



Doping titanium dioxide with palladium for enhancing the photocatalytic decontamination and mineralization of a refractory water pollutant

M. Harja, A.-M. Sescu, L. Favier, D. Lutic

► To cite this version:

M. Harja, A.-M. Sescu, L. Favier, D. Lutic. Doping titanium dioxide with palladium for enhancing the photocatalytic decontamination and mineralization of a refractory water pollutant. *Revista de Chimie*, 2020, 71 (7), pp.145-152. <10.37358/RC.20.7.8232>. <hal-02960236>

HAL Id: hal-02960236

<https://hal.science/hal-02960236v1>

Submitted on 12 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Doping Titanium Dioxide with Palladium for Enhancing the Photocatalytic Decontamination and Mineralization of a Refractory Water Pollutant

MARIA HARJA¹, AMALIA-MARIA SESCU¹, LIDIA FAVIER^{2*}, DOINA LUTIC^{3*}

¹Technical University of Iasi Gheorghe Asachi", Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 73 Prof. dr. docent Dimitrie Mangeron Str., 700050, Iasi, Romania

²Universite Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

³University of Iasi "Alexandru Ioan Cuza", Faculty of Chemistry, 11 Carol I Blvd., 700506, Iasi, Romania

Abstract: The photocatalytic performance of a commercial TiO₂ doped by incipient wet impregnation with palladium (sample named TiO₂-Pd), was evaluated in the heterogeneous degradation process using as test molecule the clofibric acid (CA), a metabolism product of a drug used as blood lipid regulator. The catalyst was characterised by XRD, SEM and UV-VIS reflectance spectroscopy. The photocatalytic potential of this new catalyst was evaluated at laboratory scale under UV-A irradiation conditions. The influence of a few key parameters was studied in order to optimize the process conditions. The results shown that TiO₂-Pd can completely remove the target pollutant under the optimal conditions (0.2 g/L catalyst, 5 mg/L CA, 6.2 mW/cm² irradiation flux). Moreover, the CA mineralization was evaluated by TOC and a 65% mineralization yield was obtained, confirming the good photocatalytic activity of TiO₂-Pd.

Keywords: Pd-doped TiO₂, clofibric acid, parametric study, mineralization

1. Introduction

Over the last years, there is an increasing interest for the removal of persistent organic compounds found in very low amounts in the wastewaters, due to their dangerous potential to modify the normal equilibrium of the water biota. The pharmaceutical compounds and their metabolites are of highest importance in this respect. Their occurrence in waters have strong negative effects on human health and on the aquatic ecosystems [1, 2].

Clofibric acid's (CA) IUPAC name is 2-(4-chlorophenoxy)-2-methylpropanoic acid (Figure 1). In pure state, CA is used as herbicide and as plant-growing controlling agent, having an opposite effect than the auxins. CA also appears in the human body as a metabolite of clofibrate, a pharmaceutical compound used as cholesterol lowering agent, and thus arrives after excretion in the wastewaters. This molecule attracted an increased attention of the scientific community due to its low biodegradability and long persistency in the environment [3].

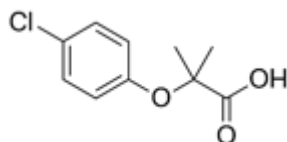


Figure 1. Chemical structure of clofibric acid

The conventional biological wastewater treatments are unable to eliminate completely this water pollutant, therefore, efforts are made in order to find new, cheap and efficient technologies in this respect [4]. Thus, advanced oxidation processes (AOPs) appear to be very promising techniques for the removal of organic pollutants. AOPs include ozonation [5], heterogeneous photocatalysis [6], Fenton and photo-Fenton reactions [7], sonolysis [8], electrochemical oxidation [9].

*email: lidia.favier@ensc-rennes.fr, doilub@uaic.ro

All these technologies are based on the generation of strong oxidants species, such as the free HO^\bullet radicals, which are aggressive enough to react with the organic compounds, even if present in low concentrations in wastewater, and mineralize them into harmless molecules [10].

Heterogeneous photocatalysis is one of the most interesting techniques, due especially to its relatively low cost and simple setup, using in most cases TiO_2 as photocatalyst. When irradiated with radiation of proper energy, the photocatalyst generates electron-hole pairs, which react with water and dissolved oxygen, to further produce hydroxyl radicals (HO^\bullet) [11]. TiO_2 is widely used for its great advantages such as: high catalytic activity, low cost, lack of toxicity, good stability in aqueous systems and readily availability [12]. On the other hand, TiO_2 has a major drawback regarding the high recombination rate of electron-hole pairs, which lower its effectiveness. Thus, a challenging purpose of material scientists is to enhance the activity of TiO_2 by doping it noble metals [13-15].

