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Endocrine disruptor degradation by photocatalytic pilot plant unit

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***Abstract*— Degradation of endocrine disruptors on an immobilized titanium dioxide photocatalyst in the presence of UV light was tested on a specially designed plug-flow reactor. The active part of this pilot plant reactor with the inner free volume of 3.5 L consisted of stainless steel annulets coated by titanium dioxide thin layers in a zig-zag arrangement. Two representative endocrine disruptors, 17-ethynyl estradiol and bisphenol A, in water solution were chosen for testing of the designed pilot plant reactor. Efficiency of the reactor was evaluated for various concentrations and flow rates. Process effectiveness and high reproducibility was also confirmed by estrogenity and toxicity tests. The designed photocatalytic treatment system was tested by purification of real waste water containing seven main endocrine disruptors and rinsed water from pharmaceutical industry. Efficiency of the photocatalytic degradation process varied between 44 – 100 % with respect to the individual endocrine disruptors and flow rates. Possible utilization of the photocatalytic reactor as the last purification unit at sewage plants was confirmed even for flow rates up to 300 L/h.**

Keywords — Endocrine disruptor; Titanium dioxide; Photocatalysis; Waste water treatment; Pilot plant photo-reactor

I. INTRODUCTION

Endocrine disruptors (EDCs) have been receiving a growing worldwide attention owing to their potential negative impacts on human health and environment. Endocrine disruptors belong to exogenous hormonally active agents influencing the hormonal system of animals and humans and can negatively affect their development. These compounds possess a very large chemical diversity, which influences their different endocrine activities. Agency for Environmental Protection (EPA) has established a list of potential substances with endocrine activity of over 10,000 molecules [1]. One of the first study focused on the EDCs is the publication written by T. Colborn (1993) [2]. The ability of EDCs to bind to steroid hormone receptors led scientists to a closer investigation of the endocrine disruptor hazard, particularly on wildlife and humans [3-6]. Moreover, endocrine disruptors may be hormonally active in very low concentrations and they may cause chronic disorders during a long-term exposure [7].

Regarding the fact that conventional methods of water and sewage treatment are not completely effective in removing the EDCs, Advanced Oxidation Processes (AOPs) have been intensively studied as really promising technologies for EDCs degradation [8-13]. Especially, heterogeneous photocatalysis has evoked a great interest in treatment of various types of organic contaminants found in polluted water or air. This method is based on the formation of highly reactive species which can degrade even the most recalcitrant molecules. The most commonly used photocatalyst is titanium dioxide (TiO_2) applied in the form of powder or immobilized as a thin layer. An intensive effort has been focused on removing single endocrine disrupting compounds (EDCs) or their mixtures which belong to the group of environmental pollutants from polluted water by TiO_2 photocatalysis.

Nevertheless, most studies were usually carried out in a laboratory scale [14-20], and studies concerning pilot scale units are rare. Moreover, the total majority of pilot plant experiments combine the TiO_2 photocatalysis with other AOPs such as Fenton or photo-Fenton treatment, the solar UV-light system or the addition of hydrogen peroxide [20-22] together with membrane processes such as cross-flow microfiltration to guarantee the TiO_2 powder removal [23]. Other pilot studies were limited to experiments with solar type pilot plants [24-27]. Thus, there is a lack of literature dealing with the application of TiO_2 photocatalysis in the pilot plant scale. Moreover, this method does not indicate the formation of estrogenically active transformation products during the treatment and, therefore, it seems to be highly effective and proficient for water purification.

Consequently, this study is focused on water treatment containing various EDCs by application of photocatalytic oxidation in a specially designed pilot plant unit with immobilized TiO_2. Efficiency of this reactor was tested not only on simulated polluted

water but also on real waste water after the sewage plant treatment or real water from pharmaceutical industry with special focus on representative EDCs such as 17b-ethynyl estradiol, bisphenol A, norethisteron, danazol *etc*.

