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THE IMPACT OF MULTIWALL CARBON NANOTUBES ON THE PHOTOCATALYTIC PROPERTIES OF IMOBILIZED TiO₂

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Preliminary note

Abstract

Industry development, Earth's population growth, ever increasing need for greater pharmaceuticals production causes irreversible changes in the environment. Photocatalysis is a process that leads to complete decomposition of pharmaceuticals to non-hazardous degradation products under the influence of solar radiation in the presence of a photocatalyst. A photocatalyst, such as titanium dioxide (TiO₂), is required for photocatalysis. The efficiency of using TiO₂ is limited due to the high energy banned zone (3-3.2 eV) so only UV-A light, which makes up 5% of solar radiation, activates the photocatalyst. In order to overcome the problem of prohibited zones and to shift the light response threshold of TiO₂ into the visible part of the spectrum, different methods can be used. One of the methods showing the potential is the use of multiwall carbon nanotubes (MWCNT).

In this paper a TiO₂ / MWCNT composites with various concentrations of MWCNT were prepared. The concentrations of MWCNT ranged from 1.5, 5, 10, 25, 50 and 100 wt. % MWCNT relative to the mass of TiO₂. It was observed that the concentration of MWCNT affects the photocatalytic activity of the composite obtained. Photocatalytic activity was followed by a degradation of salicylic acid, in a pilot reactor followed by UV-Vis spectrometry, as a model solution and an example of a pharmaceuticals present in the water. The prepared catalysts were characterized by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

Keywords: photocatalysis, TiO₂, multiwall carbon nanotubes

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INTRODUCTION

Environmental pollution and destruction are very serious problems [1]. Quality of water available for human use is increasingly deteriorated due to anthropogenic activities. Much of the pharmaceuticals used for treatment or as dietary supplements are not fully metabolized in the human body, and the vast majority of these endpoints end up in the environment. It has been found that pharmaceuticals are present in waste water after treatment also found in lakes and rivers, groundwater and drinking water. Except for wastewater, pharmaceuticals can enter the environment in a variety of ways, including disposal of unused medicines, waste disposal sites, veterinary use and fertilizer application and waste sludge from the wastewater treatment process in agriculture [2]. Conventional drinking water preparation techniques utilize physical-chemical processes to eliminate pathogens, reduce turbidity, and control taste and odor problems. These processes have a partial impact on reducing the contamination of micropollutant in ready to drink water, but incomplete, need to find new economically viable methods [3]. Two process of purification of micropollutants are used in the industrial process, which, due to their cost, requires finding new cheaper solutions. One of the solutions is an advanced oxidation process of photocatalysis where complete degradation of pollutions. Photocatalysts are used for this purpose and one of the most common is titanium (IV) oxide (TiO_2) due to their low cost, chemical and thermal stability, low toxicity and relatively high catalytic activity [4-6]. UV radiation of TiO_2 photocatalysts create hydroxyl radicals, $\bullet\text{OH}$ [7] which, as non-selective oxidants, with its oxidation potential almost completely degrade the organic matter into water and CO_2 [8,9]. Because of that fact, TiO_2 photocatalysis has recently found application to wastewater treatment [10]. Although TiO_2 is most often used in suspended form, the catalyst immobilization is considered to be more useful for easier removal of TiO_2 from the system and the ability to reuse the immobilized catalyst [11]. The efficiency of using TiO_2 is limited due to the high energy banned zone (3-3.2 eV) which causes only UV-A lights, which makes up 5 % of solar radiation to activate the photocatalyst. In order to overcome the problem of banned zones and to shift the light response threshold of TiO_2 into the visible part of the spectrum, different methods can be used. One way is to use chemical methods such as coupling with secondary semiconductors, photosensitizing and doping with transitional metals (Au, Pd, Pt, Rh) or non-metallic elements (N, S, I, F). Another way is to use physical methods such as introducing microwave or ultrasonic radiation into the photocatalysis process. The method of catalyzing the activity of the catalyst for which the scientists show an increasing interest is the use of carbon nanotubes, multiwall nanotube (MWCNT) and graphene. Significant efforts are directed towards obtaining TiO_2 / carbon nanotubes and TiO_2 / graphene composite materials. For the synthesis of the composite, the sol-gel process, the physical mixing technique and the nano-application can be used [12-14]. In this paper a TiO_2 / MWCNT composites with various concentrations of MWCNT were prepared with sol-gel method. The photocatalytic properties and morphology of the immobilized layer of the photocatalyst will be determined.