In this work, incipient wet impregnation method was employed to dope TiO_2 with palladium. The product was characterized using the common methods (XRD, SEM, UV-DR) and the photoactivity was investigated in the photodegradation of CA. In addition, the influence of some operating parameters on the reaction performance was studied, in order to define an optimal set of conditions.

2. Experimental part

2.1. Chemicals

TiO_2 with an anatase content of >98%, used in this work, was acquired from Acros Organics. Palladium chloride (PdCl_2) was purchased from Sigma Aldrich and used as Pd precursor. Hydrochloric acid (37%) and absolute ethanol (EtOH) were supplied by Silal Trading and Sigma-Aldrich, respectively. Clofibric acid (CA) used as a model pollutant was purchased from Acros Organics and used without any further purification.

2.2. Catalyst preparation

Pd-doped TiO_2 ($\text{TiO}_2\text{-Pd}$) was obtained via a simple incipient wetness impregnation (IWI) method, thus modifying the commercial TiO_2 . In a first step, 4 g of TiO_2 was dehydrated in a crucible in an oven, for at least 2h, at 200°C . Subsequently, the dopant solution prepared in concentrated HCl and EtOH (obtained by dissolving the proper amount of PdCl_2 corresponding to a Pd 0.5% molar ratio with respect to TiO_2) was rapidly poured onto the hot solid and the crucible was covered with a lid. Afterwards, the product was dried at room temperature, then calcined at 600°C for 4h ($1^\circ\text{C}/\text{min}$ heating rate). The obtained solid was further characterized and tested in the photocatalytic degradation of CA. Figure 2 shows the main steps of the catalyst preparation.

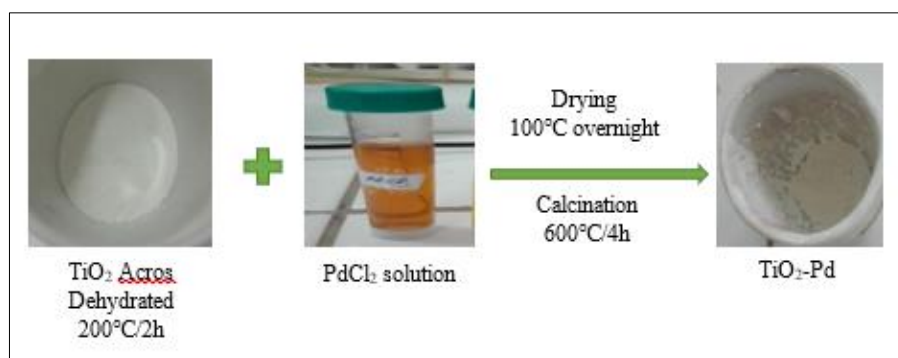


Figure 2. Schematic diagram illustrating the IWI procedure

2.3. Catalyst characterization

The morphology of the obtained catalyst was investigated by using a JEOL JSM 7100 F EDS EBSD Oxford microscope. UV-DR spectra were obtained with a Shimadzu 1700 device. The XRD patterns were obtained on a Shimadzu D6000 system, under $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

2.4. Photocatalytic tests

The photocatalytic performance of the catalysts was determined in the degradation of CA. The influence of some key parameters on the process, such as the effect of UV irradiation, the role of preliminary CA adsorption on the solid and the effect of CA concentration were investigated as well.

The experiments were carried out in a batch reactor with a working volume of 1 L, with internal irradiation, performed using a mercury vapor lamp (with maximum emission wavelength at 365 nm) and magnetic stirring. The tests were conducted at ambient temperature and at the native *pH* of the CA solution. The CA solutions were prepared daily, by dissolving a specific amount of CA in ultrapure water. Before the irradiation, the CA solution containing the photocatalyst was stirred in the dark for 30 min, in order to reach adsorption-desorption equilibrium. For the photocatalytic assays, an irradiation time of 110 min was considered. Aliquots samples were withdrawn at established reaction time intervals and filtered through 0.45 μm syringe filter to remove the catalyst. The residual concentrations of the solutions were analyzed by HPLC and the mineralization yield was monitored by TOC.

