THE REMOVAL OF NEONICOTINOID INSECTICIDE IMIDACLOPRID IN AN ANNULAR PHOTOREACTOR

Kristina Babić [1], Vesna Tomašić [1*], Ivana Grčić [2], Marina Duplančić [1], Zoran Gomzi [1]
[1]University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10000 Zagreb, Croatia
[2]University of Zagreb, Faculty of Geotechnical Engineering, Hallerova aleja 7, 42000 Varaždin, Croatia

*E-mail of corresponding author: vtomas@fkit.hr

Abstract: Heterogeneous photocatalysis has recently attracted an increasing interest of scientists and experts who deal with the waste water and air treatment. An important area of application is removal of persistent organic pollutants, which can not be easily destroyed by conventional methods. Among these pollutants are neonicotinoid insecticides, which are widely used all over the world and currently are included in the watch list of substances of the European Commission within the Water Framework Directive. Therefore, there is a need to study their influence on the environment and to develop appropriate technologies for their removal. In this work, the photolytic and photocatalytic degradation of neonicotinoid insecticide imidacloprid in an annular photoreactor with recirculation under different working conditions (irradiation source, pH, type and concentration of the catalyst) was studied. The photolytic degradation was examined using lamps that emit UVA, UVC and simulated sun light. The photocatalytic experiments in the suspension involved the use of commercial titanium dioxide (TiO_2 P25, Degussa/Evonik), commercial TiO_2 P25 pre-treated with UVC irradiation prior to use in the catalytic system and nitrogen-doped TiO_2 (CCR 200 N produced by Cinkarna Celje). The catalysts were characterized using XRD, UV/Vis-DRS and BET analysis. The most efficient photocatalyst was then immobilized on the glass woving fibre, using peroxotitanic acid (produced by Cinkarna Celje) as a binder. The degree of degradation of imidacloprid was determined using high performance liquid chromatography (HPLC). According to the obtained results, UVC-treated TiO_2 showed the best efficiency among the examined catalysts in the slurry reactor while using lamp that simulates the sun irradiation. The imidacloprid degradation rate increases with the increase in the catalyst concentration. The immobilized UVC-treated catalyst gave satisfying results in terms of stability, activity and reuse.

Keywords: heterogeneous photocatalysis, neonicotinoid insecticides, imidacloprid, annular reactor

Received: 14.02.2020./ Accepted: 4.5.2020.

Original scientific paper
https://doi.org/10.37023/ee.7.2.3

1. INTRODUCTION

Neonicotinoid insecticides are relatively new group of insecticides, widely applied for the seed treatment. Because of their high solubility in water and low adsorption to the soil, they can reach underground and surface water during rainfall rinsing. In the last ten years several investigations connected some neonicotinoids with bees poisoning all over the world (Žabar et al. 2012). At present, their use is restricted, but still not completely banned. Some insecticides from the group of neonicotinoids, e.g. imidacloprid, are included in the watch list of substances for Union-wide monitoring in the field of water policy, established by the European Commission Implementing Decision 2018/840 pursuant to Directive 2008/105/EC (Commision implementing decision (EU) 2018/840).