II. Materials and Method

A. Preparation of TiO_2 layer

TiO_2 thin layers were prepared by a sol-gel process controlled in a reverse micellar environment by a dip-coating technique. TiO_2 was synthesized by the addition of Titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$, Aldrich, > 97%) into the formed inverse micellar solution made of cyclohexane (Aldrich, 99.9+%, HPLC grade), non-ionic surfactant Triton X114 ($C_{27}H_{48}O_{7.5}$, Aldrich) and distilled water. The molar ratio of cyclohexane/Triton X114/water/$Ti(OC_3H_7)_4$ was kept at 11/1/1/1 (volume ratio TX114/cyclohexane = 0.49) [28]. Thin TiO_2 films were deposited by four cycles of a dip-coating method. The substrate was dipped into the sol during 30 s and then it was pulled out with the velocity of 6 cm min^{-1}. At the time between the single dip-coating cycles, the samples were thermally treated by calcination at 450 °C for 4 h with the temperature ramp 1 °C min^{-1} in an air flow in a muffle furnace. As a substrate, 21 stainless steel annulets of 2 different averages were used. The larger annulet had 240.5 cm^2, and the smaller one 224.2 cm^2.

B. Layer characterization

Structural analyses of the prepared thin TiO_2 films were performed by X-ray diffraction (Panalytical-MRD laboratory diffractometer with the Cu anode), Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Almega XR, 473 nm laser), scanning electron microscopy (Hitachi S4700) and atomic force microscopy (Thericroscopes). The layer resistance was measured by an abrasion tester Elcometer 1720.

C. Decomposition of endocrine disruptors

17α-ethynylestradiol (EE2; Sigma–Aldrich, ≥ 98.0 % HPLC) and bisphenol A (BPA; Sigma–Aldrich, ≥ 99.0 %) were chosen as the representative endocrine disruptors for tests with simulated water. The initial applied concentration of EE2 and BPA was 10 ppm. The average initial concentrations of the monitored EDCs in the real waste water after the sewage plant treatment are summarized in Table I. for three main contaminants (bisphenol A (BPA), irgasan (IRG) and 4-nonyphenol (4-NPH)).

TABLE I. Endocrine disruptors in real waste water

Substance	**Concentration** [ng/L]
BPA	387.2
IRG	180.2
4-NPH	59.6

Decomposition of EDCs was studied by a photocatalytic process by means of the UV light activated TiO_2 thin layers. Irradiated TiO_2 creates active radicals which can react with molecules of water or directly with endocrine disruptors and form oxidative products and intermediates. This process can be described by a simple mechanism (Equation 1 – 4).

$$TiO_2 + hv \rightarrow TiO_2\ (e^- + h^+) \quad (1)$$
$$h^+ + H_2O \rightarrow OH^{\bullet} + H^+ \quad (2)$$
$$e^- + O_2 \rightarrow O_2^{\bullet} \quad (3)$$
$$h^+/OH^{\bullet} + ED \rightarrow \text{Oxidative products} \quad (4)$$

The degradation of EDCs in water was evaluated on the basis of the concentration decrease. The analysis was performed on Waters Alliance HPLC module equipped with PDA detector, a column thermostat and Empower software. Standard retention time and UV spectra by consensus (maximum 280 nm) were used for identification.

Kinetic parameters of the reactions studied in photocatalytic system were determined by fitting experimental data to the theoretical model described by the equation (5), where, c_A represents the concentration of A in dependence on time, c_{A0} is the initial concentration of A, n represents experimental order of the reaction, k for reaction rate coefficient and τ for time.

$$c_A = c_{A0}[1+(n-1)c_{A0}{}^{n-1}k\tau]^{1/1-n} \quad (5)$$

The standardized determination of bioluminescence inhibition of *Vibrio fischeri* bacteria strain was applied [29] as a toxicity test. For this purpose, a gram of negative bacteria strain V. fischeri NRLL-B- 11177 was used as a testing microorganism. Bacteria emit the light arising in the organism during the chemical reaction and this visible light is reduced at the contact of bacteria with the contaminant.

Estrogenity was tested on a Saccharomyces cerevisiae sp. strain with an integrated receptor for human estrogen and androgen compounds. The yeast cells in contact with hormonal active agents produced luciferase, which together with luciferin present in the medium created light measured by luminometer.

