

IRANIAN JOURNAL OF CHEMICAL ENGINEERING

Chairman

Vahid Taghikhani Professor, Sharif University of Technology, Iran

Editor-in-Chief

Hassan Pahlavanzadeh Professor, Tarbiat Modares University, Iran

Executive Director

Leila Sadafi-Nejad (M.Sc.)

EDITORIAL BOARD

- ❖ Abbasian, J. (Associate Professor, Illinois Institute of Technology, USA)
- ❖ Badakhshan, A. (Emeritus Professor, University of Calgary, Canada)
- ❖ Barikani, M. (Professor, Iran Polymer and Petrochemical Institute, Iran)
- ❖ Jafari Nasr, M. R. (Professor, Research Institute of Petroleum Industry (RIPI), Iran)
- ❖ Karimi, I. A. (Professor, National University of Singapore, Singapore)
- ❖ Madaeni, S. S. (Professor, Razi University, Iran)
- ❖ Mansoori, G. A. (Professor, University of Illinois at Chicago, USA)
- ❖ Moghaddas, J. S. (Professor, Sahand University of Technology, Iran)
- ❖ Moosavian, M. A. (Professor, University of Tehran, Iran)
- ❖ Moshfeghian, M. (Professor, Shiraz University, Iran)
- ❖ Movagharnjad, K. (Professor, Babol University of Technology, Iran)
- ❖ Naseri, S. (Professor, Tehran University of Medical Sciences, Iran)
- ❖ Omidkhan, M. R. (Professor, Tarbiat Modares University, Iran)
- ❖ Pahlavanzadeh, H. (Professor, Tarbiat Modares University, Iran)
- ❖ Panjeshahi, M. H. (Professor, University of Tehran, Iran)
- ❖ Pazouki, M. (Professor, Materials and Energy Research Center (MERC), Iran)
- ❖ Rahimi, M. (Professor, Razi University, Iran)
- ❖ Rahimi, R. (Professor, University of Sistan and Baluchestan, Iran)
- ❖ Rashidi, F. (Professor, Amirkabir University of Technology, Iran)
- ❖ Rashtchian, D. (Professor, Sharif University of Technology, Iran)
- ❖ Shariaty-Niassar, M. (Professor, University of Tehran, Iran)
- ❖ Shayegan, J. (Professor, Sharif University of Technology, Iran)
- ❖ Shojaosadati, S. A. (Professor, Tarbiat Modares University, Iran)
- ❖ Soltanmohammadzadeh, J. S. (Associate Professor, University of Saskatchewan, Canada)
- ❖ Towfighi, J. (Professor, Tarbiat Modares University, Iran)

INTERNATIONAL ADVISORY BOARD

- ❖ Arastoopour, H. (Professor, Illinois Institute of Technology, USA)
- ❖ Ataai, M. M. (Professor, University of Pittsburgh, USA)
- ❖ Barghi, Sh. (Assistant Professor, University of Western Ontario, Canada)
- ❖ Chaouki, J. (Professor, University of Polytechnique Montréal, Canada)
- ❖ Ein-Mozaffari, F. (Associate Professor, Ryerson University, Canada)
- ❖ Farnood, R. R. (Professor, University of Toronto, Canada)
- ❖ Jabbari, E. (Associate Professor, University of South Carolina, USA)
- ❖ Jand, N. (Assistant Professor, Università de L'Aquila, Italy)
- ❖ Lohi, A. (Professor, Ryerson University, Canada)
- ❖ Moghtaderi, B. (Professor, University of Newcastle, Australia)
- ❖ Mohseni, M. (Associate Professor, University of British Columbia, Canada)
- ❖ Nassehi, V. (Professor, Loughborough University, UK)
- ❖ Noureddini, H. (Associate Professor, University of Nebraska, USA)
- ❖ Rohani, S. (Professor, University of Western Ontario, Canada)
- ❖ Shahinpoor, M. (Professor, University of Maine, USA)
- ❖ Soroush, M. (Professor, Drexel University, USA)
- ❖ Taghipour, F. (Associate Professor, University of British Columbia, Canada)

* This journal is indexed in the Scientific Information Database (<http://en.journals.sid.ir/JournalList.aspx?ID=3998>).

* This journal is indexed in the Iranian Magazines Database (www.magiran.com/maginfo.asp?mgID=4585).

* This journal is indexed in the Islamic World Science Citation Center (<http://ecc.isc.gov.ir/showJournal/3561>).

Language Editor: Sajjad Saberi

Art & Design: Fatemeh Hajizadeh

Iranian Association of Chemical Engineers, Unit 11, No. 13 (Block 3), Maad Building, Shahid Akbari Boulevard, Azadi Ave., Tehran - Iran.

Tel: +98 21 6604 2719 Fax: +98 21 6602 2196

Iranian Journal of Chemical Engineering

Vol. 15, No. 4 (Autumn 2018), IChE

- Degradation of Diclofenac Sodium under Solar Light Irradiation by Photocatalytic Performance of ZnO and V₂O₅** 3-16
M. Baniamer, A. Almasi, Sh. Sharifnia
- Removal of Pb (II) from Wastewater Using Henna: Optimization of Operational Conditions** 17-26
M. Shafiee, A. Akbari, B. Ghiassimehr
- Optimization of Solvothermally Synthesized ZIF-67 Metal Organic Framework and Its Application for Cr (VI) Adsorption from Aqueous Solution** 27-47
N. Mostafazadeh, A. A. Ghoreyshi, K. Pirzadeh
- Propionic Acid Extraction in a Microfluidic System: Simultaneous Effects of Channel Diameter and Fluid Flow Rate on the Flow Regime and Mass Transfer** 48-62
F. Hosseini, M. Rahimi, O. Jafari
- Evaluation of Cr (VI) Ion Removal from Aqueous Solution by Bio-Inspired Chitosan-Clay Composite: Kinetics and Isotherms** 63-80
Sh. Biswas, Md. M. Islam, M. M. Hasan, S. H. Rimu, M. N. Khan, P. Haque, M. M. Rahman
- Design and Fabrication of an Improved Single-Column Chromatographic Separation Process** 81-92
B. Medi, M. -K. Kazi
- Effect of Operating Conditions on Divinylbenzene Production in Diethylbenzene Dehydrogenation Reactor** 93-104
M. E. Zeynali, H. Abedini, H. R. Sadri
- Notes for Authors** 105

Degradation of Diclofenac Sodium under Solar Light Irradiation by Photocatalytic Performance of ZnO and V₂O₅

M. Baniamer¹, A. Almasi², Sh. Sharifnia^{1*}

¹ Catalyst Research Center, Chemical Engineering Department., Razi University, Kermanshah, Iran

² Social Development and Health Promotion Research Center, Public Health School, Kermanshah University of Medical Sciences, Kermanshah Iran

ARTICLE INFO

Article history:

Received: 2017-09-10

Accepted: 2018-08-20

Keywords:

Photocatalysis,
Pharmaceutical Active
Ingredient,
Wastewater Treatment,
Solar Energy

ABSTRACT

Pharmaceutical pollutants are one of the most important issues of modern life, and their negative effects on the environment and human health are undeniable. In the present work, the effectiveness of the photocatalytic process was studied by two semiconductors (ZnO and V₂O₅) in order to remove the Diclofenac Sodium completely under solar irradiation. The study examined the impact of parameters such as the high-level range concentration of pharmaceutical, catalyst dosage, pH changes, and time on the photodegradation of Diclofenac Sodium in aqueous solution. All the experiments were carried out under solar and UV irradiation to compare the two circumstances. The optimum conditions obtained for photodegradation of Diclofenac Sodium include a reaction time of 180 min, zinc oxide and vanadium pentoxide = 1 g L⁻¹, Diclofenac Sodium concentration = 300 mg L⁻¹, and pH of 4. In addition, chemical oxygen demand removal was investigated for all the conditions, and total degradation was observed by V₂O₅ under optimum conditions. The study of reaction kinetics was carried out in optimum conditions, and a pseudo-first-order kinetic model was approximately in agreement with experimental results in each case.