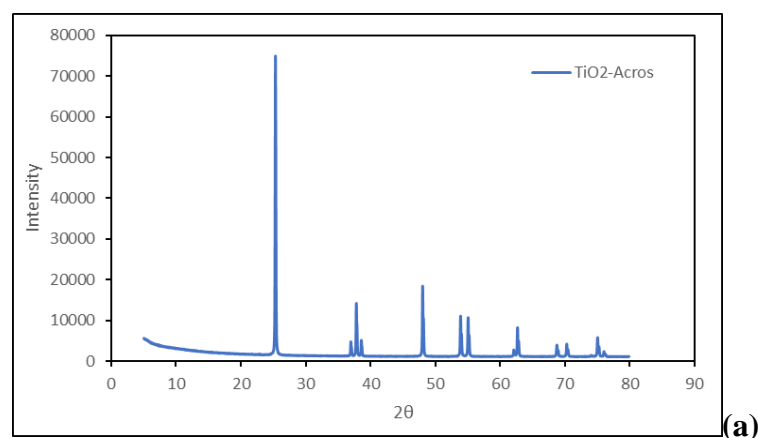
2.5. Sample analysis

The residual CA concentrations from the samples were measured by high performance liquid chromatography (HPLC) using a WATERS® system with a photodiode array detector (WATERS™ 996). The mobile phase consisted of a mixture of 60% acetonitrile and 40% ultrapure water. The detection of CA was performed by measuring the absorbance at 227 nm and its retention time was around 6.4 min. In order to monitor the mineralization of CA, the total organic carbon was traced during the photocatalytic tests, using a Shimadzu TOC-5000-A device.

3. Results and discussions

3.1. Material characterization

The crystalline character of the samples was highlighted by tracing the XRD patterns (Figure 3). The patterns are very similar for both samples, displaying the main maxima specific for pure anatase phase. The very sharp peaks and smooth baseline unveil high crystalline materials. The maxima situated at 2θ diffraction angles of 25° , 38° , 48° , 54° , 55° , 62.7° and 68.8° , can be indexed, respectively, to the characteristic planes of anatase (101), (004), (200), (105), (211), (204) and (116), in agreement with the standard pattern (JCPDS no. 84-1286). The low degree of doping did not allow to detect diffraction characteristics due to the presence of palladium, suggesting its presence as nanoparticles on the surface.



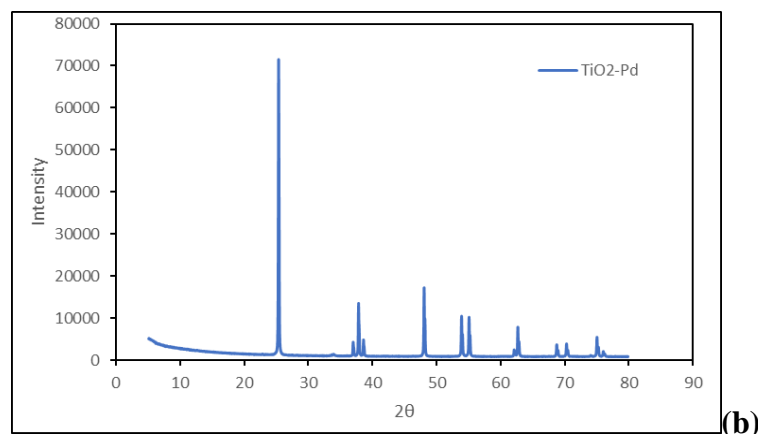


Figure 3. XRD patterns of (a) commercial TiO₂-Acros, (b) TiO₂-Pd

This fact is supported by the values of the particle size, calculated using the Debye-Scherrer equation:

$$D_{\text{cryst}} = 0.94 \lambda / (h_{1/2} \cos \theta_{hkl}) \quad (1)$$

where λ is the CuK α wavelength, $h_{1/2}$ is the width at the half peak height of the most intense peak due to the (hkl) diffraction plane.

The values found were 55.66 nm for pure TiO₂ and 55.98 nm for TiO₂-Pd; there is only a very slight particle size increase as an effect of the dopant.