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MATERIALS AND METHODS

Multiwall carbon nanotubes (MWCNT), Chengdu Organic Chemicals, P.R. China with outer diameter of 10 – 30 nm, TiO₂, Aeroxide® P25, Evonik, Germany, tetraethoxysilane (TEOS), VWR Cematic, USA, acetic acid from VWR Chemicals, France, salicylic acid (SA), Kemika Croatia and ethanol, GramMol, Croatia used as received. As a carrier the glass mesh from Keltex, Croatia (CM 300/300, $\rho = 610 \text{ g / m}^2$) was purchased.

TiO₂ and MWCNT is applied to the glass mesh using sol-gel method, for the preparation of the immobilized layer. Glass meshes are cut into the reactor's dimension and weighed. The suspension from which TiO₂ and MWCNT is applied to the glass mesh is prepared by mixing TiO₂ and MWCNT with distilled water and ethanol (water: ethanol = 1 : 1) on a magnetic stirrer. Six different solutions with different concentrations of MWCNT were produced. The concentrations of MWCNT ranged from 1.5, 5, 10, 25, 50 and 100 wt. % MWCNT relative to the mass of TiO₂. The pH of the suspension was adjusted by adding acetic acid with stirring to pH 1.5-2. After achieving the desired pH, the suspension was mixed for a period of 15 minutes, after which the homogenization was performed with ultrasound for 6 minutes (ultrasonic bath 120W, frequency 40 kHz). After homogenization, TEOS was added and further stirred over a period of 60 minutes at a temperature of 50 °C. Glass mesh is immersed in the prepared suspension and dried. Drying was carried out in a 70 °C drier for 30 minutes. The immersion and drying procedure was repeated 4 times. Schematic illustration of preparing immobilized layer on glass mesh is shown on Figure 1. The prepared glass meshes were left in air for 7 days, after which they were washed with distilled water, dried and weighed to determine the mass of the applied layer. Clean meshes and meshes with TiO₂ / MWCNT obtained by the described procedure were recorded by scanning electron microscope (SEM, TESCAN VEGA 5136MM) operated at 20kV. The presence of TiO₂ and/or MWCNT on fiber glass mesh was determined by using energy dispersion spectroscopy (EDX) mapping analysis. For mapping analysis SEM microscope was operating at 20 kV while working distance was set at 20 mm. Mesh for SEM / EDX analysis were previously fixed to the carrier using double-sided self-adhesive carbon-guided stripes and a gold-platinum layer. The photocatalytic properties of the catalyst were investigated through the degradation of salicylic acid in the prepared 0.2 mmol / dm³ model solution. The UV-VIS spectrophotometer (Perkin Elmer LAMBDA 35, 200-700 nm with a recording speed of 480 nm / min) was used to monitor the photocatalytic degradation reaction. Tests for photocatalytic properties were carried out in a batch pilot photoreactor of rectangular geometry (size 4.5 x 17.5 cm) with recirculation with peristaltic pumps with a flow rate of 48 cm³ / min. The source of the simulated solar radiation (UV-B 2% / 13 W) is placed 7 cm above the surface of the reaction solution and is covered with a shadow / reflective surface of Al-sheet in order to evenly illuminate the reactor space.

The immobilized photocatalyst meshes were placed at the bottom of the reactor and a model solution of SA 100 cm³ was added. At the beginning of the procedure, a sample of SA 2 cm³ was taken, after which the reactor was left in the dark for 30 minutes and the sampling was repeated. At the end of the phase in the dark, the source of the simulated solar radiation was included, and the samples were taken periodically 15, 30, 60, 90 minutes. Also, tests of a

blank probe without a catalyst, that is, the influence of light radiation on the potential photolysis of salicylic acid, were conducted.