1. Introduction

From an environmental point of view, pharmaceuticals have been a new category of pollutants in the environment in recent years [1]. Since the impacts of pharmaceutical contaminants on the health are still not thoroughly recognized, there are concerns about their introduction into the environment. In fact, the main problem of the pharmaceutical presence in the environment is the growth of bacteria and microorganisms resistant to them, even at low concentrations

[2]. Although the amount of drug concentration in the environment is not notable, organisms are exposed to their accumulation and risks over time [3].

Nonsteroidal anti-inflammatory drugs are a special group of medicines that are often found as a constant toxic waste and largely available. A well-known member of this family that is usually consumed as a pain reliever, anti-arthritic, and anti-rheumatic is DS (Diclofenac Sodium). This pollutant enters the environment from various sources

*Corresponding author: sharif@razi.ac.ir

such as pharmaceutical manufacturing plants, direct domestic disposal, and excretion of the pharmaceutical amount which has not been metabolized in humans and animals body. Recent studies on the toxicity of this drug found its harmful effects, even at a low concentration [4, 5]. A significant decrease in the vulture population has been reported in some parts of the world due to the devastating environmental effects of DS [6, 7].

Most of the water and wastewater treatment plants have used conventional techniques to remove contaminants [8, 9], especially activated sludge and trickling filter. Although many of these methods are suitable and successful treatment techniques, they commonly are very inefficient at eliminating pharmaceuticals. In this field, Nakada et al. [10] examined the removal efficiency of 24 different medications by the trickling filter technique. The results indicated that the removal of pharmaceutical substances by the trickling filter occurred at a very low speed, while pharmaceutical pollutants can be removed by utilizing the ozonation process, even by 80 %. Although different treatments have been utilized to eliminate some pharmaceuticals such as using activated carbon adsorption [11], membrane filtration [12], and advanced oxidation [13, 14], the complete removal of these pollutants has not been achieved in recent years. In this context, Rohricht et al. [15] achieved 65 % of diclofenac and 10 % of carbamazepine removing using nanofiltration. Xue et al. [12] studied membrane bioreactor in order to investigate the fate of 19 organic contaminants after passing through an anaerobic-aerobic reactor. According to the obtained results, contaminants were removed by 50 to 100 %, while there was not any elimination by only biological methods. By

this treatment process, the removal of Diclofenac was achieved less than 20 %.

Hence, it is obligatory to develop a proper treatment technique in order to achieve the total removal of pharmaceutical contaminants from wastewater [16, 17]. Destruction of DS using advanced oxidation processes (AOPs) has been reported by many researchers lately [5, 18-20]. In this regard, Mendez-Arriaga et al. [21] studied and compared the destruction of three non-steroidal anti-inflammatory drugs (including Ibuprofen, Diclofenac, and Naproxen) by photocatalytic TiO_2 in a Xe-lamp reactor. Although the amount of Ibuprofen is greatly reduced by the photocatalytic process, no significant removal was observed for Diclofenac. Perez-Estrada et al. [22] also evaluated the oxidation of Diclofenac and the kinetics of processes in a pilot plant by photo-Fenton and TiO_2 . They found that a significant decomposition rate of Diclofenac could occur at pH 2.7, and that this value of pH was incompatible to Diclofenac solubility.

To the best of our knowledge, attaining the photocatalysts that can degrade more amount of this pharmaceutical will be an efficient endeavor under not only UV irradiation but also the natural solar light. To achieve this purpose, two metal oxides were utilized as photocatalysts under UV and the natural solar light: Zinc oxide (ZnO) and Vanadium pentoxide (V_2O_5). In this study, the capability of ZnO and V_2O_5 to remove DS in aqueous solution was investigated by UV-vis diffuse reflectance spectroscopy (UV-vis) measurement and by evaluating chemical oxygen demand (COD). In addition, metal oxide characterizations including FT-IR, SEM, and UV-vis were reported in order to compare the performances of two photocatalysts and the effects of UV and solar

irradiation. Irradiation time, catalyst dosage, initial pharmaceutical concentration, and pH changes were studied to achieve the optimum features of maximum degradation. Ultimately, the kinetic order of the photodegradation processes was measured.

2. Materials and methods

2.1. Chemicals and pharmaceutical

All chemicals were used without any further purification. Zinc oxide (ZnO) and Vanadium pentoxide (V₂O₅) (the size of the particles was between the range of 40 to 70 micrometer) powders were purchased from Merck Co. Sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) used for pH adjustment were purchased from Merck Co. Diclofenac Sodium with - CAS 15307-79-6 (Merck Co) was used as a pharmaceutical. Double distilled water, which was produced in the laboratory, was utilized in order to prepare synthetic wastewater.

2.2. Analytical methods

In the present study, spectroscopy analysis was used to monitor the concentration of DS in aqueous solution, and the absorbance was measured in the range of 200 to 400 nm by a spectrophotometer. The maximum absorbance wavelength was obtained at 275 nm for a solution containing 3 mg L⁻¹ of DS. Different concentrations of DS were prepared for the calibration curve. UV-vis diffuse reflectance spectroscopy (UV-vis) measurements were performed on a Hitachi UV-365 spectrophotometer equipped with an integrating sphere attachment. Fourier transform infrared (FT-IR) spectra were recorded from pressed KBr pellets (containing ca. 8 mg sample and 150 mg KBr) using a Nicolet 6700 FT-IR spectrometer. The surface morphology of two

catalysts was characterized using a scanning electron microscope (SEM, model HITACHI-S4160). Chemical oxygen demand (COD) was investigated based on the available reports in the literature [23].

2.3. Pharmaceutical aqueous solution

The pharmaceutical aqueous solution was prepared by dissolving specific amounts of DS in distilled water. The aqueous solution features include DS concentration range between 100-500 mg L⁻¹, COD 100-500 mg L⁻¹, which is checked by potassium phthalate namely COD measurement, and pH range between 4-8. The pharmaceutical solution was stored at 25-30 °C.

