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Scale-up of photoreactor with TiO_2 thin layer for wastewater treatment

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ABSTRACT

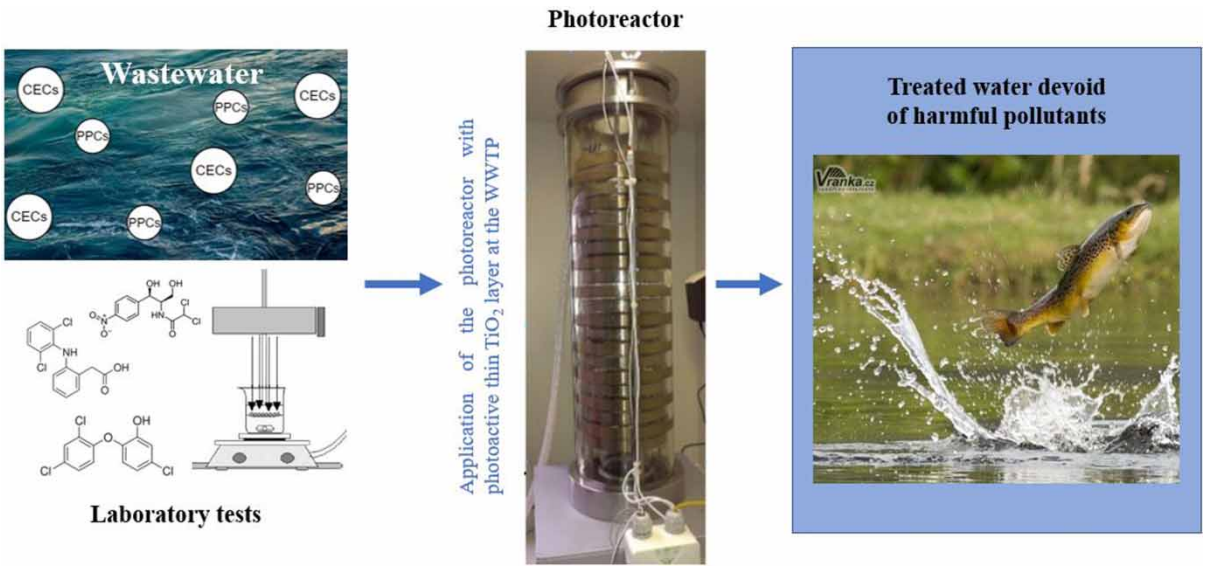
This study is devoted to the scale-up potential of TiO_2/UV photocatalyst for real wastewater treatment including its durability tests. The activity of the prepared TiO_2 layers was first tested in a laboratory reactor on key representative pollutants diclofenac, chloramphenicol and triclosan. A special pilot plant reactor of a two-tube system with 21 stainless steel annulets covered by TiO_2 thin layers and the inner volume of 3.5 L was constructed. Pilot tests were performed with wastewater from the pharmaceutical industry containing danazol and norethisterone with the concentration varying between 4 and 7 mg L^{-1} at the flow 18 L h^{-1} and municipal wastewater at the output sewage plant for 67,000 inhabitants containing bisphenol A, 4-nonyphenol, estron, ethinylestradiol and triclosan in the concentrations of the individual contaminants varying between 50 and 600 ng L^{-1} at the flow 200 L h^{-1}. After the treatment during the pilot photocatalytic test, the concentration of individual contaminants decreased by 82–100%, while no decrease in the efficiency of the photocatalytic process was recorded during the long-term tests lasting for 3–6 months.

Key words: chloramphenicol, diclofenac, photocatalytic degradation, titanium dioxide, waste pharmaceuticals

HIGHLIGHTS

- A new type of pilot plant reactor was designed for TiO_2/UV photocatalysis scale-up.
- Excellent durability of TiO_2 layer on annulets was corroborated on a durability tester.
- Efficiency of pilot reactor was tested on various drugs and real wastewater successfully.
- The lifespan of the photocatalyst was corroborated by a 3-month-long test.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Alarming levels of water pollution have been a serious problem in most countries all over the world. Various micropollutants have negative impacts on the environment regarding their permanent presence not only in wastewater but also in surface water, groundwater and drinking water. Among many water purification technologies currently in use, advanced oxidation processes (AOPs) have a great potential to remove a wide range of emerging contaminants. AOPs include the in-situ generation of highly reactive oxygen species, such as hydroxyl radicals (HO•), H_2O_2, O_3, and superoxide anionic radicals ($O_2^{\bullet -}$), which provide pathways of mineralization to CO_2, H_2O, and inorganic ions or acids, or at least, destroy contaminants to residual compounds which are no longer ecotoxic. Reactive hydroxyl radicals are produced by one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). AOPs are currently of great interest and are being extensively studied for their potential use in removing non-biodegradable and highly stable pollutants from water (Feng *et al.* 2013; Kanakaraju *et al.* 2018; Cuerda-Correa *et al.* 2019; Sbardella 2019; Garrido-Cardenas *et al.* 2020; Pino *et al.* 2020; Mahdi *et al.* 2021 and many others).