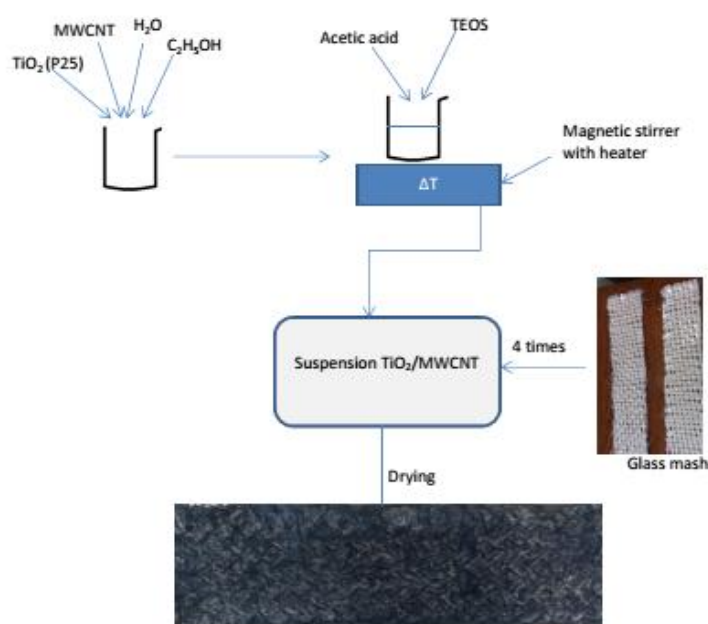


Figure 1. Schematic illustration of immobilization TiO_2 / MWCNT on glass mesh

RESULTS AND DISCUSSION

To demonstrate the immobilized of TiO_2 and TiO_2 / MWCNT composite on the surface of glass mesh samples were recorded with SEM (Figure 2) after photocatalysis.

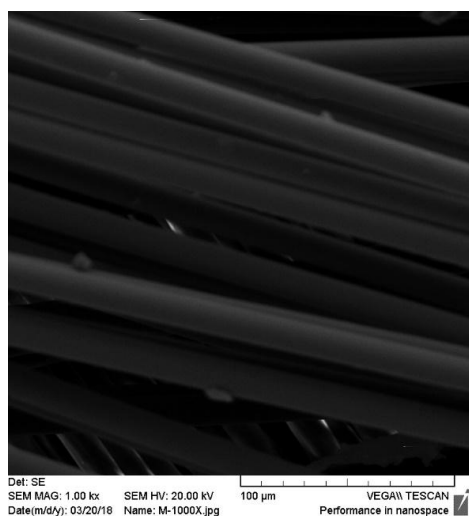
Comparing Figures 2a, 2b and 2c it can be concluded that TiO_2 and TiO_2 / MWCNT immobilization on glass mesh with sol-gel methods was successful. Furthermore, from Figures 2b and 2c it can be seen that particles are of similar size. The presence of TiO_2 / MWCNT was determined by EDX analysis on the glass meshes after immobilization. Results of EDX analysis showed on Figure 3. On Figures 3b it can see results EDX analysis where showed presence TiO_2 and carbon. Presence of carbon is results of immobilization MWCNT.



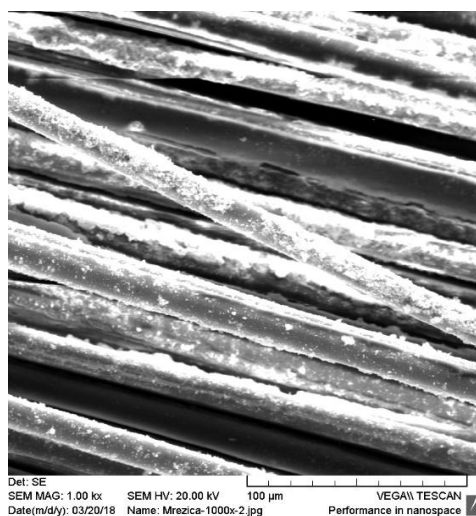
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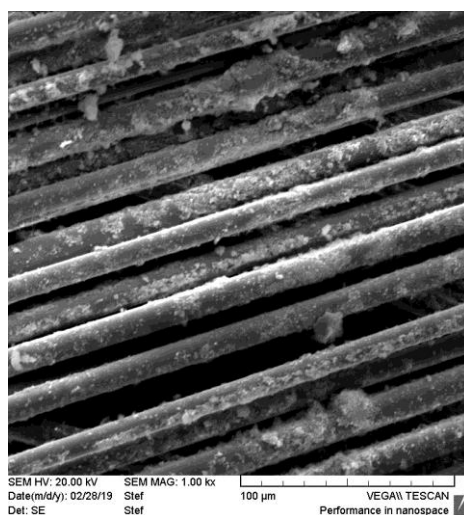
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(a)