2.4. Experimental procedure

A 250 mL diclofenac solution was placed in a 500 mL reactor with the required amount of ZnO and V₂O₅ and was blended by a magnetic stirrer during the reaction time. pH was regulated to the required value by H₂SO₄ 1N or NaOH 1N. Thus, the solution was exposed to UV and solar irradiations. The system was illuminated by a 125 W Hg lamp with a peak light intensity at 280-380 nm in the case of UV irradiation experiments. All the experiments under solar irradiation were performed on the campus of Razi University, Kermanshah, Iran (latitude 34823.3050 longitude 4786.6950 E) in May 2015, between 11 AM to 2 PM. In addition, the range of time was chosen based on the previous work [24].

3. Results and discussion

3.1. Effect of UV and solar irradiation

Photolysis occurred when solutions were subjected to light either solar or UV without the presence of any catalyst in the solution. The photolysis degradation of DS under UV

and solar irradiation was investigated with the initial conditions of concentration 300 mg L^{-1} of DS and pH 6. With 5 h of exposure to solar or UV irradiation, photolysis degradation rates were 15.5 and 12.5 %, respectively. According to the results, a peak was clearly observed at 275 nm wavelength, and weak disintegration occurred via photolysis.

3.2. Effect of irradiation time

The photodegradation efficiency of DS at different irradiation times was studied. The solutions contain 300 mg L^{-1} contaminants, 1 g L^{-1} of the catalysts (V_2O_5 and ZnO), and pH 6, which were exposed to UV and solar irradiation for 5 h. A high rate of decomposition is observed in the initial stages of photodegradation. This is probably due to a large number of active species generated at the initial time. In all cases, the destruction reached equilibrium during the first 180 min; after that, the rate of DS degradation became slower. In fact, the passage of time reduces the concentration of the pollutant. In other words, significant changes in the DS decomposition have not been observed after 180 to 300 min. Therefore, the time of 180 min was considered as the optimum time for photocatalytic degradation of DS in the following experiments.

3.3. Characterizations of catalysts

FT-IR spectrum is a method superior to infrared spectroscopy. The FT-IR spectra of pure V_2O_5 and ZnO particles are shown in Fig. 1 (a), the band at 3749, 3408, 2017, 1631, 1408, 1018, 812, 532, and 474 cm^{-1} is clearly visible. The bands observed at 3749 and 3408 cm^{-1} correspond to regular and irregular tension vibrations of O-H that have probably been allocated to the water hydration, respectively. The bands which

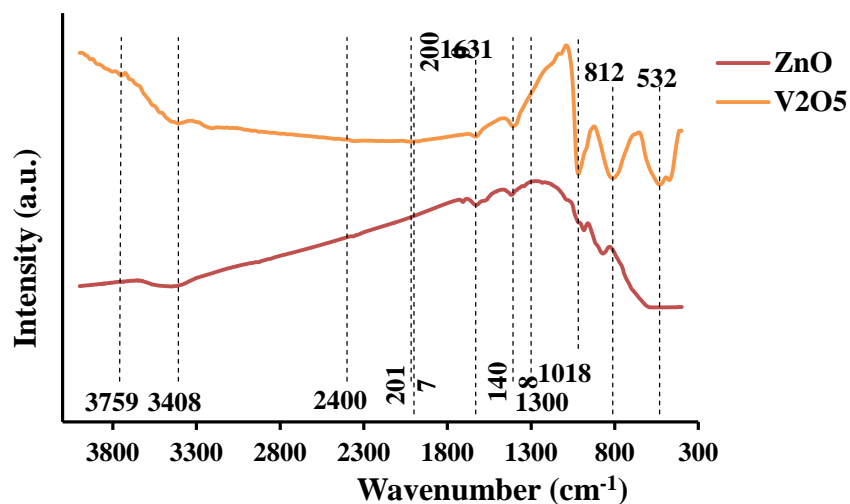
exist at 1631 to 1300 cm^{-1} are also related to the O-H vibration of H_2O [25]. The two regions representative of O-H confirm the existence of water molecules in the samples that come with the absorbing environment moisture or amount that is in the structure of particles. The peaks in the range of 2000 to 2400 cm^{-1} are dedicated to CO_2 compounds in the air that are shown in two graphs [25]. The bands at 1018 and 812 cm^{-1} have been allocated to V-O bands in V_2O_5 particles [26]. Regions close to 476 and 1000 cm^{-1} are representatives of Zn-O bands [27]. UV-vis analysis was also carried out to introduce a range of catalyst absorptions between 200-1000 nm (Fig. 1 (b)). According to UV-vis spectra of V_2O_5 and ZnO, ZnO has absorbed both of the visible and UV light. Although V_2O_5 absorption is mostly dedicated to UV region, ZnO has had an acceptable photocatalytic performance under not only UV but also solar light. Moreover, natural solar light includes both visible and UV irradiations; therefore, catalyst activation is predictable under natural solar irradiation.

The SEM images taken by a scanning electron microscope are demonstrated with different magnifications in Fig. 2. Based on the SEM pictures, the shape of the catalyst surface is well shown. Fig. 2 (a and b) indicates ZnO particles, and Fig. 2 (c and d) indicates V_2O_5 particles. According to the outcome obtained, the surface of V_2O_5 shows irregular dimensions, leading to defects on the catalyst surface and a better catalyst performance in electron trapping. In fact, the defects would produce active sites for the adsorption-activation of the reacted molecules and would be responsible for higher catalytic activity [28]. Although the surface of ZnO shows more regular dimensions in comparison with V_2O_5 surface, it may cause

high contact surface between the catalyst particles and the pollutant. On the other hand, highly dispersed and regular dimensions of

particles lead to easy access to the pollutant particle; hence, the chance for the contact between catalyst particles is high.

a)



b)

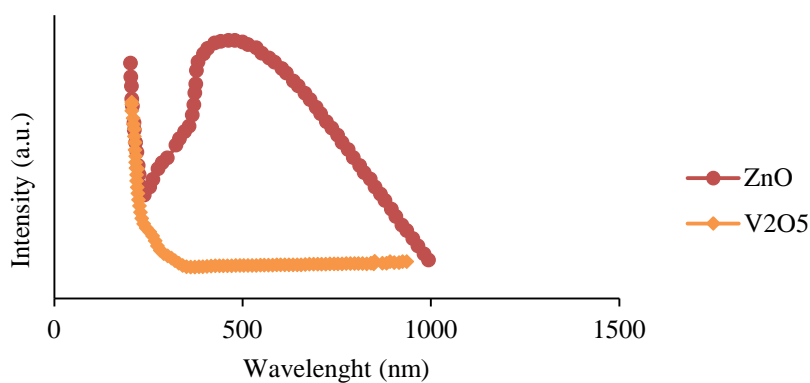
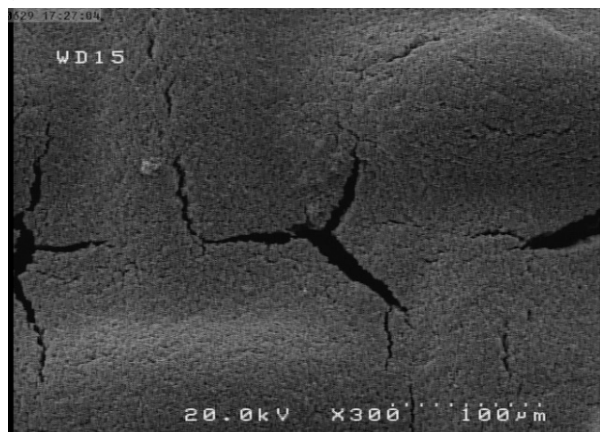
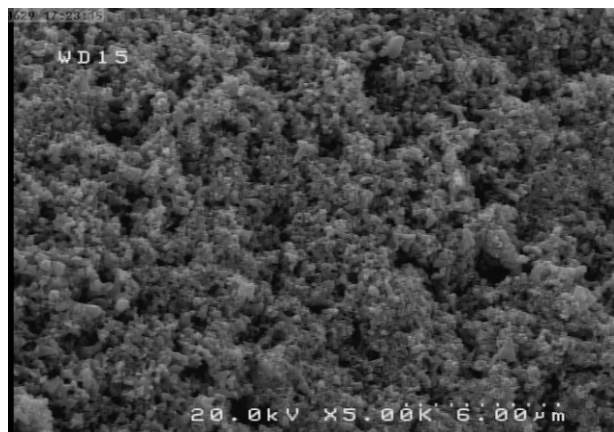