D. Pilot plant experiments

According to the obtained data and knowledge based on the flow and batch reactors [30], a pilot reactor was built up. Photocatalytic experiments were performed in this special pilot plant reactor (Fig. 1) [31] placed at the sewage treatment plant area. The active part of the pilot plant reactor with the inner free volume of 3.5 L consisted of 21 stainless steel annulets coated by TiO_2 active thin layers. The reactor body uses a system of two tubs - an inner quartz tube and outer borosilicate glass tube. A medium pressure mercury lamp Philips HOK 25/120 with technical data: Overall Length C 367 mm; Diameter 21.6 mm; Lamp Wattage 2500 W; Lamp Voltage 440 V is situated inside the quartz tube. This UV lamp emits the polychromatic light beam which is cooled by air blowing in the inner tube and actuated by a ventilator.

The photocatalytic reactor is covered by a metal case to prevent UV light emission.

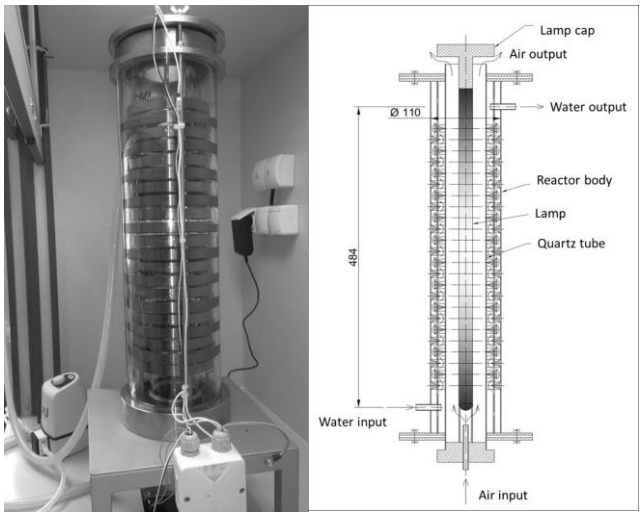

Fig. 1. *Pilot plant photocatalytic reactor*

The space between the inner tube and the outer tube is filled by rings with immobilized TiO_2 nanoparticles in a thin layer form. The contaminant water was pumped into the reactor at a constant rate and flow through the reactor annulus from the bottom upwards. The system of coated annulets was created by alternated organized bigger and smaller rings characterized by the shape of an isosceles triangle in a vertical sectional view (Fig. 2). This special arrangement provided the unique zigzag stream mode of contaminant water which ensured higher photocatalytic efficiency due to the increased UV irradiation transmittance and the larger irradiated area of the photocatalyst. The UV light emitted by the lamp homogenously irradiated the skew upper and lower area of the small and big rings, which caused photocatalysis and photolysis of organic compounds in the flowing contaminated water. The special zigzag water flow in the reactor led to a better transfer of the matter between molecules of contaminants and the photocatalyst surface, which also increased the photocatalytic activity.

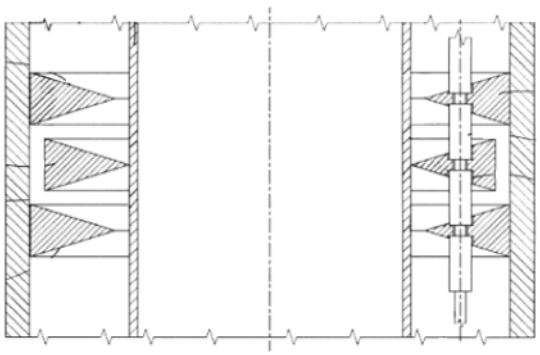

Fig. 2. *The coated annulets system with thin TiO_2 films*

III. RESULTS AND DISCUSSION

A. Layer's characterization

The prepared thin TiO_2 layers deposited on the metal rings possess the anatase crystalline structure, which was determined by XRD analysis and Raman spectroscopy. The thickness of three deposited layers was evaluated from images made by SEM and it was estimated at 330 nm. The layer surface morphology was studied by AFM analyses and the obtained value of RMS factor (< 1) indicated a smooth surface of layers. A more detailed characterization of layers was described in our previous work [32].

Regarding any application, layer resistance belongs to the most important properties. Therefore, the abrasion test was performed. A frictional element- felt disc with the density of 0.56 g cm-3 was applied as a tester. The abrasion resistance was tested by 1160 cycles with the weight of 0.25 kg and 2900 cycles with the weight of 0.5 kg. After these 4060 cycles, only 40-50 % of TiO_2 layers were removed, which corresponds to high abrasion resistance.