The bare TiO₂ is a white powder, while TiO₂-Pd is slightly grey, illustrating a change of catalyst surface and its optical properties. The UV-DR spectra (Figure 4) allowed the calculation of the band gap, by the extrapolation of the linear portion of the spectrum and identifying the x-axis crossing value. A slightly change in the band-gap from 3.2 eV in the case of TiO₂, to 2.98 eV in the case of TiO₂-Pd, was observed.

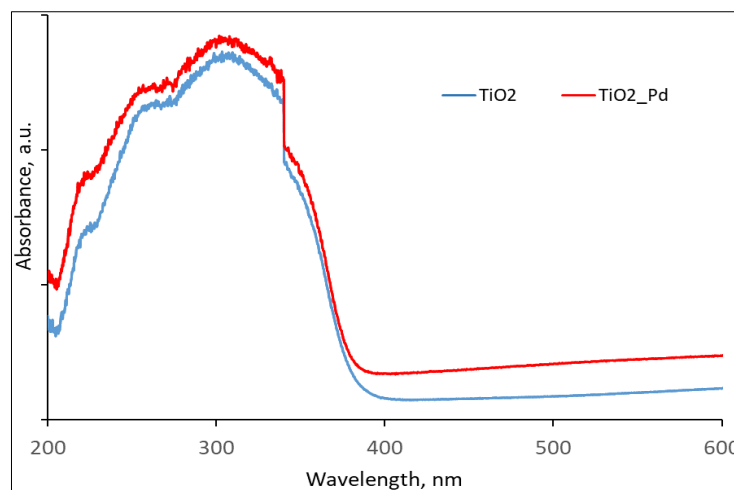


Figure 4. UV-DR spectra of TiO₂-Acros and TiO₂-Pd

The morphology of the doped catalyst highlighted by SEM (Figure 5) reveals that the sample consists of agglomerations of particles having quite irregular shapes with many edges, but relatively uniform sizes of 3-4 μm . The elemental mapping (Figure 5b) for TiO₂-Pd sample indicate the uniform dispersion of the Pd particles on TiO₂ surface, supporting the XRD data which indicate the lack of peaks due to Pd metal phase.

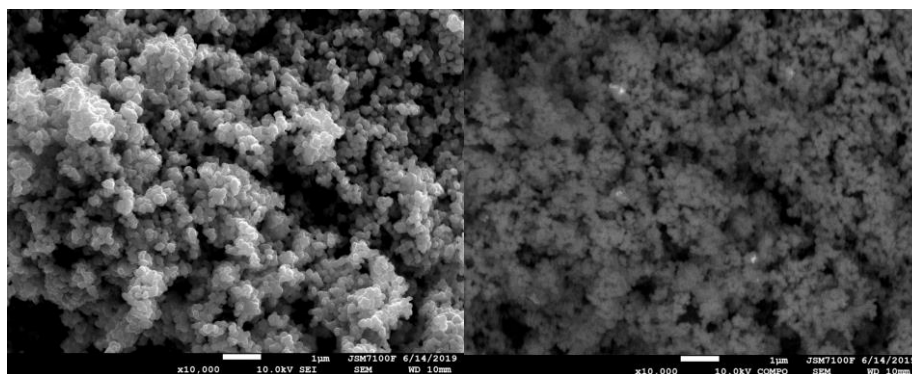


Figure 5. SEM images a. $\text{TiO}_2\text{-Pd}$ sample light field
b. Pd mapping of $\text{TiO}_2\text{-Pd}$

3.2. Photocatalytic activity

The activity of $\text{TiO}_2\text{-Pd}$ was tested in the heterogeneous photocatalysis process for the degradation of CA. In order to prove that associating the UV irradiation and the use of a photocatalytic solid is really necessary, blank tests were performed preliminarily. The blank tests made by measuring the CA concentration after the solid was simply stirred for 110 min in CA solution, without irradiation and, respectively, by applying the UV-light without photocatalyst addition under simple stirring, for the same duration. These blank tests, as well as a complete photocatalytic experiment, were carried out at an initial CA concentration of 25 mg/L, a catalyst loading of 0.2 g/L and an irradiation flux of 6.2 mW/cm^2 .

Palladium had been reported in literature as a reliable disinfection agent against *E. coli* AN 387, when used as dopant on N-doped TiO_2 , and the mechanism for this behavior was explained by the decrease of the electron-hole recombination rate. Furthermore, the XPS study revealed that palladium is present in the metallic form on the surface [16]. Therefore, in an eventual practical application, palladium brings not only an improvement of the photocatalytic activity, but also a valuable biological decontamination, highly desirable for the advanced wastewater treatment.