Figure 1. (a) FT-IR spectra and (b) UV-vis spectrum of V₂O₅ and ZnO.

a)



b)



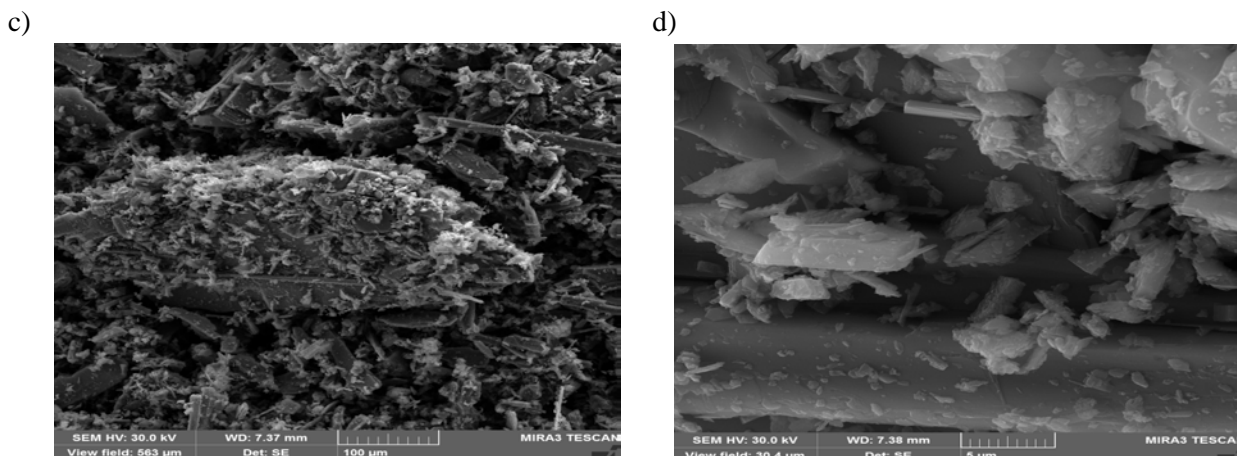


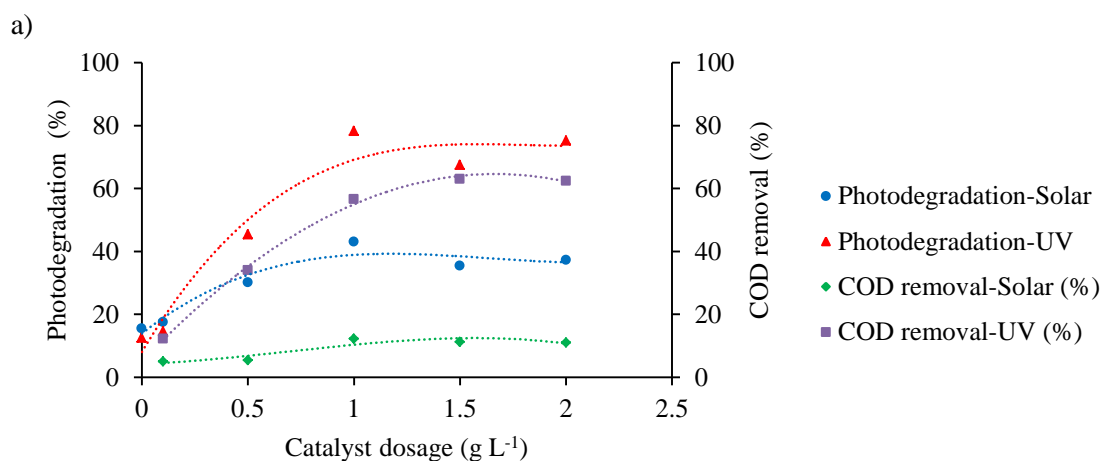
Figure 2. SEM images of (a) and (b) ZnO, (c) and (d) V₂O₅.

3.4. Effect of catalyst dosage

The investigation of the effect of catalyst dosage on the contamination removal in the wastewater is necessary to determine the optimum amount of catalyst for the desirable removal of contamination. Fig. 3 (a and b) shows the DS removal by both ZnO and V₂O₅ under UV and solar irradiations with initial pH 6 and DS concentration of 300 mg L⁻¹, while the catalyst dosage has changed in the range of 0.5 to 2.0 g L⁻¹. As is obvious from the results, increasing catalyst dosage up to 1 g L⁻¹ leads to an increase in the rate of DS decomposition by absorbing more photons on its surface (ZnO appears to remove DS more efficiently than V₂O₅). On the other hand, the content of ZnO and V₂O₅ more than 1 g L⁻¹ has no significant effect on DS

decomposition. It may be due to the catalyst accumulation and light scattering. In addition, Fig. 3 demonstrates the effect of both ZnO (Fig. 3 (a)) and V₂O₅ (Fig. 3 (b)) dosage on DS degradation after 180 min solar and UV irradiation in terms of COD removal. The trend of COD removal is similar to that of DS removals. It is obvious that photodegradation of DS not only causes decomposition of pharmaceuticals, but also has a significant effect on COD removal. It appears that in a high amount of catalyst dosage, a decrease in COD removal occurs due to higher toxicity obtained by DS degradation.

Based on the experimental data, the optimum amount of catalyst for photodegradation of DS in aqueous solution is about 1 g L⁻¹ in each case.