B. Degradation of simulated water

Two representative endocrine disruptors in water solutions were chosen for photocatalytic degradation in the designed pilot plant reactor with the volume of 3.5 L. EE2, which represents the pharmaceutical substance of hormonal contraception, and BPA, which is released e.g. from food packages, were selected as model EDCs. The efficiency of the degradation process was studied on simulated water with the initial concentration of both contaminants of 10 ppm. This model concentration of EDCs was chosen on the basis of the laboratory tests made in a flow photoreactor. The chosen concentration of EE2 similarly as BPA in simulated water was significantly higher than the usual sum of endocrine disruptors in real water at the output of sewage plant. Thus, the certainty of absolute purification of real water could be guaranteed even at high velocities.

Photocatalytic degradation of EE2 was measured for three various flow rates - 6, 9 and 14 L/h with corresponding retention time of 35, 24 and 15 min. The reaction course of EE2 decomposition during photocatalytic reaction in the reactor is depicted in Fig. 3. The efficiency of EE2 degradation process at flow rates 6 and 9 L/h achieved 95 % and 90 % respectively, while at 14 L/h the decomposition efficiency decreased to 78 %. The difference in efficiency between the flow rate 6 and 14 L/h is almost 20 % and it is evident that the degradation efficiency strongly depends on a used flow rate. In fact, the most important quantity is the retention time; a higher retention time causes a longer time of photocatalytic reaction of the solution on the TiO_2 layer surface and thus higher degradation efficiency.

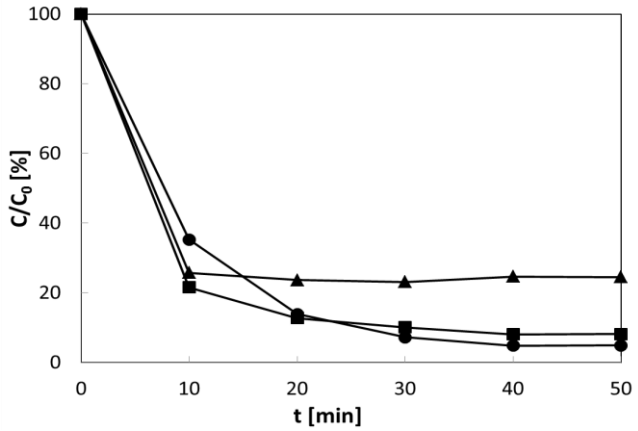

Fig. 3. *Decomposition of EE2 from model water at various flow rates, ● – 6 L/h, ■ – 9 L/h, ▲ – 14 L/h*

The photocatalytic degradation of BPA at three various flow rates - 5, 11 and 14 L/h is depicted in Fig. 4. The retention time of the solution during irradiation in the reactor was 45, 19 and 15 min, respectively. The highest conversion was reached at flow rate 5 L/h and the efficiency was 80 %. It can be seen that BPA is a more resistant compound to the photocatalytic process than EE2. Comparing the reached results at flow rate 14 L/h after 1 reaction cycle (15 min), it is obvious that degradation efficiency of EE2 is 78 % while BPA only 44 %; thus, EE2 degradation is nearly twice more efficient than BPA.

To obtain reproducibility of the measurements the photocatalytic experiments were repeated and the determined deviation was lower than 5 %. Nevertheless, this deviation includes not only reproducibility of the experiments but also the error of the analytical method and analytical determination. Therefore, it can be concluded that reproducibility of photocatalytic experiments is evidently very good.

Kinetic parameters of EE2 and BPA degradation in photocatalytic reactor were calculated acording the eq. (5) and are summarized in Table II. The obtained kinetic data of EDCs decomposition in the photo-reactor evinced the pseudo first order reaction for both compounds.