The existing water treatment processes cannot remove persistent organic compounds sufficiently, which is why the advanced oxidation processes (AOPs) are increasingly explored as an alternative to conventional methods. Among the most investigated AOPs is heterogeneous semiconductor photocatalysis based on the excitation of semiconductor particles in the aqueous media using corresponding source of irradiation (UV or visible irradiation) (Ibhadon & Fitzpatrick 2013). First photocatalytic studies began with titanium dioxide (TiO_2), which has been the most studied photocatalyst till now. TiO_2 has many advantages, for instance high chemical stability, non-toxicity, availability, environmental acceptability and low prices compared to other semiconductor oxides. The most commonly studied TiO_2 catalyst is commercial P25 (80% anatase structure, 20% rutile structure) from Evonik/Degussa. The bandgap energy of the TiO_2 P25 is about 3.2 eV, corresponding to the wavelength of activation $\leq$ 390 nm. High bandgap energy and the ability to absorb only UV radiation, which consists only 5 % of the solar spectrum, limits the use of TiO_2 for commercial purposes (Yang et al. 2018). Therefore, there is a large number of photocatalytic investigations directed to the modification of TiO_2 in order to achieve photocatalytic activity in the visible area of the solar spectrum (λ> 390 nm). These procedures include the modification of surface TiO_2 by sensitization to organic dyes, polymers or surface-bound organic complexes and creating composites with other semiconductor materials (Rehman et al. 2009). In addition to surface modification, the activity of TiO_2 in the visible part can be achieved by narrowing the bandgap by doping/codoping TiO_2 with nonmetals and transition metals (Zaleska-Medynska 2008). Also, some studies have shown that reduction of Ti^{4+} to Ti^{3+} ions results in creating oxygen vacancies due to the release of oxygen ions from the band structure. These vacancies are formed between the valence and conduction bands in the TiO_2 band structure and they act as an electron captures from the valence band, which consequently enhances photocatalytic activity of TiO_2 in the visible region (Zuo et al. 2010). Reduction of TiO_2 in this way was carried out in several studies using different strategies, for instance plasma, vacuum TiO_2 heating, steam chemical vapor deposition or bombarding TiO_2 with high energy particles.

In this paper we studied pretreating of TiO_2 with UVC light in order to obtain reduced TiO_2 with enhanced photoactivity in the visible part of the sun spectrum. The obtained catalyst, the so called UVC-TiO_2 was compared to two commercial catalysts in the suspended form. Also, some experiments were performed using UVC-TiO_2 in the immobilized form.

2. MATERIALS AND METHODS

2.1. Chemicals

An analytical standard imidacloprid, used for HPLC analysis was purchased from Sigma Aldrich Company Ltd. The experiments were performed using commercial plant protection product Boxer 200 SL supplied by Sharda Ltd. Peroxotitanic acid (PTA) and nitrogen-doped TiO_2 (N-TiO_2, CCR 200 N) were donated by Cinkarna Celje. TiO_2 P25 was purchased from Evonik. Formic acid 98 % p.a. and acetonitrile HPLC grade were purchased from VWR. All aqueous solutions were prepared with ultra-pure water.

2.2. Characterization of the catalysts

The specific surface area, total pore volume and average pore diameter of the powder samples were determined with nitrogen adsorption-desorption isotherms, using the Brunauer–Emmet–Teller (BET) method on the Micrometrics ASAP 2000. The crystalline phase composition of the prepared samples was determined by X-ray diffraction measurements (Shimadzu 6000) with CuKα radiation. The UV–vis spectra of the prepared powder samples were obtained using DRS (Perkin-Elmer Lambda 35) equipped with an integrating sphere. The spectra were recorded at room temperature in the wavelength range of 200–800 nm. $BaSO_4$ was used as a reference.

2.3. Apparatus

The photocatalytic experiments were performed in an annular batch reactor (including recirculation in a closed system) with the source of irradiation placed in the central part of the reactor. The same reactor was used for 2-hour pretreatment of commercial TiO_2 using UVC lamp before photocatalytic reaction. The reaction mixture was recirculated using recirculating pump and the temperature was kept constant using a thermostat (Julabo–Model ED, Heating Immersion Circulator). The reaction conditions were given in the **Table 1**.