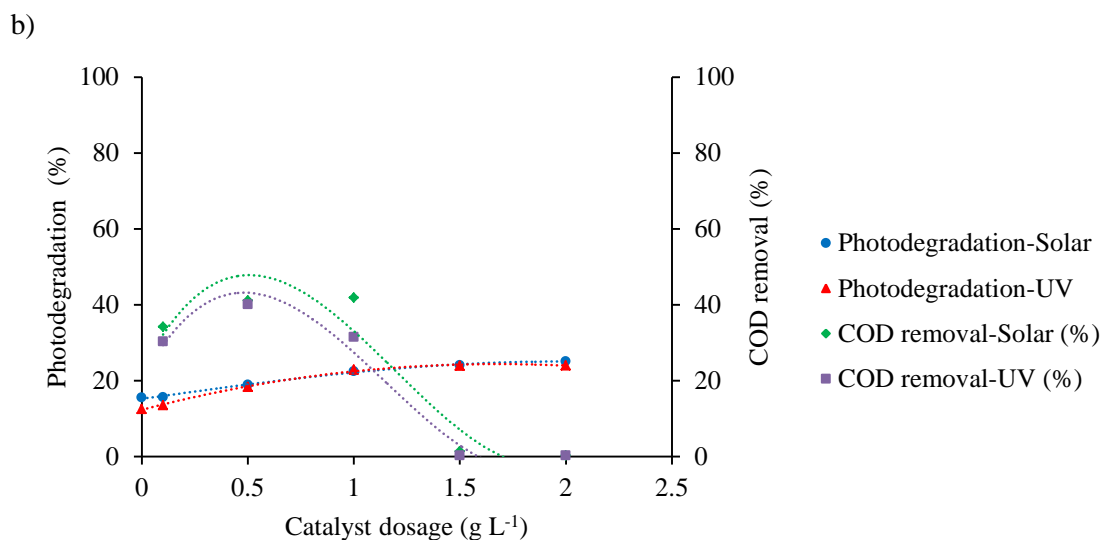


Figure 3. Effect of catalyst dosage on DS photodegradation and COD removal under UV and solar irradiation by (a) ZnO and (b) V₂O₅ (initial concentration of DS = 300 mg L⁻¹, pH of 6).

3.5. Effect of initial pharmaceutical concentration

The effect of the initial concentration on the photodegradation of DS was evaluated (Fig. 4 (a and b)). DS concentration, utilized for synthetic wastewater photocatalytic degradation, ranged from 100 to 500 mg L⁻¹. The investigation of the DS concentration effect on the photodecomposition experiments was accomplished using 1 g L⁻¹ of ZnO and V₂O₅ exposed to solar and UV irradiation that was gained from catalyst dosage optimization mentioned above at pH 6. As can be seen in Fig. 4 (a and b), the initial concentration of DS is an effective parameter in the photodecomposition efficiency. By increasing the initial concentration of DS up to 300 mg L⁻¹, the removal efficiency increases, because the initial concentration gradient as a driving force improves substantially and leads to greater transfer of DS molecules to the catalyst surface. At a higher DS concentration more than 300 mg L⁻¹, the removal efficiency did not exert any significant change. Although increasing DS concentration improves the driving force, the accumulation

of contaminants on the catalyst surface also increases. Hence, low light irradiation reaches the catalyst surface, resulting in a fewer number of effective holes formed. This factor produces an unfavorable impact on the removal efficiency in contrast to the favorable impact of the initial concentration gradient enhancement. Considering that the photodecomposition efficiency did not exert any significant changes in the range of DS concentration between 300 to 500 mg L⁻¹, the optimum point of DS concentration was set at 300 mg L⁻¹.

COD removal investigation was also carried out as another effective factor in the DS photodestruction. The results are in accordance with the presented reports of initial concentration effects on DS removal efficiency. Fig. 4 illustrates COD removal under the optimized conditions (catalyst concentration of 1 g L⁻¹ and pH 6). It is noteworthy that the higher COD removal of solutions can be achieved when the concentration is between 300 and 500 mg L⁻¹.

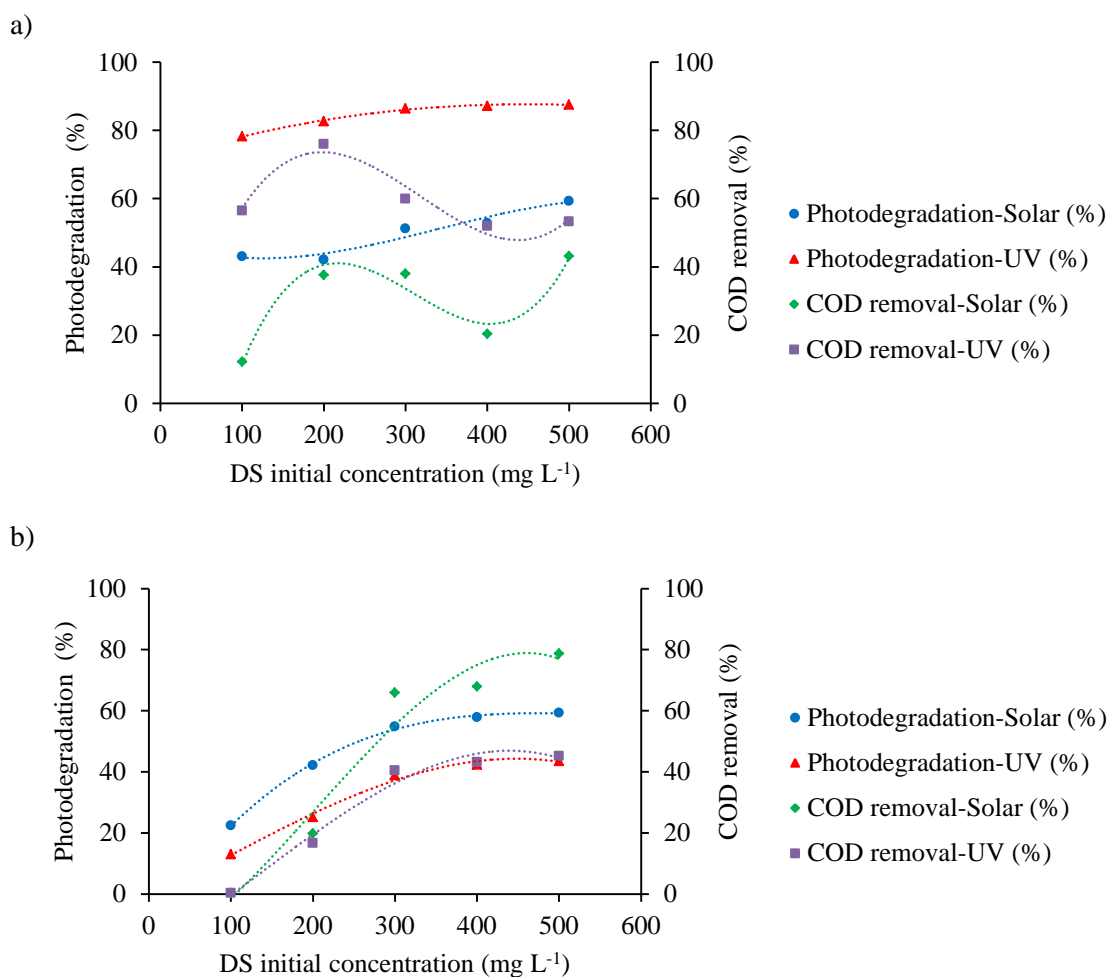


Figure 4. Effects of the initial concentration of DS on DS photodegradation and COD removal under UV and solar irradiation by (a) ZnO and (b) V₂O₅ (catalyst dosage = 1.0 g L⁻¹, pH of 6).