In Figure 6 are displayed the results from the CA removal by photolysis (UV light), adsorption procedure without irradiation ($\text{TiO}_2\text{-Pd}$ /dark) and under photocatalysis conditions ($\text{TiO}_2\text{-Pd}$ and UV-A light). The data indicate that the adsorption in dark and the photolysis alone could remove only low amounts from the initial CA; after a run time of 110 min, the pollutant removal was only 3% by the adsorption on the solid and respectively of 5% by photolysis. In contrast, the complete removal of the pollutant was achieved when the photocatalytic process was run, in 110 min. This result is in line with the similar effect for the removal of phenol [17] and of methyl orange dye [18], using pure and modified TiO_2 .

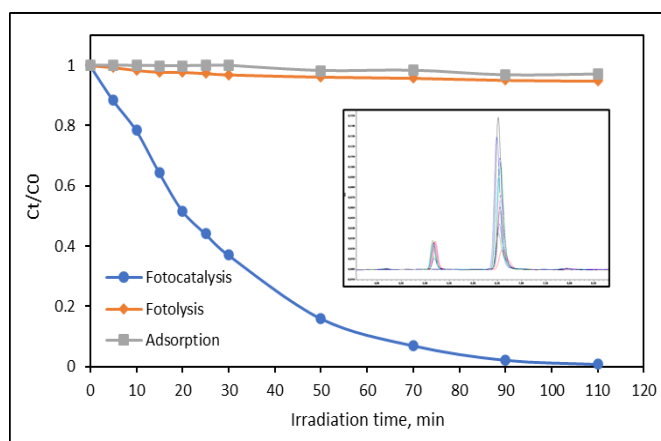


Figure 6. CA degradation by photocatalysis ($\text{TiO}_2\text{-Pd}$ /UV light), photolysis (UV light) and adsorption. (initial CA concentration = 25 mg/L; $\text{TiO}_2\text{-Pd}$ = 0.2 g/L; irradiation flux = 6.2 mW/cm^2)

3.2.1. Influence of the initial CA concentration

The initial pollutant concentration is one of the key parameters that influence its photocatalytic degradation, due on one part, on the transparency of the solution in the UV range and, on another part, on the adsorption of the organic compound on the solid, which competes for the holes from the valence band with water molecules. The tests were conducted at initial CA concentrations of 5 mg/L and 25 mg/L and the same 0.2 g/L of catalyst and irradiation flux of 6.2 mW/cm². As expected, the results shown in Figure 7 prove that the CA degradation yield is lower when the initial solution concentration is higher. However, the efficiency of the photocatalyst is noticeable, since for a decrease by 50% of the initial CA concentration ($C_t/C_0 = 0.5$), the time difference between the two solutions used in the test, having the concentrations ratio of 5 relative to each other, is revealed to be of only 5 min. When the concentration of the organic compound is higher, a strong competition occurs between this molecule absorbed on the photocatalyst surface and the water molecules, which are an important source of HO• radicals delivery, they being the key species in the initiation of organic molecules degradation [19].

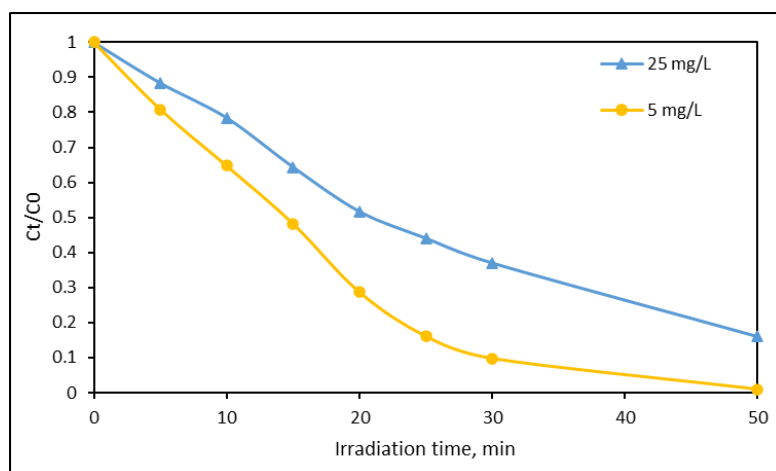


Figure 7. Effect of CA initial concentration on its degradation in presence of TiO₂-Pd (0.2 g/L) at an irradiation flux of 6.2 mW/cm²

Further, the TiO₂-Pd mineralization potential of the target pollutant was evaluated by TOC. The results (Figure 8) show that the mineralization efficiency is much higher for an initial CA concentration of 5 mg/L (65% mineralization yield), compared to 32% in the case of 25 mg/L CA, during 110 min.