Table 1. Reaction conditions

INITIAL CONCENTRATION OF IMIDACLOPRID, ppm	10		
TEMPERATURE, °C	30		
REACTOR VOLUME, mL	450		
INITIAL pH OF THE SOLUTION	6.5-7.0		
RECIRCULATION FLOW RATE, (L/min)	1.4		
FORM OF THE CATALYST	suspended	immobilized	without catalyst-photolysis
TYPE OF THE CATALYST	TiO_2 P25, N-TiO_2 (CCR 200 N), UVC-TiO_2	UVC-TiO_2	-
CATALYST CONCENTRATION, (g/L)	0.05-0.5	0.036-0.110	-
IRRADIATION SOURCE	Arcadia Natural Sunlight 8 W	Arcadia Natural Sunlight 8 W	UVC 8 W, UVA 8 W, Arcadia Natural Sunlight 8 W

The immobilized type of the catalyst was prepared using peroxotitanic acid (PTA) as a binder. The suspension of catalyst and binder was prepared by mixing 1 g of catalyst in 100 ml of PTA. The prepared mixed solution was applied in thin layers on the glass woving fibre. Different amount of catalyst on the support was achieved by applying several layers and drying between each layer. The immobilized TiO_2 layer was placed close to the reactor walls using specially designed inert photocatalyst holder. After "dark" period (establishing of the adsorption equilibrium), the reaction mixture was illuminated with the corresponding lamp. The concentration of model compound imidacloprid was analyzed at different reaction times on a 5 µm, 250 x 4.6 mm Zorbax SB-C18 column by high performance liquid chromatography (Shimadzu LC 20AT Prominence) equipped with an autosampler and diode array detector (DAD).

3. RESULTS AND DISCUSSION

3.1. Characterization of the powder catalysts

Figure 1 presents UV-Vis spectra of the commercial nitrogen doped TiO_2, N-TiO_2 (produced by Cinkarna Celje) and UVC-treated TiO_2 P25 (UVC-TiO_2). The band gap energy, E_g, was estimated by plotting modified Kubelka-Munk function for indirect electron transition, $(F(R)h\nu)^{1/2}$ vs. photon energy ($h\nu$), the so–called Tauc's plot, followed by extrapolation of the linear region onto the energy axis (Valencia et al. 2010). The estimated band gap energies, together with wavelength of activation, are shown in **Table 2**. Pretreatment of TiO_2 P25 with UVC radiation during 2 hours led to decreasing of E_g to 2.6 eV compared to 3.2 and 3 eV as characteristic values for the anatase and rutile phase of TiO_2 P25, respectively. The decrease in value of E_g resulted in a change of wavelength activation from 390 nm for TiO_2 P25 to 476 nm for UVC-TiO_2 and, consequently, enabled photocatalytic experiments in the visible part of solar spectrum ($\lambda > 390$ nm).

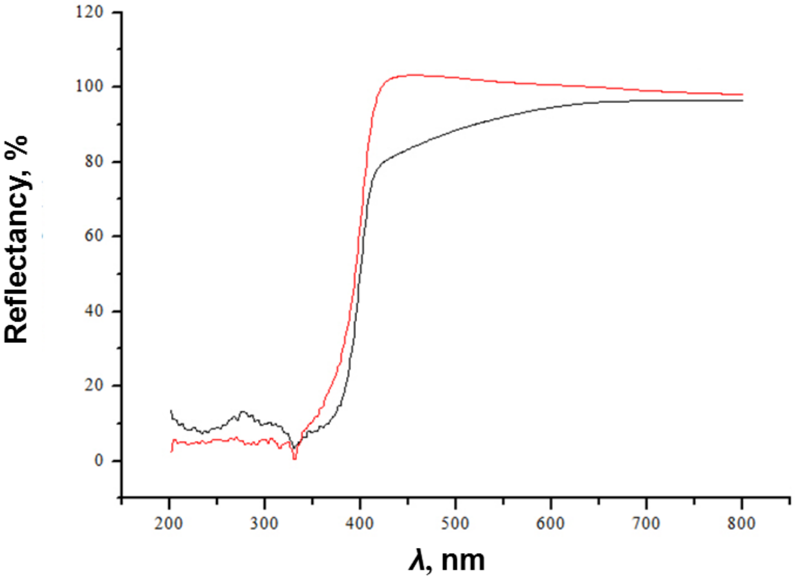

Figure 1. Diffuse reflectance spectra of N-TiO_2 (black line) and UVC-TiO_2 (red line)