3.6. Effect of pH

Since the holes and hydroxyl radicals generated are the main pillars of photocatalytic processes and are affected strongly by pH, the pH of the solutions plays an important role in the photodegradation processes. Therefore, the role of pH in photocatalytic degradation and COD removal was investigated in the pH range of 4-8 under solar and UV light for both catalysts: ZnO and V₂O₅. With regard to the zero-point charge of catalysts and the structure of DS, the highest amount of pH was selected 8, because no noticeable photocatalyst performance was observed in pH > 8 (since the zero-point charge of ZnO is 9.0, the surface of the catalyst is positive below pH

9.0 [29]). On the other hand, corresponding to the reported literature, the lowest level of pH is chosen 4, because when pH is under 4, DS will precipitate [22]. The pH experiments were carried out in the optimum conditions under both solar and UV irradiation during 180 min; therefore, the DS concentration was considered 300 mg L⁻¹; in addition, 1 g L⁻¹ of ZnO and V₂O₅ powders were added.

The results of pH effects on the destruction of DS are shown in Fig. 5 (a and b). Generally, it is difficult to explain the pH effects on the photodegradation process due to three possible reactions that can occur, leading to the release of hydroxyl radicals, oxidation of the positive holes, and the reduction of electrons isolated from the

conduction band. Photocatalytic transformations on the surface of these catalysts also appear to be mainly due to hydroxyl radicals; thus, direct oxidation by positive holes seems to be operating [30]. In the present study, direct oxidation by positive holes is more likely to overcome other reactions; hence, the optimum pH for all conditions was adjusted in acidic and neutral pHs. According to Fig. 5 (a and b), pH 4 has been optimized for ZnO under solar and UV irradiation. The high photodegradation performance also took place at pH 4 for V₂O₅. These results were anticipated based on the catalyst and pharmaceutical nature. Acidic

ambiance is not only favorable for photocatalysts but also suitable for DS degradation. When DS dissolves in water, sodium separates by hydrolysis in aqueous solution; therefore, diclofenac is charged negatively. Hence, the acidic condition is ameliorative in the photodegradation of DS.

The same procedure for DS removal was also observed for COD removal of DS, as shown in Fig. 5 (a and b). The high decomposition of pharmaceutical occurred in neutral pH for ZnO and acidic ambiance for V₂O₅. In addition, this condition is the best pH point to optimize the COD removal.

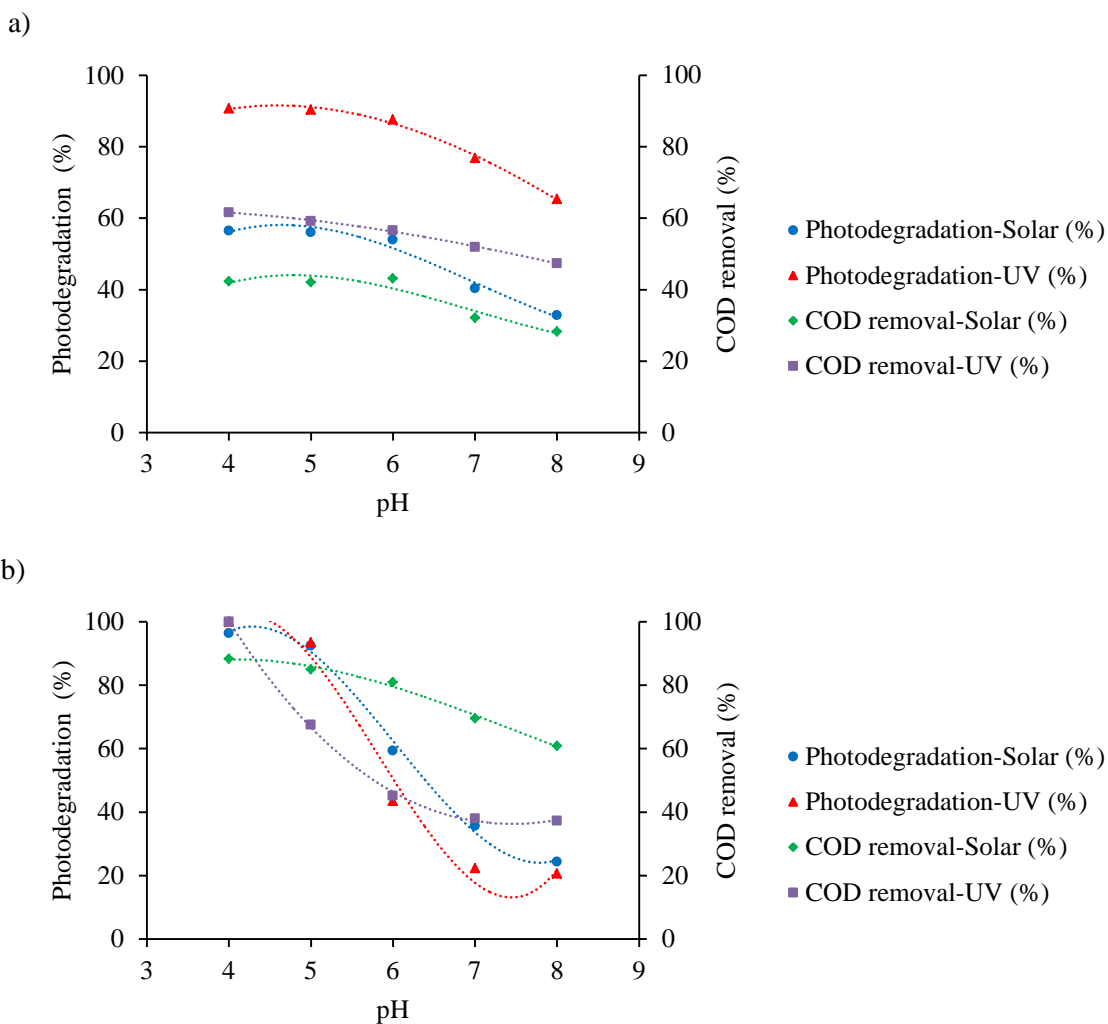


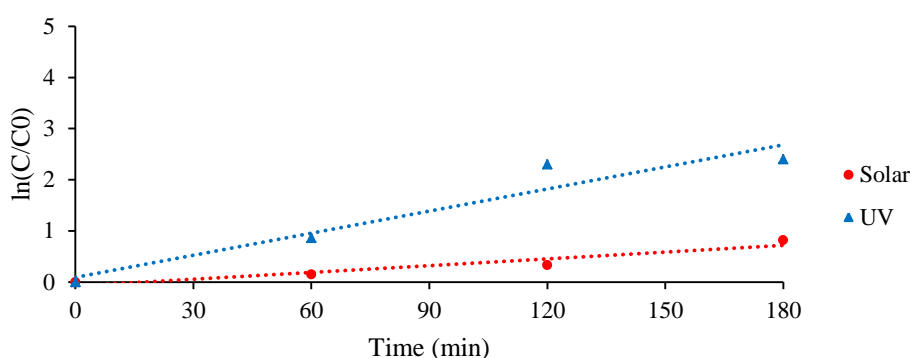
Figure 5. Effects of pH on DS photodegradation and COD removal under UV and solar irradiation by (a) ZnO and (b) V₂O₅ (catalyst dosage = 1.0 g L⁻¹, initial concentration of DS = 300 mg L⁻¹).

