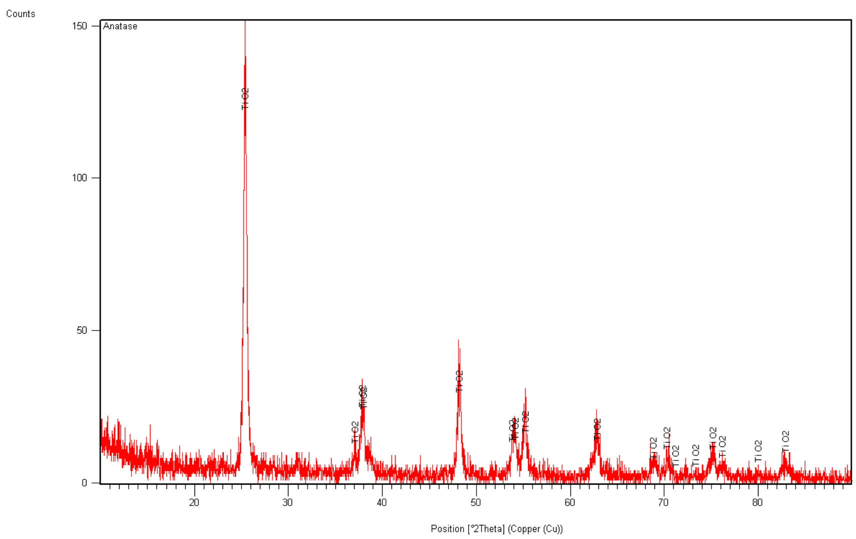

Fig. 2. X-ray diffraction graph

The validation of the diffraction performed was performed by comparing with the product sheet the characteristic of the anatase, according to the existing database [10]. According to the Debye-Scherrer ratio (1), the average crystallite size of TiO_2 powder is approximately 11.29 nm.

$$\tau = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

The surface characteristics of the synthesized powder were determined by atomic force microscopy analysis. TiO_2 was identified as an agglomeration of fine particles with heights above 6 nm (Fig. 3)

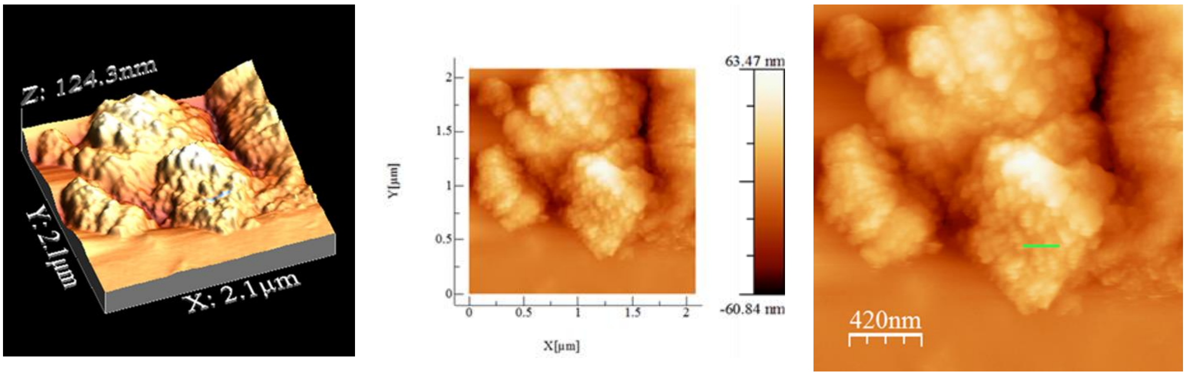

Fig. 3. SEM images obtained for TiO_2 samples obtained by the sol-gel method

Morphology and structural characteristics were determined by scanning electron microscopy (SEM) coupled with dispersive energy spectroscopy (EDS). SEM analysis indicates at magnifications of 60.000 x and 120.000 x ordered agglomerates of spherical TiO_2 particles of average dimensions of 26 nm (Fig 4). The sizes indicated that the nanoparticles were agglomerated and the values are in accordance with crystallite size from XRD analysis.

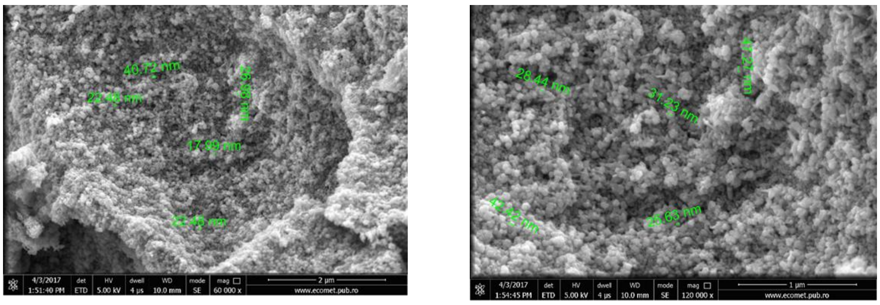

Fig. 4. SEM analysis at magnification of 60.000 and 120.000 x

The EDS analysis aimed to identify the majority elements on the analyzed surface, as well as to distribution them (Fig 5).