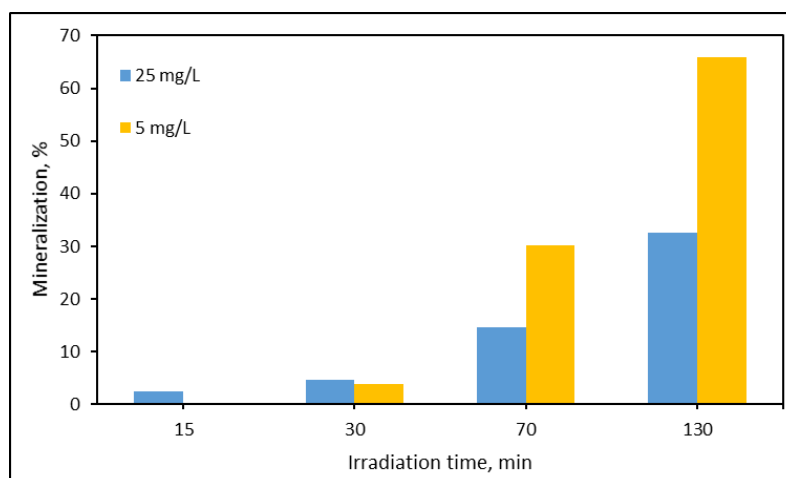


Figure 8. CA mineralization at different irradiation times in presence of TiO₂-Pd (0.2 g/L) at an irradiation flux of 6.2 mW/cm²

These results confirm the high activity of TiO₂-Pd in the fragmentation and quite high mineralization extent of CA. The heterogeneous photocatalysis is a suitable tool for the elimination of organic pollutants from water, especially when their concentrations are very low. The fact that the mineralization is high at higher concentrations makes the heterogeneous photocatalysis on this material a potential practical strategy to remove trace pollutants with high efficiency from wastewaters.

4. Conclusions

A photocatalytic process was used for the advanced removal of clofibric acid (CA) from diluted solutions (ppm to tens of ppm range), using the commercial TiO₂ from Acros, doped with Pd by incipient wet impregnation. CA is a non-biodegradable compound reaching wastewater either from pesticides or from drugs.

The CA molecule splitting from a 25 ppm solution in the presence of 0.2 g/L Pd-TiO₂ and under UV irradiation proved by HPLC was complete after 110 min, while the mineralization degree after 130 min reached 32%. When a solution of 5 ppm was used for the tests, the complete fragmentation of the molecule occurred in 50 min, while the mineralization reached 65% after 130 min.

These results show that the performance of the photocatalyst makes it suitable especially for the removal of rebel toxic organic species found in traces in water.