Leyva-Díaz *et al.* (2021) studied 2,938 articles published related to the pollutant disposal from wastewater in the period of 1979–2020. They monitored the development of individual scientific methods to find the best practices. They found that the most commonly used oxidation process was photocatalysis on titanium dioxide (TiO_2) as the photocatalyst. However, in addition to it, many other heterogeneous photocatalysts based on metal oxides were tested, such as V_2O_5, ZnO, ZnS, Fe_2O_3, CdO, CdS, $SrTiO_3$, WO_3, and Al_2O_3. The mineralization of organic pollutants into CO_2, NH_4^+, NO_3^-, and SO_4^{2-} took place by the formation of radicals such as O_2^-, HOO•, or OH• through a multistep reduction. Moreover, the mechanism of photocatalysis has also been widely studied, and basic principles of the method are sufficiently described (Ameta & Ameta 2018; Konstas *et al.* 2019; Fanourakis *et al.* 2020; Varma *et al.* 2020; Barros *et al.* 2021). Furthermore, photocatalysts can be combined, for example, with magnetic material coated with optical fibers, adsorbents or membranes, which improve their efficiency in water treatment. Advances in the research of photocatalytic materials have enabled the development of highly effective materials capable of degrading various contaminants, as well as the development of photocatalysts in visible light (Benotti *et al.* 2009; Ek *et al.* 2014; Fanourakis *et al.* 2020; Mansouri *et al.* 2021).

Titanium dioxide, either in its mineral forms or in a composite system, revealed a high potential as a photocatalyst due to its favourable physicochemical properties. In addition, compared to many other candidates, TiO_2 is almost the only material suitable for industrial applications, due to its effective photoactivity, high stability and low cost (Krakowiak *et al.* 2021). For this reason, there are many studies using TiO_2 as a photocatalyst aimed at determining optimal operating conditions in order to achieve the highest efficiency of degradation of pharmaceutical compounds (Kanakaraju *et al.* 2018; Shi *et al.* 2018; Zhu *et al.* 2019). In fact, there are many studies (Gusain *et al.* 2020; Kumar *et al.* 2020; Yamazaki *et al.* 2020) focusing on the application of photocatalysis for degradation of chemical pollutants. However, from the analysis of the results, it is evident that the decontamination efficiency differs significantly from author to author. It is obvious that the oxidation rate together with the efficiency of the photocatalytic system are highly dependent on a number of operating parameters which control the photodegradation of organic molecules. The basic parameters include substrate concentration, photocatalyst amount, solution pH, reaction medium temperature, light irradiation time, light intensity, photocatalyst surface, dissolution of oxygen in the reaction medium, nature of photocatalyst, nature of substrate, doping of metallic and nonmetallic ions, and structure of photocatalyst and substrate, their crystallinity, and crystallite size (Kumar & Pandey 2017; Gusain *et al.* 2020; Niu *et al.* 2020; Yamazaki *et al.* 2020). Moreover, the rate of photocatalytic degradation also depends on the type of pollutant, i.e., on its chemical structure, concentration, and the presence of other substances in water (Doll & Frimmel 2003; Karungamye 2020). Regrettably, the vast majority of these studies are carried out only on a laboratory scale.

Analyzing hundreds of studies devoted to this issue, it is clear that, essentially, the only scale-up solutions have been focused on so-called solar reactors (Abdel-Maksoud *et al.* 2016; Fendrich *et al.* 2019) either mostly tubular or falling film type. Glass tubes were placed in parabolic bells concentrating real solar radiation into the treated contaminated water, which is in contact with the photocatalyst. Water usually flowed through the irradiated tubes along with the TiO_2 nanoparticles. Glass tubes 1,250 mm long with the diameter of 32 mm and wall thickness of 1.4 mm were arranged on an aluminum base that reflects sunlight onto the tubes. The reactor volume was 7.7 L, while the liquid was in the recirculation mode at 20 L/min (Diaz-Angulo *et al.* 2020). Solar collector areas usually achieved units of m^2 (Prieto-Rodriguez *et al.* 2012; Cabrera-Reina *et al.* 2019). Another tested arrangement involved tubes with the irradiated area of 3.08 m^2 (Saggioro *et al.* 2014) or as a recirculating glass tube type model, with their radiated area of 0.91 m^2 (Pereira *et al.* 2011).