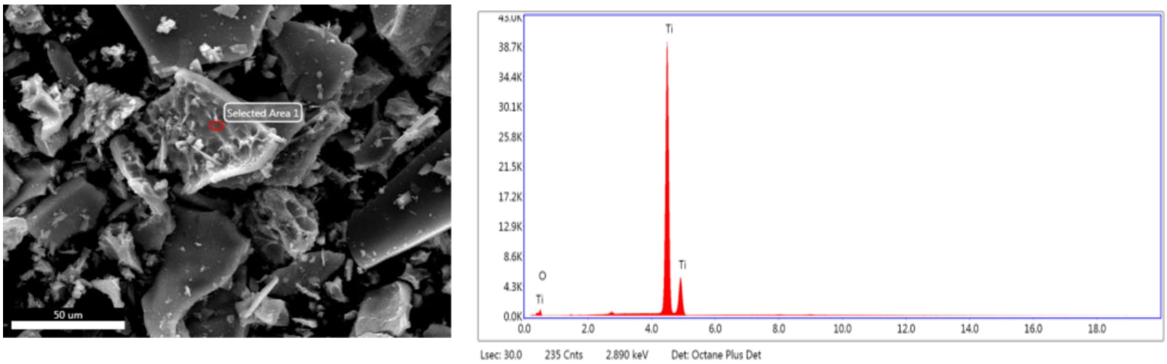

Fig. 5. Surface analysis

Ti and O are evenly distributed on the surface, thus explaining the formation of TiO_2, thus validating the previous results of XRD and SEM type investigations (Fig. 6)

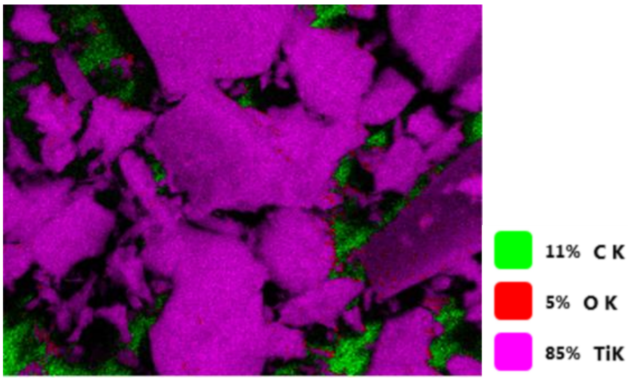

Fig. 6. Distribution of elements for the TiO_2 sample

To evaluate the effectiveness of the material, a dye present in the wastewater of the chemical industry was used, namely MB [11]. It was degraded under UV light in the presence of nano-TiO_2. A 100 mL sample with a methylene blue content between 0.1 and 0.2 mg/L which was treated with 0.2 g TiO_2, was analyzed. After thirty minutes, a 100 ml sample was taken, which was analyzed on a UV-Vis spectrometer.

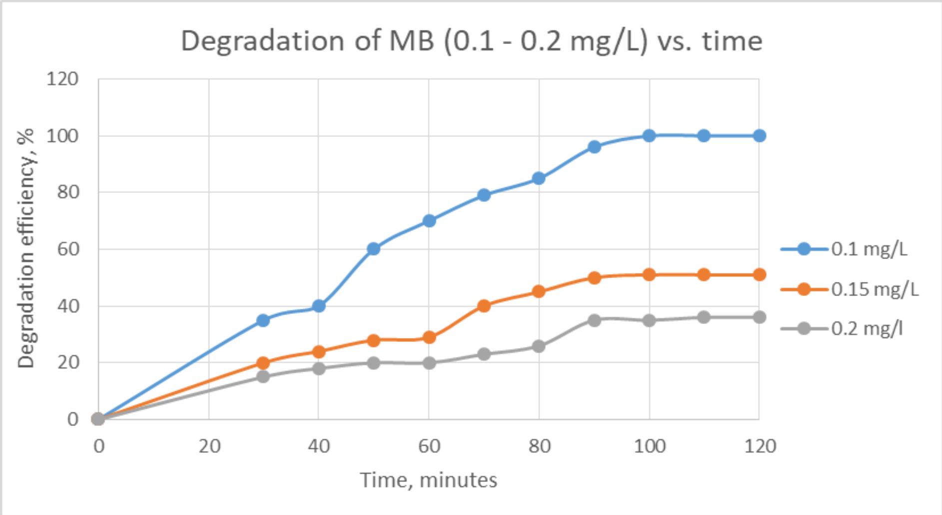

Fig. 7. Graph of dye degradation

The results are an average of three replicates (Fig. 7). The efficiency of using such particles in powder form in the photocatalytic degradation of MB, indicated a degree of degradation of 100% in case of 0.1 mg/L methylene blue, with the following order of degradation: 100% (0.1 mg/L) > 50% (0.15 mg/L) > 30% (0.2 mg/L)

According to the literature, methylene blue was successfully degraded when TiO2 nanoparticles are used, the final degradation (100% efficiency) is being achieved after few hours [12]. Also, the literature indicates the micro-and nano-scale design of TiO_2 nanoparticles and doping process improved time of degradation and efficiency [12, 13, 14]. Based on these results next steps will consist in development of such structures.

4. Conclusions

In the present paper, the classical sol-gel method was used to obtain titanium dioxide nanoparticles. In X-ray diffraction (XRD) investigations, a single phase of TiO_2 in the form of anatase was identified. The particle size obtained, and their morphology were identified by microstructural analyzes. SEM analysis indicates at magnifications of 60.000 x and 120.000 x ordered agglomerates of spherical TiO2 particles of average dimensions of 26 nm. Ti and O are evenly distributed over the surface of the analyzed sample. The efficiency of using such particles in powder form in the photocatalytic degradation of dyes (such as MB), indicated a degree of degradation of 100%. Given the results obtained using TiO_2 nanoparticles in the degradation of methylene blue dye, future research directions will be to develop a working protocol on the use of this nanomaterial in real waters containing organic pollutants, to study the photocatalysis capacity under conditions of chemical interference and dynamic working regime and will be focused on kinetics mechanism, recovery efficiency of nano-TiO_2 from system.

Acknowledgment

This research was supported by Doctoral Studies Contract no 11/19/05.10.2020

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