References

1. GOGOI, A., MAZUMDER, P., TYAGI, V. K., CHAMIDA, G. T., AN, A. K., KUMAR, M, Occurrence and fate of emerging contaminants in water environment: a review, *Groundwater for Sustainable Development*, **6**, 2018, 169-180.
2. FAVIER, L., RUSU, L., SIMION, A. I., HLIHOR, R. M., PACALA, M. L., AUGUSTYNIAK, A, Efficient degradation of clofibric acid by heterogeneous photocatalytic oxidation process, *Environmental Engineering and Management Journal*, **18**(8), 2019, 1683-1692.
3. DORDIO, A. V., DUARTE, C., BARREIROS, M., CARVALHO, A. P., PINTO, A. P., DA COSTA, C. T, Toxicity and removal efficiency of pharmaceutical metabolite clofibric acid by *Typha* spp.—potential use for phytoremediation?, *Bioresource Technology*, **100**(3), 2009, 1156-1161.
4. WANG, Y., LI, H., YI, P., ZHANG, H., Degradation of clofibric acid by UV, O₃ and UV/O₃ processes: Performance comparison and degradation pathways, *Journal of Hazardous Materials*, **379**, 2019, 120771.
5. PATEL, S., AGARWAL, R., MAJUMDER, S. K., DAS, P., GHOSH, P., Kinetics of ozonation and mass transfer of pharmaceuticals degraded by ozone fine bubbles in a plant prototype, *Heat and Mass Transfer*, **56**(2), 2020, 385-397.
6. LEE, C. M., PALANIANDY, P., DAHLAN, I., Pharmaceutical residues in aquatic environment and water remediation by TiO₂ heterogeneous photocatalysis: a review, *Environmental Earth Sciences*, **76**(17), 2017, 611.
7. MIAO, W., LIU, Y., CHEN, X., ZHAO, Y., MAO, S, Tuning layered Fe-doped g-C₃N₄ structure through pyrolysis for enhanced Fenton and photo-Fenton activities, *Carbon*, **159**, 2020, 461-470.
8. RAYAROTH, M. P., ARAVIND, U. K., ARAVINDAKUMAR, C. T., Ultrasound based AOP for emerging pollutants: from degradation to mechanism, *Environmental Science and Pollution Research*, **24** (7), 2017, 6261-6269.
9. LOOS, G., SCHEERS, T., VAN EYCK, K., VAN SCHEPDAEL, A., ADAMS, E., VAN DER BRUGGEN, B., DEWIL, R., Electrochemical oxidation of key pharmaceuticals using a boron doped diamond electrode, *Separation and Purification Technology*, **195**, 2018, 184-191.
10. KANAKARAJU, D., GLASS, B. D., OELGEMOLLER, M., Advanced oxidation process-mediated removal of pharmaceuticals from water: A review, *Journal of Environmental Management*, **219**, 2018, 189-207.
11. LUTIC, D., CRETESCU, I., Optimization study of rhodamine 6G removal from aqueous solutions by photocatalytic oxidation, *Rev. Chim.*, **67**, 2016, 134-138.



12. MAHMOUD, W. M., RASTOGI, T., KUMMERER, K., Application of titanium dioxide nanoparticles as a photocatalyst for the removal of micropollutants such as pharmaceuticals from water, *Current Opinion in Green and Sustainable Chemistry*, **6**, 2017, 1-10.
13. MAICU, M., HIDALGO, M.C., COLON, G., NAVIO, J.A., Comparative study of the photodeposition of Pt, Au and Pd on pre-sulphated TiO₂ for the photocatalytic decomposition of phenol, *Journal of Photochemistry and Photobiology A: Chemistry*, **217**, 2011, 275-283.
14. ALAUI, O. T., HERISSAN, A., LE QUOC, C., EL MEHDI ZEKRI, M., SORGUES, S., REMITA, H., COLBEAU-JUSTIN, C., Elaboration, charge-carrier lifetimes and activity of Pd-TiO₂ photocatalysts obtained by gamma radiolysis, *Journal of Photochemistry and Photobiology A: Chemistry*, **242**, 2012, 34-43.
15. DUDUMAN C.N., HARJA M., BARRENA PÉREZ M.I., DE CASTRO C.G., LUTIC D., KOTOVA O., CRETESCU I., Preparation and characterization of nanocomposite material based on TiO₂-Ag for environmental applications. *Environmental Engineering and Management Journal*, **17**, 2018, 925-936.
16. LI, Q., LI, Y.W., WU, P., XIE, R., SHANG, J.K., Palladium Oxide Nanoparticles on Nitrogen-Doped Titanium Oxide: Accelerated Photocatalytic Disinfection and Post-Illumination Catalytic "Memory", *Advanced Materials*, **20**(19), 2008, 3717-3723.
17. RETI, B., KISS, G. I., GYULAVARI, T., BAAN, K., MAGYARI, K., HERNADI, K., Carbon sphere templates for TiO₂ hollow structures: Preparation, characterization and photocatalytic activity, *Catalysis Today*, **284**, 2017, 160-168.
18. MAKDEE, A., UNWISIT, P., CHANAPATTARAPOL, K. C., KIDKHUNTHOD, P., Effects of Ce addition on the properties and photocatalytic activity of TiO₂, investigated by X-ray absorption spectroscopy, *Materials Chemistry and Physics*, **213**, 2018, 431-443.
19. CHANU, L. A., SINGH, W. J., SINGH, K. J., DEVI, K. N., Effect of operational parameters on the photocatalytic degradation of Methylene blue dye solution using manganese doped ZnO nanoparticles, *Results in Physics*, **12**, 2019, 1230-1237

Manuscript received: 20.05.2020