Within the falling film arrangement, water flows in a thin film along the irradiated wall (falling film solar reactors) (Colina-Marquez *et al.* 2016; Shnain *et al.* 2021). As a photocatalyst, nanoparticles of anatase, rutile, or their mixture, in concentrations of approximately 10–400 mg/L, were usually used. The areas of falling film reactors used to be over 1 m^2 (e.g. Abdel-Maksoud *et al.* 2018; Shnain *et al.* 2021). The largest detected irradiated area for the solar photocatalytic reactor of 25 m^2 was precisely for the falling flow type (Zayani *et al.* 2009). The mentioned solar photocatalytic reactors should be energetically advantageous; however, their applications are limited due to the possibility of these reactors to work only in specific geographical climatic conditions with sufficient solar radiation and only during the day (Chafie *et al.* 2018). Another solution, which is considered usable for so-called gray water, is a research membrane bioreactor with ultrafiltration and solar photocatalysis with a volume of 3 L, where photocatalysis with anatase particles is simultaneously applied (Ojobe *et al.* 2021).

Apart from the experimental modified membrane bioreactor mentioned above, we have not been able to find any pilot or operational solutions for the photocatalytic removal of pollutants with a TiO_2 photocatalyst, modified, for example, into a catalytic film in a closed reactor and irradiated with a suitable radiation emitter (UV, LED lamps) enabling the photocatalytic decomposition of pollutants, which would be capable of a scale-up for at least a pilot arrangement.

For these reasons, this study is devoted to the potential of TiO_2/UV photocatalyst for a scale-up. The efficiency of the catalyst was first studied on selected common pollutants in laboratory scale and compared with the classic sorption method further. Moreover, the study shows the potential of TiO_2 as a simple photocatalyst suitable for scale-up. The article is also focused on verifying the sufficient resistance and long life of the photocatalytic TiO_2 layer. The developed reactor will enable the continuous removal of emerging pollutants from real wastewater, especially from point sources using an end-of-the-pipe solution. The novelty of this reactor lies in a robust, however simple, and inexpensive device with simple operation and non-conflicting scale-up.

2. EXPERIMENTAL

2.1. Preparation of TiO_2 layers and used chemicals

TiO_2 photocatalyst was prepared by a sol-gel method based on the formation of an inverse micellar system by mixing non-polar solvent cyclohexane (99.9%, Carl Roth GmbH Co.), non-ionic surfactant Triton X 114 (TX114; laboratory grade, Sigma-Aldrich) and distilled water. Subsequently, by the addition of the metal precursor (Titanium (IV) isopropoxide; ≥97.0%, Sigma-Aldrich), its hydrolysis and polycondensation took place. The prepared sol was applied on two different types of substrates – glass beads for a laboratory unit and stainless-steel annulets for a pilot unit. Regarding the laboratory scale, glass beads with the diameter of 1.5 mm were put into a stirred beaker, where the deposition was performed. Stainless steel annulets were covered by TiO_2 layer and dipped into the sol under defined conditions (residence time in the sol 30 sec, pulling-out velocity 6 cm min^{-1}). In both cases, the prepared amorphous gel layers were calcinated at 400 °C for 4 h with the temperature ramp 1 °C min^{-1} in a muffle furnace to form crystalline TiO_2. The whole preparation of one layer was repeated four times, and the resulting TiO_2 photocatalyst contained only a pure anatase crystalline phase. The prepared photocatalyst was used for photocatalytic degradation of two drugs – diclofenac sodium salt (an analytical standard, Sigma-Aldrich) and chloramphenicol (VETRANAL®, analytical standard, Sigma–Aldrich) – and triclosan (certified reference material, TraceCERT®, Sigma–Aldrich) widely used as an antibacterial and antifungal agent present as an additive in medicinal cosmetics, medical soaps, etc. (Daughton & Ternes 1999). The Figure 1 shows the structural formulas of the tested substances.

2.2. Characterization of photocatalyst and sorbents

A crystallographic characterization was performed by XRD (panalytical-MRD diffractometer with the Cu anode) and by Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Almega XR, with wavelength 473° nm). XRD patterns for

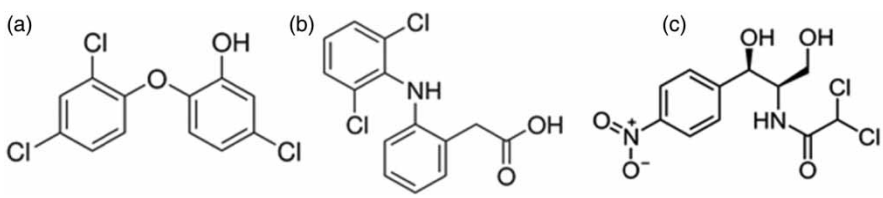


Figure 1 | Chemical structure of tested pollutants in laboratory tests: (a) triclosan (TCS), (b) diclofenac (DFC), (c) chloramphenicol (CAM).

glass beads covered by three and four layers of TiO_2 were nearly identical with the main diffraction lines of anatase (Figure 2). Other crystalline structures of TiO_2 were not revealed. Moreover, Raman spectra showed the attendance of characteristic vibration lines with 640, 525, 400, and 150 cm^{-1}, which confirmed the pure anatase structure. The detailed characterization of prepared layers was published in our previous study, e.g. in Solcova *et al.* (2018).