The XRD patterns of the N-TiO_2 and UVC-TiO_2 are shown in **Figure 2.** The XRD spectra of the UVC-TiO_2 correspond to the spectra of TiO_2 P25 before UVC irradiation that was found in literature (Wang et al. 2011). It can be concluded that irradiation of TiO_2 P25 with UVC light did not affect the crystalline structure of the photocatalyst, but probably led to formation of oxygen vacancy states between the valence and conduction bands in the TiO_2 band structure, that take part in the photoexcitation process. That is, the electron may be excited to the oxygen vacancy states from the valence band even with the energy of visible light (Nakamura et al. 2000). DRS spectroscopy of N-TiO_2 (Fig. 1) showed that this photocatalyst is also active in the visible part of spectrum, but from the XRD spectra it is visible that this photocatalyst consists only of rutile crystal phase, which is less active than anatase (**Figure 2**). The lower activity of N-TiO_2 was confirmed while performing photocatalytic experiments, as mentioned later in the text. The results of the N_2 adsorption/desorption analysis showed that treating TiO_2 P25 with UVC light did not affect the textural properties of the catalyst (**Table 3**) As expected, addition of PTA as a binder for immobilization of TiO_2 on a glass woving fibre lead to decreasing of specific surface area of prepared UVC-TiO_2/PTA sample in comparison to the pure UVC-TiO_2. This decrease can be explained in partial blocking of pores of TiO_2. The specific BET surface area for N-TiO_2 was higher than for TiO_2 P25.

Table 2. Values of indirect band gap energy for the examined TiO_2 photocatalysts

MATERIAL	**E_g, eV**	**λ, nm**
TiO_2 P25	A: 3.2; R: 3.0	390
UVC-TiO_2	2.6	476
N-TiO_2	2.8	443