(b)



(c)

Figure 2. SEM images: (a) clean glass mesh, (b) glass mesh with TiO₂,
(c) glass mesh with TiO₂ / MWCNT



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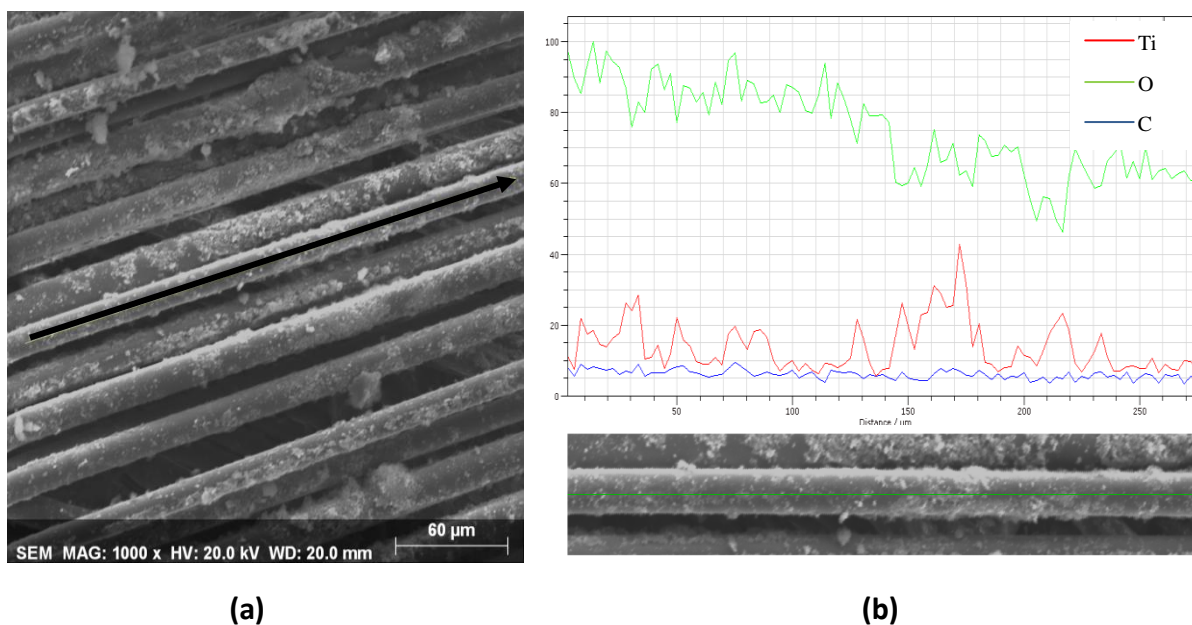


Figure 3. (a) SEM image for EDX analysis, (b) results EDX analysis

The photocatalytic properties were carried out in a batch pilot photoreaction with recirculation were investigated through the degradation of salicylic acid (SA). On Figure 4 is show degradation of SA with TiO_2 and TiO_2 / MWCNT composites with various concentrations of MWCNT.