Surface imaging was performed using a scanning electron microscope (Tescan Indusem). The images were taken at accelerating voltage 15 kV. From the pictures of the layer edge is also possible to estimate the layer thickness (Figure 3(b)).

Two activated commercial charcoal Norit (grain 0.16–0.25 mm, S_{BET} 733 $m^2\,g^{-1}$) and Supersorbon (pellets 4–7 mm, S_{BET} 1,258 $m^2\,g^{-1}$) were used for the sorption comparable experiments. Specific surface areas (S_{BET}) were determined by physical adsorption of nitrogen at −195.8 °C on ASAP 2050 and 2020 instruments (Micromeritics) from the adsorption-desorption isotherm using a modified BET equation (Schneider 1995). The comparative sorption experiments were realized in a batch

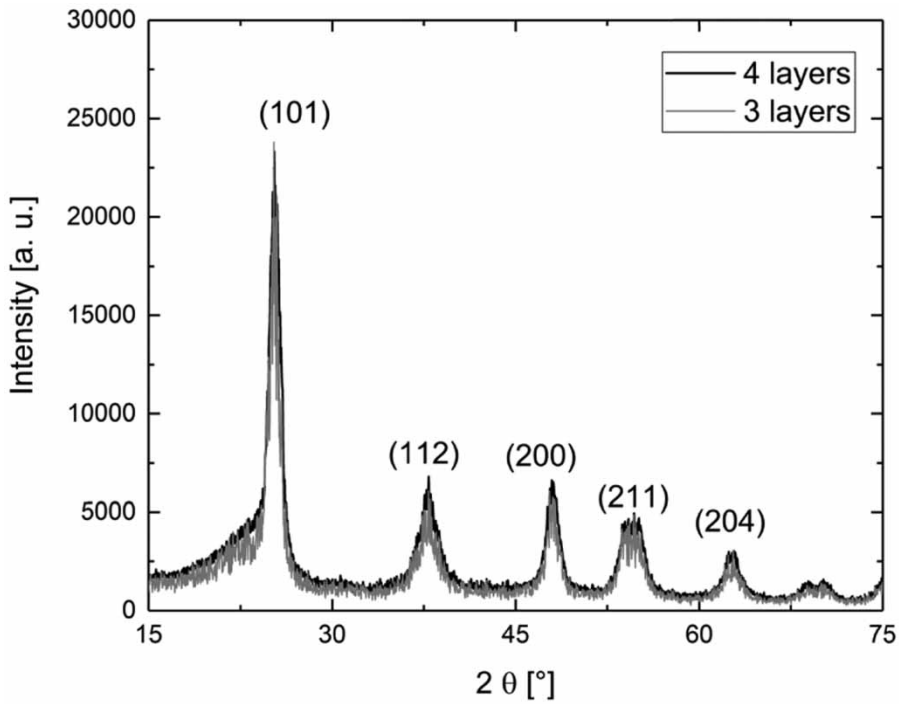


Figure 2 | XRD of prepared layers (3 and 4). Only the main diffraction lines of anatase are depicted. Other crystalline structures of TiO_2 were not revealed. Particle size is lower than 10 nm.

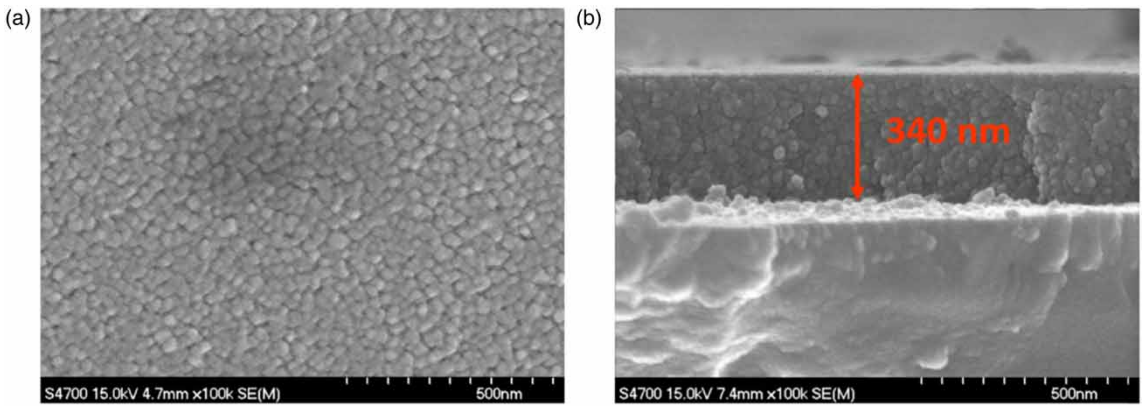


Figure 3 | (a) SEM image of surface and (b) cross-section morphologies of prepared TiO_2 thin film.

reactor using the orbital shaker GFL 3005, 300 rpm (Lauda DR. R. Wobser GMBH, Germany) with the volume of the reaction solution at 100 mL and amount of sorbent 1 g.