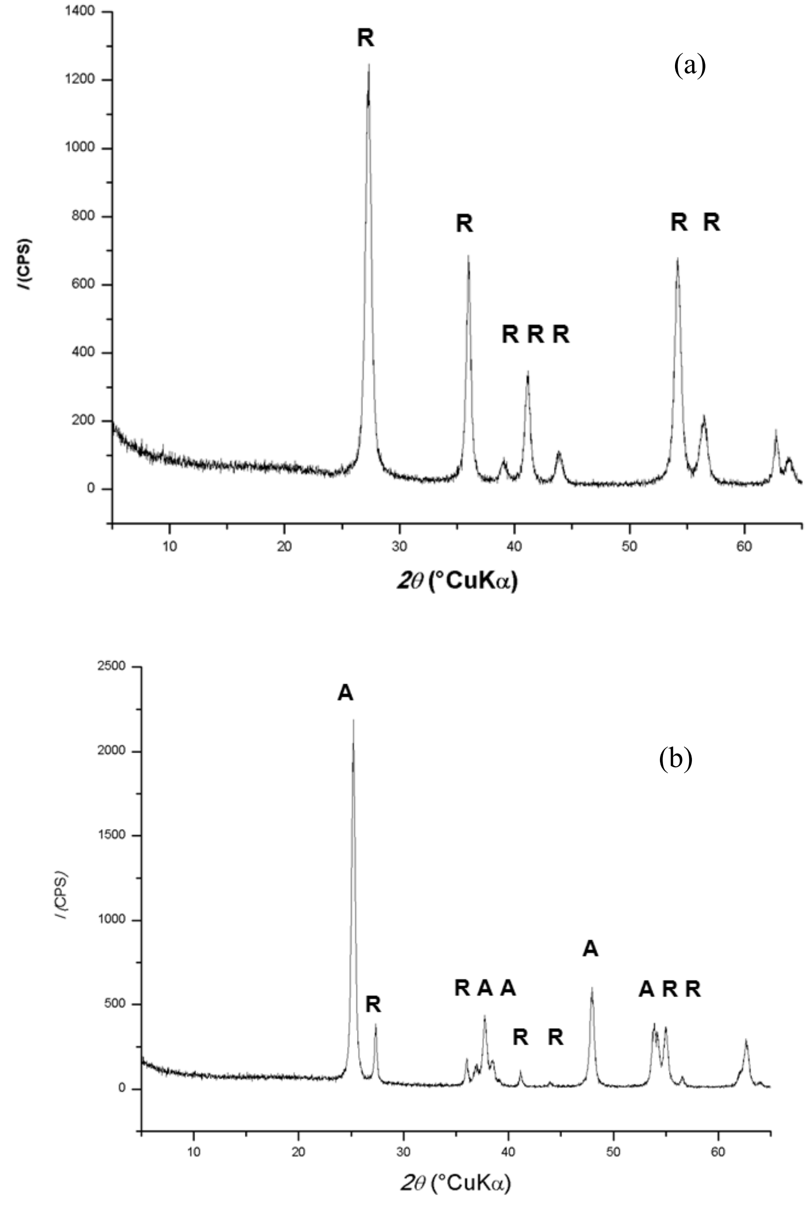

Figure 2. *XRD spectra of N-TiO_2 (a) and UVC-TiO_2 (b)*

Table 3. Textural properties of powder catalysts determined using the nitrogen adsorption/desorption analysis

MATERIAL	**S_{BET}, (m^2/g)**	**V_P, (cm^3/g)**	**d_P, nm**
TiO_2 P25	56	0.25	17.50
UVC-TiO_2	54.28	0.27	20.22
UVC-TiO_2/PTA (50 g/L TiO_2)	17.93	0.05	11.44
N-TiO_2	87.92	0.47	21.40

3.2. Testing of the photocatalytic properties

The photolytic and photocatalytic activity of the suspended and immobilized TiO_2 photocatalysts is evaluated by photodegradation of imidacloprid in the simulated sunlight conditions. In order to study the contribution of photolysis on the degradation of imidacloprid, three different irradiation sources were examined. The results showed that the lamp of interest (Arcadia natural sunlight), that closely simulates sun spectrum, did not degrade imidacloprid even after 3.5 hours of irradiation in an annular photoreactor. On the other side, the strong UVC light completely degraded imidacloprid after 1 hour of irradiation (**Figure 4**).

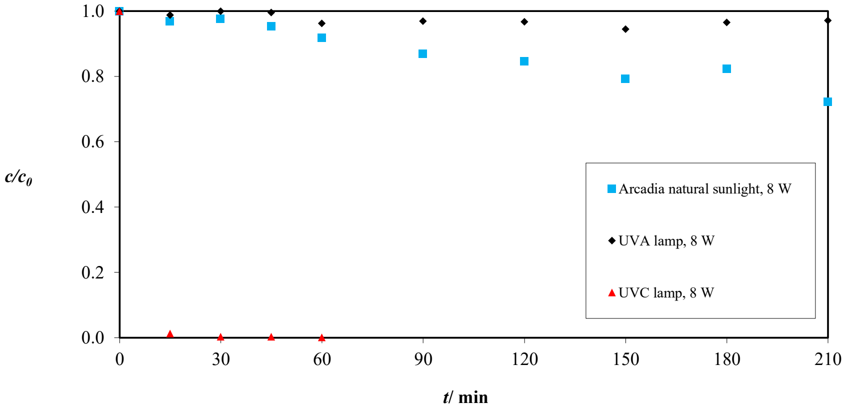

Figure 4. *Photolytic degradation of imidacloprid using different irradiation source*

Further experiments were performed using simulated sunlight under the presence of photocatalysts. Three TiO_2 catalysts in the suspended form were compared in the same reaction conditions and it was shown, according to our expectations, that the best efficiency was obtained using UVC-TiO_2 (**Figure 5**). N-TiO_2 was not efficient in our reaction system, although the same photocatalyst exhibited excellent photocatalytic activity in the presence of natural or artificial UV and visible light for the decomposition of nitrogen monoxide (NO).