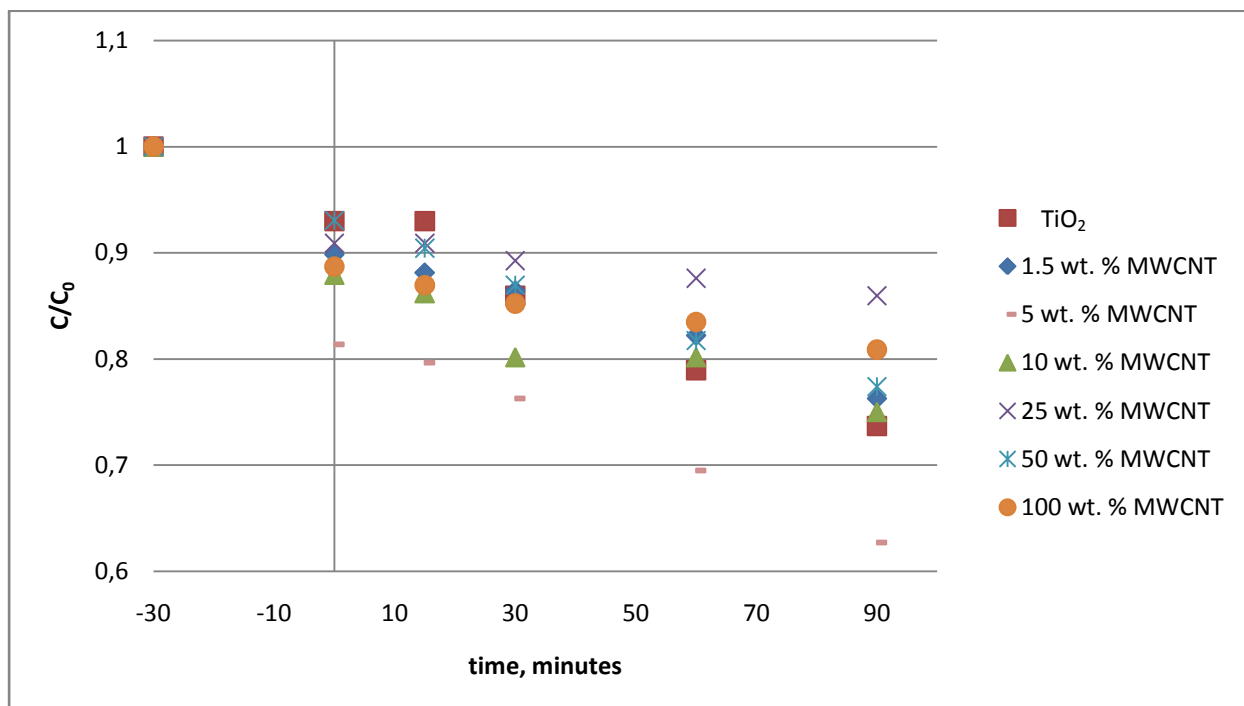


Figure 4. Photocatalytic degradation of SA over TiO_2 and TiO_2 / MWCNT under visible light irradiation



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Results are given as normalized SA concentration vs irradiation time. Negative time is the time spent in the dark for the decrease of the concentration resulting from adsorption to the photocatalyst as described in the chapter of materials and methods.

Comparing the results of the photocatalytic degradation of salicylic acid it is concluded that it is the best result achieved when using the composite TiO₂ / MWCNT with 5 wt. % MWCNT concentrations while the weakest degradation when using the composite with higher concentrations MWCNT. Comparing the results of the photocatalysis with the mass of the immobilized layer (Table 1), it can be seen that photocatalysis doesn't depend on the mass of the immobilized layer but on the concentration of MWCNT.

Table 1. Mass of immobilization layer

| Concentrations of wt.% MWCNT | m (glass mesh clean)/ g | m (glass mesh + TiO ₂ /MWCNT)/g | m (immobilization layer)/g |
|------------------------------------|----------------------------|---|----------------------------------|
| 0 | 5.7764 | 5.9781 | 0.2017 |
| 1.5 | 6.4251 | 6.6492 | 0.2241 |
| 5 | 4.5922 | 4.8158 | 0.2236 |
| 10 | 5.9035 | 6.1226 | 0.2191 |
| 25 | 7.5188 | 7.6999 | 0.1811 |
| 50 | 5.7496 | 6.1090 | 0.3594 |
| 100 | 5.4641 | 5.9050 | 0.4409 |

CONCLUSIONS

In this paper a new photocatalysts, glass meshes with the immobilized TiO₂ and TiO₂ / MWCNT with various concentrations of MWCNT, were prepared and subsequently compared. The concentrations of MWCNT ranged from 1.5, 5, 10, 25, 50 and 100 wt. % MWCNT relative to the mass of TiO₂. After preparation, photocatalytic properties were investigated through the degradation of salicylic acid in pilot reactor. Comparing the results of the photocatalysis it was concluded that the best result is achieved using the composite TiO₂ / MWCNT with 5 wt. % MWCNT.

After photocatalysis, SEM and EDX analysis of prepared photocatalysts demonstrated the presence of TiO₂ and MWCNT on glass meshes that confirm the stability of immobilized TiO₂ and TiO₂ / MWCNT.

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