2.3. Laboratory photocatalytic and photolytic tests

The initial concentrations of pollutants were 1 mg L^{-1} for Diclofenac, Chloramphenicol and Triclosan in laboratory experiments. The reactions were carried out in a stirred beaker (volume of reaction solution 200 mL) with the prepared photocatalyst (5 g glass beads contained 2.5 mg active amount of TiO_2) or without a photocatalyst at laboratory temperature in the presence of UV light (UV lamp Philips HOK 4/120 SE, 400 W medium pressure mercury lamp (Phillips, the Netherlands) with a wavelength in the range of 250–420 nm). Pollutants concentrations were analysed on Waters Alliance HPLC module equipped with PDA detector, a column thermostat and Empower software. Toxicity tests were evaluated from bioluminescence inhibition of *Vibrio fischeri* bacteria. Analytical parts (pollutant concentrations and toxicity) were performed in external commercial laboratories. All laboratory experiments were duplicated and the standard deviation never exceeded 5%. The figures show the calculated average values.

2.4. Pilot photocatalytic tests

A special pilot plant reactor, depicted in Figure 4(b), with a two-tube system (an inner quartz tube and outer borosilicate glass tube) was used. Twenty-one stainless steel annulets covered by TiO_2 thin layers were placed into the inner volume of 3.5 L. The UV light source (mercury lamp Philips HOK 25/120 with technical data: overall length C 367 mm; diameter 21.6 mm; lamp wattage 2,500 W; lamp voltage 440 V) was inserted into the centre of the reactor. Emitted heat was cooled by flowing air. Polluted water flowed through the space with an active photocatalyst by zigzag system from the bottom to the top of the reactor. An aluminium casing was placed on the outer wall of the reactor during experiments to prevent emission of UV light. The detailed description of the reactor can be found in Spacilova *et al.* (2016). Tests with the pilot photocatalytic unit were performed on two real water samples – wastewater from the pharmaceutical industry containing danazol and norethisterone with the concentration varying between 4 and 7 mg L^{-1} at the flow 18 L h^{-1} and municipal wastewater as the last purification unit at the output sewage plant for 67,000 inhabitants containing bisphenol A, 4-nonyphenol, estron, ethinylestradiol and triclosan in the concentrations of the individual contaminants varying between 50 and 600 ng L^{-1} at the flow 200 L h^{-1}. Resistance to abrasion was measured with ELCOMETER 1720, a durability tester with the frictional element-felt disc of

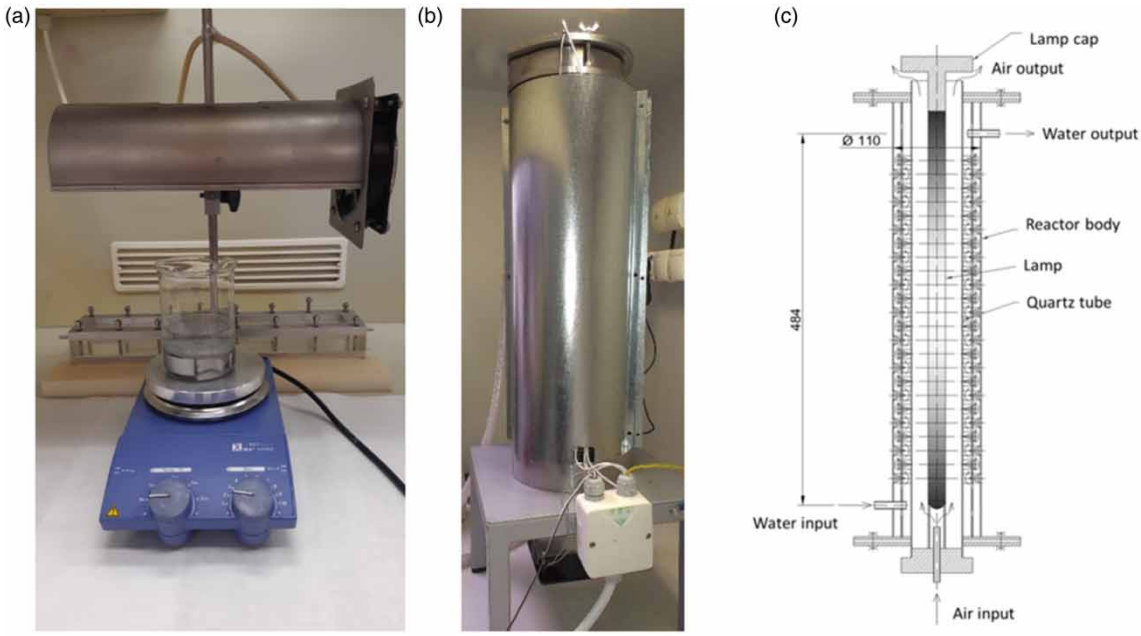


Figure 4 | (a) The laboratory unit arrangement; (b) the pilot scale reactor with protective casing; (c) diagram of the coated annulets system with thin TiO_2 films in the pilot plant reactor.