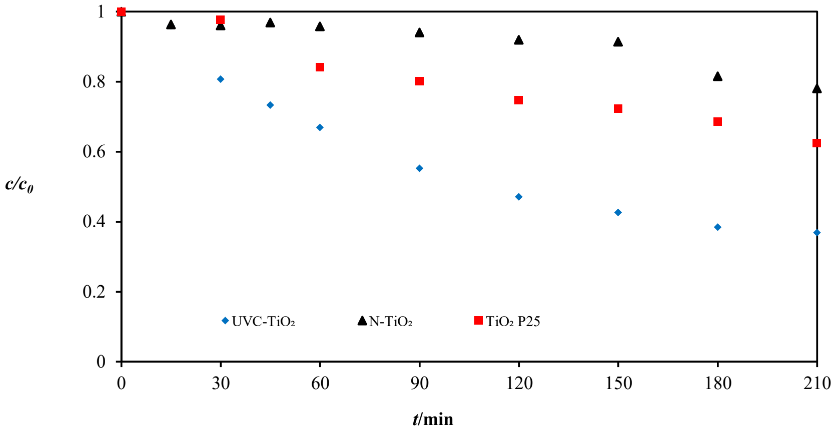

Figure 5. *Comparison of three TiO_2 catalysts in the suspended form at the same reaction conditions*

Furthermore, the influence of different concentration of UVC-TiO_2 photocatalyst on the degradation efficiency was examined. The higher catalyst concentration led to greater decrease in the imidacloprid concentration (**Figure 6**). This is obvious since the higher catalyst concentration leads to more photocatalytically active sites available for the photoexcitation process. Some authors have reported on the optimal catalyst concentration in the suspended form that gives the best degradation efficiency. In these studies higher concentration than optimal led to decrease in the degradation rate of model pollutant (Kitsiou et al. 2009). This was explained with possible agglomeration of TiO_2 particles and decreased system opacity, which consequently blocked reaching of light to the surface of catalyst particles (Affam & Chaudhuri 2013). This phenomenon was not noticed in the concentration range of TiO_2, studied in this paper (0.05 – 0.5 g/L).

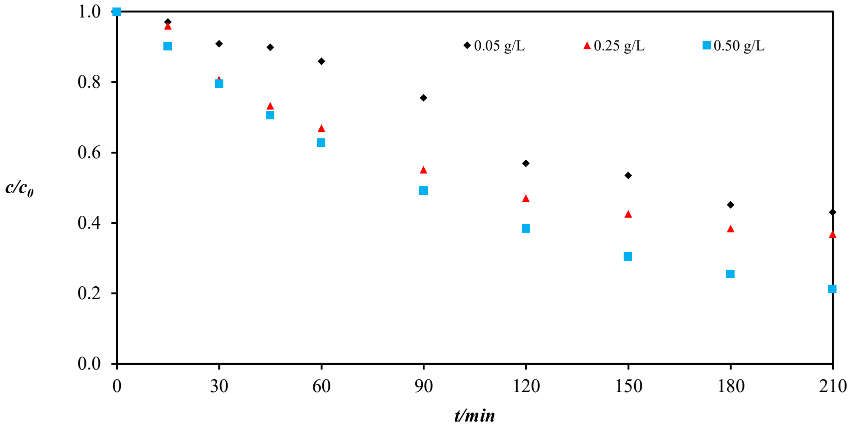

Figure 6. *Influence of the concentration of UVC-TiO_2 on the degradation of imidacloprid*

Afterwards, the immobilized UVC-TiO_2 was evaluated in the photocatalytic degradation of imidacloprid in the same reaction conditions as in the suspended form (concentration of imidacloprid, irradiation source, recirculation flow rate and reaction temperature). „Dark“ experiment during 1 hour showed that the adsorption process did not contribute to decrease of imidacloprid concentration (**Figure 7**).