3.7. Kinetics of photocatalytic degradation of DS

Reaction kinetics was studied to evaluate the factors (pH, DS concentration, and catalyst dosage) that affect the rate of the photocatalytic decomposition process of DS. Kinetic investigation of processes was conducted at optimum points (180 min irradiation time, catalyst dosage 1 g L^{-1} , initial DS concentration 300 mg L^{-1} , and pH of 4). Fig. 6 ((a) and (b)) can demonstrate the plots

of $\ln(C/C_0)$ vs. irradiation time under solar and UV light that most likely follow pseudo-first-order kinetic model ($C(t) = C_0 \cdot \exp(Kt)$). The value of the rate constant (K) and R^2 can be observed under UV and solar light by ZnO and V_2O_5 in Table 1. According to the higher amount of calculated rate constant (K) under UV light, it is clear that catalysts are highly active under UV irradiation than solar light, and the higher DS photodegradation is obtained.

a)



b)

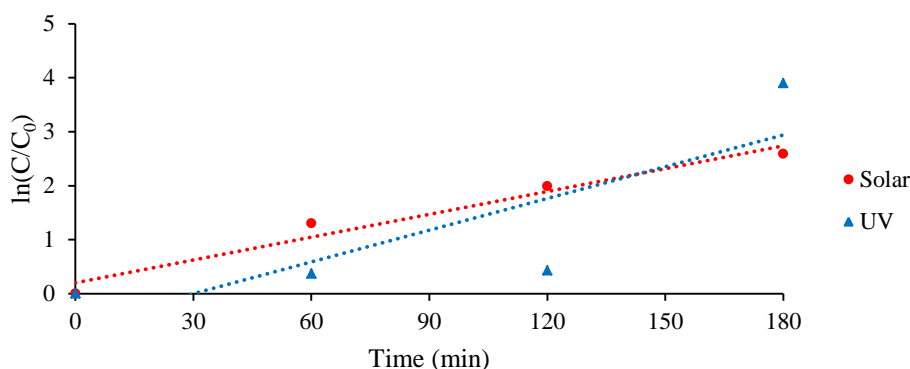


Figure 6. Kinetic analysis of DS photodegradation by (a) ZnO and (b) V_2O_5 under optimum point (catalyst dosage = 1.0 g L^{-1} , initial concentration of DS = 300 mg L^{-1} , and pH = 4).

Table 1

The pseudo-first-order kinetic parameters in the DS photodegradation.

Irradiation source	Catalyst	$K(\text{min}^{-1})$	R^2
UV	ZnO	0.0144	0.9191
UV	V_2O_5	0.0196	0.6908
Solar	ZnO	0.0044	0.9139
Solar	V_2O_5	0.0141	0.9634

The mechanism of the DS photocatalytic degradation is very complex; however, it may be greatly simplified as that demonstrated in Fig. 7. It appears that the generation of electron-hole pairs that migrate to the surface of the particles is the first step following the radiation absorption by the catalyst. Moreover, they can participate in redox on the surface of the catalyst. According to the mechanism of the photocatalytic reaction, the oxidation of organic species is included in the trapping reaction of the positive holes with

adsorbed water or with hydroxyl groups to form OH[•] radicals responsible for the initial oxidant attack in aqueous solutions [31]. In addition, the values of both catalysts band gap are reported in Fig. 7. The values of band gap energy (E_{bg}) will likely show that V₂O₅ ($E_{bg}=2.5$ eV) has an acceptable performance under solar irradiation compared with ZnO ($E_{bg}=3.2$ eV). Therefore, different activities of both catalysts are associated with their different band gap values.

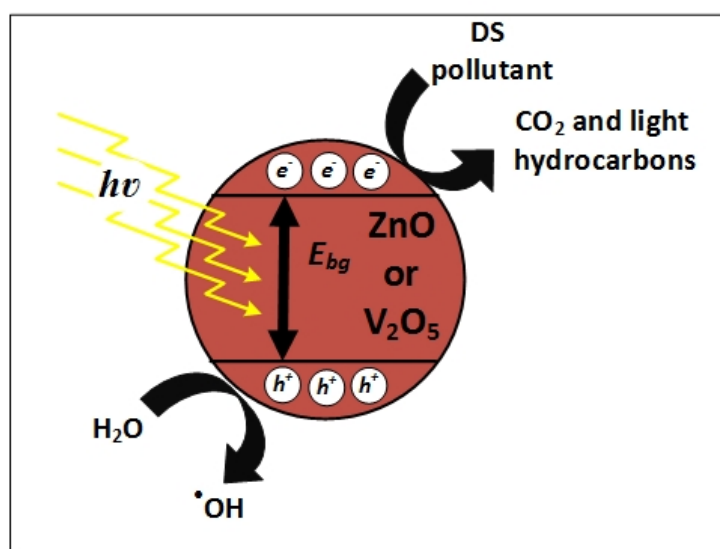


Figure 7. The photocatalytic reaction mechanism of ZnO and V₂O₅.

4. Conclusions

One of the most efficient ways to eliminate the pharmaceutical pollutants from wastewater is photocatalytic decomposition. In the current work, the impact of solar irradiation on the destruction of DS was evaluated using two photocatalysts with different band gaps. The maximum extent of photodestruction was obtained at a catalyst dosage of 1.0 g L⁻¹, the initial concentration of DS 300 mg L⁻¹, and pH 4 for each catalyst and under both light sources during 180 min irradiation time. Based on the results obtained, pH of solutions has a vital role in DS decomposition. Fortunately, the optimal

photodegradation percentage reached 100 % not only in removal efficiency but also in terms of COD removal for V₂O₅ under solar irradiation. Moreover, photodecomposition efficiency by ZnO reached 90.7 and 56.5 % and, also, 61.6 and 42.3 % in terms of COD removal under UV and solar irradiation, respectively.