the density 0.56 g cm^{-3}. A disc newly covered by TiO_2 was used for the abrasion test. It consisted of two parts, 1,160 cycles with the weight of 0.25 kg and 2,900 cycles with the weight of 0.5 kg.

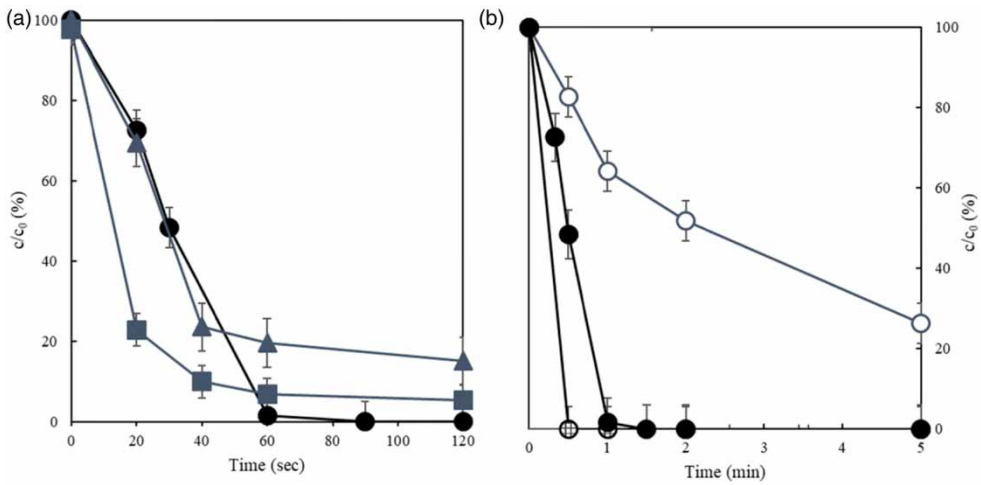
3. RESULTS AND DISCUSSIONS

Two widely used drugs, diclofenac (DFC) and chloramphenicol (CAM), in addition to one bacterial agent used in personal care products, triclosan (TCS), were selected for laboratory tests. Prior to the start of the photocatalytic reaction, reaction solution with photocatalyst was stirred and kept for 15 min in the dark. Only then the reaction solution was located under UV light. The sorption of the pollutant on the surface of the photocatalyst was low, up to a maximum of 2.5% of the initial concentration; 0.2% for DFC, 0.3% for CAM and 2.3% for TCS.

The obtained results of photocatalytic decomposition for all three contaminants (DFC, CAM and TCS) in the laboratory batch reactor are shown in Figure 5(a) in normalized concentration $c.c_0^{-1}$. It is evident that the photocatalytic decomposition of all tested pollutants ran really fast. The decomposition of DFC was the fastest, and its concentration dropped to zero in 60 seconds. The decomposition of TCS was the quickies at the start of the reaction and decreased to 20% in the first 20 seconds. With respect to the scale-up of the process, the efficiency of photocatalysis was compared with the sorption on two commercially activated carbons, Supersorbon and Norit, see Figure 5(b). When comparing the effectiveness of both methods, it must be taken into account that during sorption there is no decomposition of pollutants, but only their adsorption on the surface of the sorbent, which must be subsequently regenerated or disposed of, usually by incineration. However, in the case of sorption, pollutants are completely removed, whereas in the case of photocatalysis, similarly to photolysis, pollutants are decomposed and the resulting substances may be more toxic than the original ones. Solcova *et al.* (2018) found that direct photolytic decomposition brought significantly increasing values of toxicity for bisphenol A, 4-nonylphenol and ethinylestradiol compared with the photocatalytic process. In all cases, the presence of TiO_2 photocatalyst reduced the resulting toxicity. For this reason, photolytic and photocatalytic decomposition of diclofenac were performed together with toxicity determination of the resulting solutions. The obtained results are shown in Figure 6.

It is evident that decomposition of diclofenac was nearly the same involving photolysis, as well as photocatalysis (Figure 6(a)); however, toxicity of the resulting solutions revealed significant differences (Figure 6(b)). In the case of a photocatalytic reaction, the toxicity did not increase nor varied around zero, whereas in the case of the purely photolytic reaction, there was a significant increase in toxicity during the course of the photocatalytic reaction.