The influence of different number of layers of immobilized UVC-TiO_2 that consequently led to different amount of catalyst on the support, was examined (**Table 1**). It was shown that there was no significant change in the degradation rate with catalyst concentration in the prepared layer (**Figure 8**). The degradation rate obtained with the immobilized TiO_2 was much lower than with suspended TiO_2 as expected. Regardless of the lower efficiency, the prepared immobilized layer of TiO_2 showed good stability and no Ti leaching. Peroxotitanic acid as a binder ensured good adherence strength of the immobilized photocatalyst layer to the substrate surface.

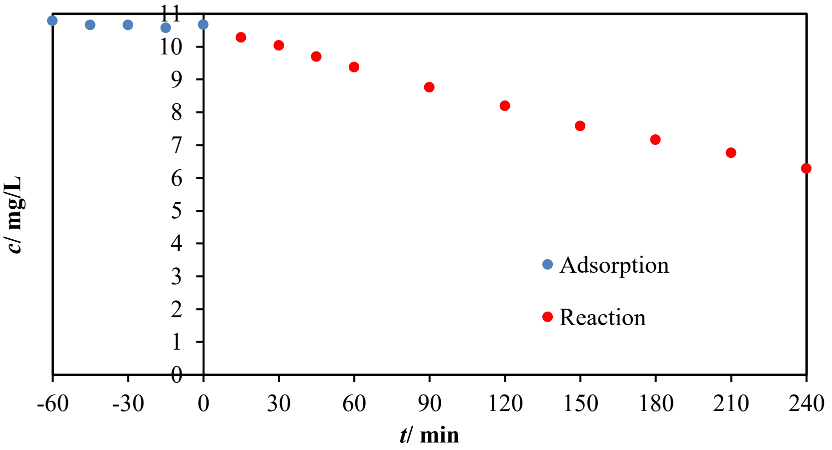

Figure 7. *Contribution of adsorption process to the elimination of imidacloprid*

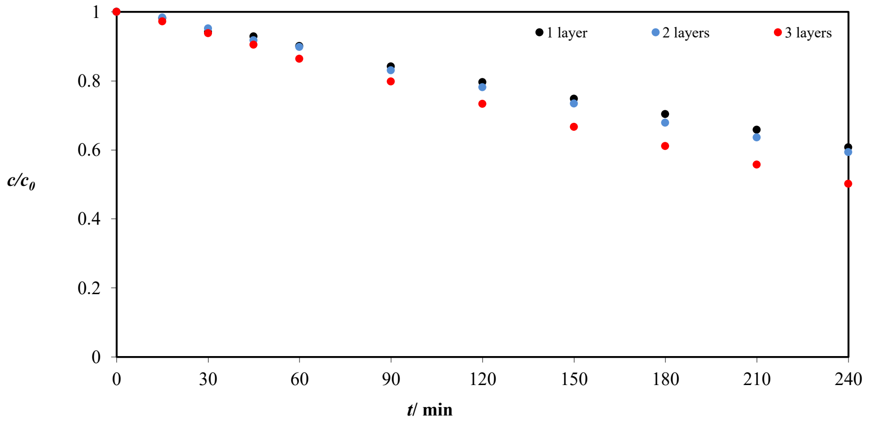

Figure 8. *Influence of the number of layers of UVC-TiO_2 impregnated on glass vowing fibre on the degradation of imidacloprid*