References

- [1] Radosavljević, K. D., Lović, J. D., Mijin, D. Ž., Petrović, S. D., Jadranin, M. B., Mladenović, A. R. and Ivić, M. L. A., "Degradation of azithromycin using Ti/RuO₂ anode as catalyst followed by

- DPV, HPLC–UV and MS analysis”, *Chemical Papers*, 1 (2017).
- [2] Walter, M. V. and Vennes, J. W., “Occurrence of multiple-antibiotic-resistant enteric bacteria in domestic sewage and oxidation lagoons”, *Applied and Environmental Microbiology*, **50** (4), 930 (1985).
- [3] Boxall, A. B., Kolpin, D. W., Halling-Sørensen, B. and Tolls, J., Peer reviewed: Are veterinary medicines causing environmental risks?, ACS Publications, (2003).
- [4] Bort, R., Ponsoda, X., Jover, R., Gómez-Lechón, M. J. and Castell, J. V., “Diclofenac toxicity to hepatocytes: A role for drug metabolism in cell toxicity”, *Journal of Pharmacology and Experimental Therapeutics*, **288** (1), 65 (1999).
- [5] Artmann, J., Bartels, P., Mau, U., Witter, M., Tumpling, W. V., Hofmann, J. and Nietzsche, E., “Degradation of the drug diclofenac in water by sonolysis in presence of catalysts”, *Chemosphere*, **70** (3), 453 (2008).
- [6] Oaks, J. L., Gilbert, M., Virani, M. Z. and Watson, R. T., “Diclofenac residues as the cause of vulture population decline in Pakistan”, *Nature*, **427** (6975), 630 (2004).
- [7] Taggart, M., Senacha, K., Green, R., Jhala, Y., Raghavan, B., Rahmani, A., Cuthbert, R., Pain, D. and Meharg, A., “Diclofenac residues in carcasses of domestic ungulates available to vultures in India”, *Environment International*, **33** (6), 759 (2007).
- [8] Takáčová, A., Mackluřak, T., Smolinská, M., Hutňan, M. and Olejníková, P., “Influence of selected biowaste materials pre-treatment on their anaerobic digestion”, *Chemical Papers*, **66** (2), 129 (2012).
- [9] Pasquini, L., Munoz, J.-F., Rimlinger, N., Dauchy, X., France, X., Pons, M.-N. and Görner, T., “Assessment of the fate of some household micropollutants in urban wastewater treatment plant”, *Chemical Papers*, **67** (6), 601 (2013).
- [10] Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N. and Takada, H., “Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant”, *Water Research*, **41** (19), 4373 (2007).
- [11] Grover, D., Zhou, J., Frickers, P. and Readman, J., “Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: Impact on receiving river water”, *Journal of Hazardous Materials*, **185** (2), 1005 (2011).
- [12] Xue, W., Wu, C., Xiao, K., Huang, X., Zhou, H., Tsuno, H. and Tanaka, H., “Elimination and fate of selected micro-organic pollutants in a full-scale anaerobic/anoxic/aerobic process combined with membrane bioreactor for municipal wastewater reclamation”, *Water Research*, **44** (20), 5999 (2010).
- [13] Esplugas, S., Bila, D. M., Krause, L. G. and Dezotti, M., “Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents”, *J. Hazard. Mater.*, **149** (3), 631 (2007).
- [14] Achilleos, A., Hapeshi, E.,

- Xekoukoulotakis, N. P., Mantzavinos, D. and Fatta-Kassinos, D., "Factors affecting diclofenac decomposition in water by UV-A/TiO₂ photocatalysis", *Chemical Engineering Journal*, **161** (1-2), 53 (2010).
- [15] Röhricht, M., Krisam, J., Weise, U., Kraus, U. R. and Düring, R.-A., "Elimination of pharmaceuticals from wastewater by submerged nanofiltration plate modules", *Desalination*, **250** (3), 1025 (2010).
- [16] Deegan, A., Shaik, B., Nolan, K., Urell, K., Oelgemöller, M., Tobin, J. and Morrissey, A., "Treatment options for wastewater effluents from pharmaceutical companies", *International Journal of Environmental Science & Technology*, **8** (3), 649 (2011).
- [17] Bagal, M. V. and Gogate, P. R., "Degradation of diclofenac sodium using combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis", *Ultrasonics Sonochemistry*, **21** (3), 1035 (2014).
- [18] Madhavan, J., Kumar, P. S. S., Anandan, S., Zhou, M., Grieser, F. and Ashokkumar, M., "Ultrasound assisted photocatalytic degradation of diclofenac in an aqueous environment", *Chemosphere*, **80** (7), 747 (2010).
- [19] Rizzo, L., Meric, S., Kassinos, D., Guida, M., Russo, F. and Belgiorno, V., "Degradation of diclofenac by TiO₂ photocatalysis: UV absorbance kinetics and process evaluation through a set of toxicity bioassays", *Water Research*, **43** (4), 979 (2009).
- [20] Naddeo, V., Belgiorno, V., Kassinos, D., Mantzavinos, D. and Meric, S., "Ultrasonic degradation, mineralization and detoxification of diclofenac in water: Optimization of operating parameters", *Ultrasonics Sonochemistry*, **17** (1), 179 (2010).
- [21] Mendez-Arriaga, F., Esplugas, S. and Gimenez, J., "Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO₂ and simulated solar irradiation", *Water Res.*, **42** (3), 585 (2008).
- [22] Pérez-Estrada, L., Maldonado, M., Gernjak, W., Agüera, A., Fernández-Alba, A., Ballesteros, M. and Malato, S., "Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale", *Catalysis Today*, **101** (3), 219 (2005).
- [23] Federation, W. E. and Association, A. P. H., Standard methods for the examination of water and wastewater, American Public Health Association (APHA), Washington D.C., USA, (2005).
- [24] Shavisi, Y., Sharifnia, S., Zendezhaban, M., Mirghavami, M. L. and Kakehazar, S., "Application of solar light for degradation of ammonia in petrochemical wastewater by a floating TiO₂/LECA photocatalyst", *Journal of Industrial and Engineering Chemistry*, **20** (5), 2806 (2014).
- [25] Muthukumaran, S. and Gopalakrishnan, R., "Structural, FTIR and photoluminescence studies of Cu doped ZnO nanopowders by co-precipitation method", *Optical Materials*, **34** (11), 1946 (2012).
- [26] Wei, Y., Ryu, C.-W. and Kim, K.-B., "Improvement in electrochemical performance of V₂O₅ by Cu doping", *Journal of Power Sources*, **165** (1), 386

- (2007).
- [27] Byrappa, K., Dayananda, A., Sajan, C., Basavalingu, B., Shayan, M., Soga, K. and Yoshimura, M., "Hydrothermal preparation of ZnO: CNT and TiO₂: CNT composites and their photocatalytic applications", *Journal of Materials Science*, **43** (7), 2348 (2008).
- [28] Liu, Y., Lu, Y., Liu, S. and Yin, Y., "The effects of microwaves on the catalyst preparation and the oxidation of o-xylene over a V₂O₅/SiO₂ system", *Catal. Today*, **51** (1), 147 (1999).
- [29] Samaha, M., Merabet, S., Bouguerra, M., Bouhelassa, M., Ouhenia, S. and Bouzaza, A., "Photo-oxidation process of indole in aqueous solution with ZnO catalyst: Study and optimization", *Kinet. Catal.*, **52** (1), 34 (2011).
- [30] Richard, C., Boule, P. and Aubry, J. M., "Oxidizing species involved in photocatalytic transformations on zinc oxide", *J. Photochem. Photobiol., A: Chem.*, **60**, 235 (1991).
- [31] Pelizzetti, E. and Serpone, N., (Eds.), *Homogeneous and Heterogeneous Photocatalysis*, Reidel, Dordrecht, (1988).