Thus, it can be concluded that the photocatalytic process is an effective way of removing drugs from water, and its practical application depends on the scale-up of the process and the durability, as well as the lifespan of the catalyst. Based on these



Figures 5 | (a) Comparison of photocatalytic decomposition of diclofenac —●—, chloramphenicol —▲— and triclosan —■— (amount of photocatalyst was 5 g of glass beads with 2.5 mg active amount of TiO_2, $V = 200$ mL); (b) comparison of photocatalytic decomposition and sorption of diclophenac; Norit —⊗—, Supersorbon, —○—, photocatalysis —●— (amount of sorbent was 1 g, $V = 100$ mL); initial concentration of all pollutants was 1 mg L^{-1}.

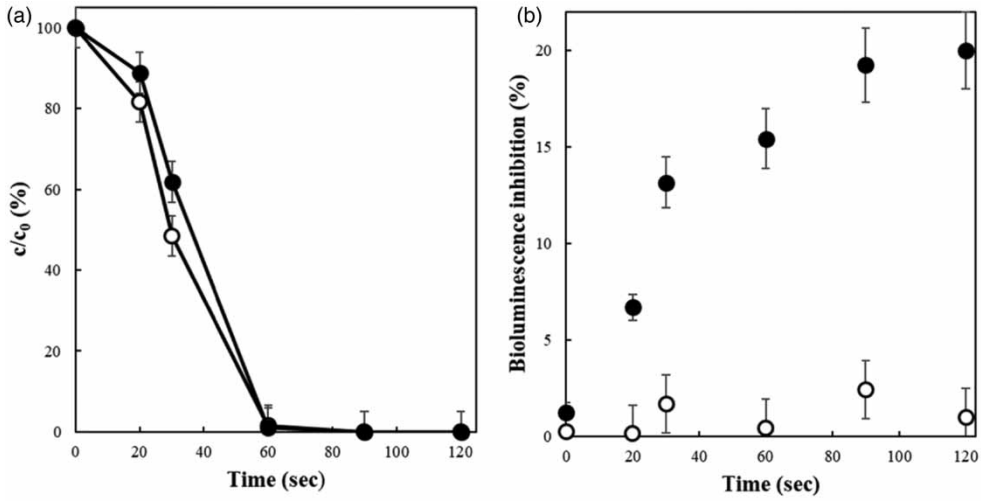


Figure 6 | (a) Time dependence of normalized DFC concentration for photolytic (•) and photocatalytic (○) reactions and (b) inhibition of bioluminescence for photolytic (•) and photocatalytic (○) reactions over time.

results, a specially designed pilot unit was employed, for which a new methodology was developed for covering large areas by titanium oxide layers without the loss of surface strength and quality.

Real water samples were used for the pilot tests regarding a photocatalyst durability and a lifespan. The long-term photocatalytic experiments lasting nearly a quarter of a year were performed at a sewage plant, where the photocatalytic pilot plant reactor (Figure 4(b)) was placed as the last purification unit. The treated water contained the main contaminants: bisphenol A, 4-nonylphenol, estrone, ethinylestradiol and triclosan within the concentrations of the individual contaminants varying between 50 and 600 ng L^{-1}. The initial concentration of all contaminants varied slightly in the range of maximum 10% for two samples in the interval of a quarter of a year. The comparison of the catalyst efficiency for the mentioned samples is shown in Figure 7. The concentration of all contaminants decreased rapidly with the efficiency of 82–100% for both types of samples. In addition, no differences in catalyst efficiency were found between two samples tested after a quarter of a year. It can be stated that even after the intensive use during the quarter of a year, the photocatalyst did not show a loss of the catalytic efficiency.

The second test with the pilot photocatalytic unit concerning a photocatalyst durability and a lifespan was performed with wastewater from the production of specific contraceptive components, namely danazol and norethisterone with the concentrations varying between 4 and 7 mg L^{-1}. The obtained results related to the photocatalytic efficiency are summarized in Figure 8. It is important that in all cases, the residual concentration was below the officially allowed limit, 0.5 mg L^{-1} for