4. CONCLUSION

The UVC-treated TiO_2 photocatalyst showed the higher visible light activity for imidacloprid removal among the examined TiO_2 catalysts under simulated sunlight conditions. Neither the crystal structure nor the specific surface area was observed to change between the commercial TiO_2 P25 and UVC-treated TiO_2 P25 photocatalyst. The appearance of the visible light photocatalytic activity in UVC-treated TiO_2 is due to a new photoexcitation process by the formation of the oxygen vacancy state located between the valence and the conduction bands. This phenomenon will be confirmed performing ESR measurements in the future work. The imidacloprid degradation rate increased with the increase in the catalyst concentration in the studied concentration range. The immobilized UVC-treated TiO_2 gave satisfying results in terms of stability, activity and reuse.

5. ACKNOWLEDGEMENT

This work has been supported by Croatian Science Foundation under the project IN-PhotoCat (IP-2018-01-8669) and by EU European Regional Development Fund, KK.01.1.1.04.0006 as a part of the project "Waste & Sun for photocatalytic degradation of micropollutants in water" (OS-Mi). Special thanks go to Dejan Verhovšek and Cinkarna Celje for the supply of N-TiO_2 (CCR 200 N) and PTA samples.

6. REFERENCES

Affam AC, Chaudhuri M (2013) Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by TiO_2 photocatalysis. J Environ Manage 130: 160–165. doi: 10.1016/j.jenvman.2013.08.058.

Commision implementing decision (EU) 2018/840, https://eur-lex.europa.eu/eli/dec_impl/2018/840/oj (Accessed June 26, 2019).

Ibhadon AO, Fitzpatrick P (2013) Heterogeneous photocatalysis: recent advances and applications. Catalysts 3: 189–218. doi: 10.3390/catal3010189.

Kitsiou V, Filippidis N, Mantzavinos D, Poulios I (2009) Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solutions. Appl Catal, B 86: 27–35. doi: 10.1016/j.apcatb.2008.07.018.

Nakamura I, Negishi N, Kutsuna S, Ihara T (2000) Role of oxygen vacancy in the plasma-treated TiO_2 photocatalyst with visible light activity for NO removal. J Mol Catal A: Chem 161: 205–212. doi: 10.1016/S1381-1169(00)00362-9.

Rehman S, Ullah R, Butt AM, Gohar ND (2009) Strategies of making TiO_2 and ZnO visible light active. J Hazard Mater 170: 560–569. doi: 10.1016/j.jhazmat.2009.05.064.

Valencia S, Marin J M, Restrepo G (2010) Study of the bandgap of synthesized titanium dioxide nanoparticles using the sol-gel method and a hydrothermal treatment. TOMSJ 4: 9–14. doi: 10.2174/1874088X01004010009.

Wang G, Xu L, Zhang J, Yin T, Han D (2012) Enhanced photocatalytic activity of TiO_2 powders (P25) via calcination treatment. Int J Photoenergy 2012: 1–9. doi: 10.1155/2012/265760.

Yang X, Min Y, Li S, Wang D, Mei Z, Liang J, Pan F (2018) Conductive Nb-doped TiO_2 thin films with whole visible absorption to degrade pollutants. Catal Sci Technol 8: 1357–1367. doi: 10.1039/C7CY02614E.

Zaleska-Medynska A (2008) Doped-TiO_2: a review. Recent Pat Eng 2: 157–164. doi: 10.2174/187221208786306289.

Zuo F, Wu T, Zhang Z, Borchardt D, Feng P (2010) Self-doped Ti^{3+} enhanced photocatalyst for hydrogen production under visible light. J Am Chem Soc 132: 11856–11857. doi: 10.1021/ja103843d.

Žabar R, Komel T, Fabjan J, Bavcon Kralj M, Trebše P (2012) Photocatalytic degradation with immobilised TiO_2 of three selected neonicotinoid insecticides: imidacloprid, thiamethoxam and clothianidin. Chemosphere 89: 293–301. doi: 10.1016/j.chemosphere.2012.04.039.