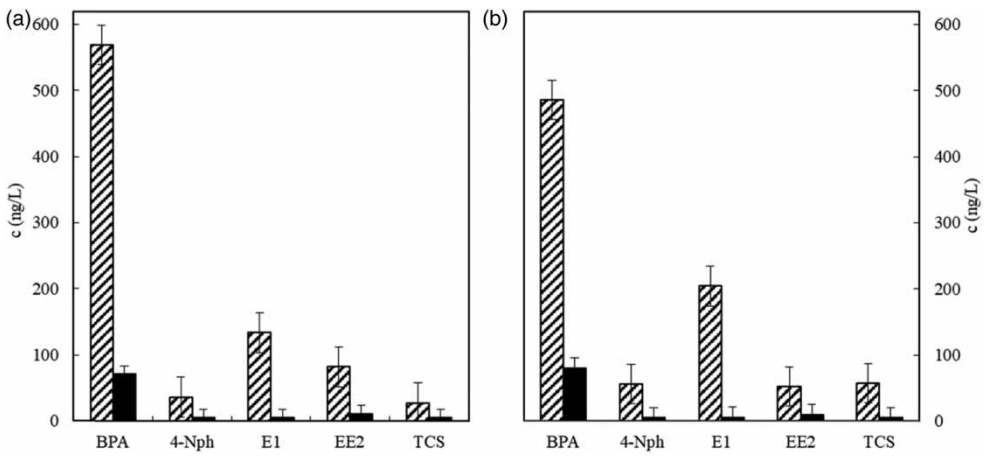


Figure 7 | Comparison of the catalytic efficiency for two samples of wastewater in the interval of two months.

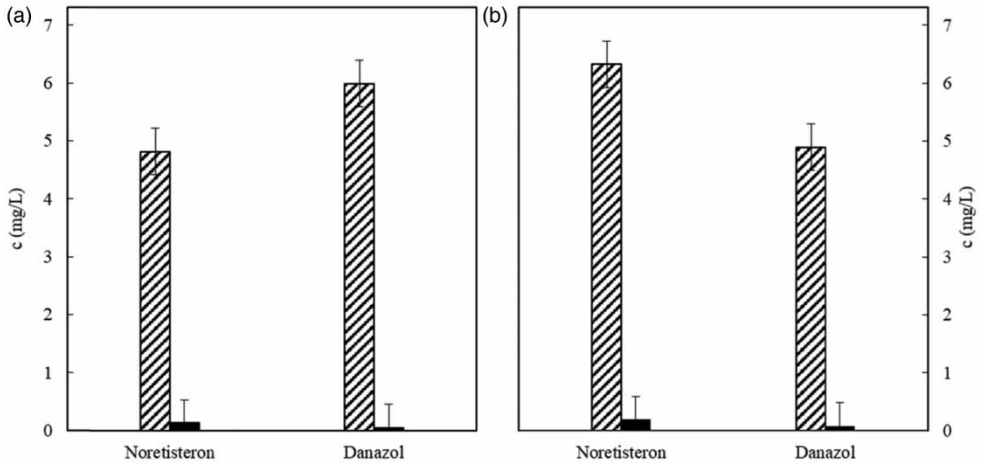


Figure 8 | Comparison of the catalytic efficiency wastewater from pharmacy production containing danazol and noretisteron in the interval of the half year.

both drugs. It is an excellent result regarding the fact that between testing both samples, there was a time interval of six months, during which the pilot reactor was used daily. Based on both tests, it can be concluded that the prepared TiO_2 photocatalyst showed not only high activity but also considerable abrasion resistance, so that even after half a year, there was no decrease in its efficiency.

Based on these positive results, the prepared photocatalyst was subjected to an abrasion test. A disc newly covered by TiO_2 was used for the abrasion test. It consisted of two parts, 1,160 cycles with the weight of 0.25 kg and 2,900 cycles with the weight of 0.5 kg. After 4,060 cycles, only 40–50% of the TiO_2 layer was removed, which is an excellent result.

4. CONCLUSION

This study verified the potential of TiO_2/UV photocatalysis to remove various pollutants, i.e. diclofenac, chloramphenicol and triclosan, in laboratory and pilot plant tests using a new type of pilot plant reactor. Long-time tests with the pilot photocatalytic unit, which were successfully performed on two real water samples, wastewater from the pharmaceutical industry containing danazol and norethisterone with the concentration varying between 4 and 7 mg L^{-1} and municipal wastewater containing emerging pollutants bisphenol A, 4-nonylphenol, estron, ethinylestradiol and triclosan in the concentrations between 50 and 600 ng L^{-1}, confirmed not only the efficiency of the photocatalytic system but also the durability and lifespan of the prepared TiO_2 photocatalytic layers. In all cases, the residual concentration was below the officially allowed limits even after six months of operation of the pilot plant photocatalytic unit. Durability of TiO_2 layers was corroborated on a durability tester, with an excellent result. The obtained results document that photocatalysis using TiO_2-based catalyst (mostly anatase) synthesized by a sol-gel technique is an effective method to remove emerging pollutants including pharmaceuticals, and can be conveniently scaled-up.

This study confirmed that the developed reactor enables the continuous removal of emerging pollutants from real wastewater, especially from point sources using an end-of-the-pipe solution from smaller ones, while it is a robust but simple and inexpensive device with simple operation. Further scale-up is possible by vertical setting or parallel addition of additional units. The incorporation of photocatalyst nanoparticles into the film enables long-term operation of the device with constant high remediation efficiency, as well as eliminating demanding separation of titania nanoparticles.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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