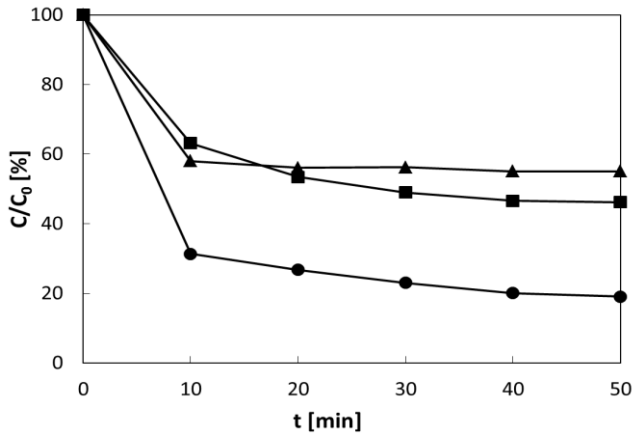

Fig. 4. *Decomposition of BPA from model water at various flow rates, ● – 5 L/h, ■ - 11 L/h, ▲ – 14 L/h*

Comparison of the rate constants (Table II.) clearly shows higher efficiency for EE2 degradation. Degradation of EE2 solution was approximately 3.5 times faster than for BPA solution.

TABLE II. KINETIC PARAMETERS OF EE2 AND BPA SOLUTION DEGRADATED IN PILOT PLANT UNIT

ED	k [min^{-1}]	n [-]	c_{A0} [$mg \cdot L^{-1}$]
EE2	0.091	1.011	11.31
BPA	0.026	1.194	11.83

Many researchers have investigated the degradation of BPA using various series of oxidants and described the oxidation kinetics but only in a laboratory scale [33-35]. In fact, there is a real lack of literature providing similar results for pilot plant scale; nevertheless, J.Sharma [36] studied photolysis of BPA with and without H_2O_2 addition under similar conditions. They achieved without H_2O_2 addition under UV radiation efficiency of 30% during 350 min and with H_2O_2 addition under UV radiation the efficiency increased up to 80% in dependence of H_2O_2 concentration (1.47 -11.76 mM). The reported results for BPA degradation with UV/H_2O_2 showed pseudo-first-order kinetics for the oxidation reactions. Regrettably, important information concerning toxicity and/or estrogenity before and after a degradation process is really missing.

C. The effect of EDCs degradation on toxicity and estrogenity

During photocatalytic degradation of EDCs some new intermediates or by-products are created and these compounds can possess higher estrogenity and toxicity than the original contaminants. Therefore, we focused on estrogenity and toxicity of EE2 and BPA decomposition. The obtained results for the flow rate of 14 L/h are summarized in Fig. 5, where the vertical dashed line represents retention time of the reactor.

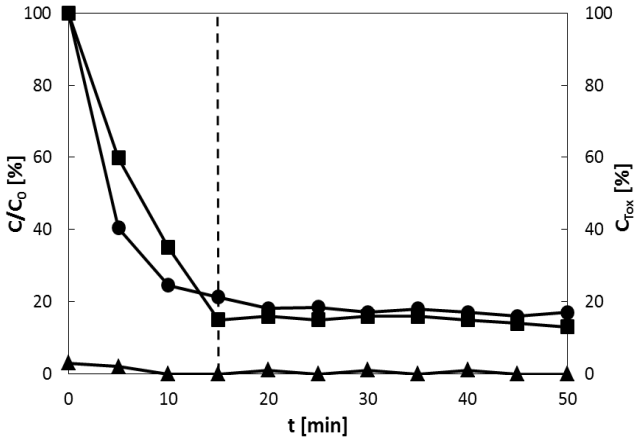

Fig. 5. *Estrogenity and toxicity of EE2 during the photocatalytic experiment, ● – Concentration at 14 L/h, ■ – Estrogenity, ▲ – Toxicity, -- 1 cycle (15 min)*

It is evident that the estrogenic activity of EE2 was reduced to 20 % and the toxicity value ranged from 0 % to 3 %, which falls to error of analytical determination and can be evaluated as a zero toxic effect during the reaction. The measured values of toxicity and the residual concentration in EE2 solution also demonstrated rapid equilibration (15 min) corresponding to the residence time at a given flow. It follows that no emerging products, intermediates or by-products which reveal any estrogenic activity were created.

Similar results were also obtained for BPA degradation. The decrease of estrogenity corresponds to BPA degradation rate and the significant decrease of toxicity was also detected, see Fig. 6. Toxicity and estrogenic activity of BPA solution during the experiment was measured at a flow rate of 5 L/h, which corresponds to the residence time of 45 minutes and the highest degradation efficiency (Fig. 4).

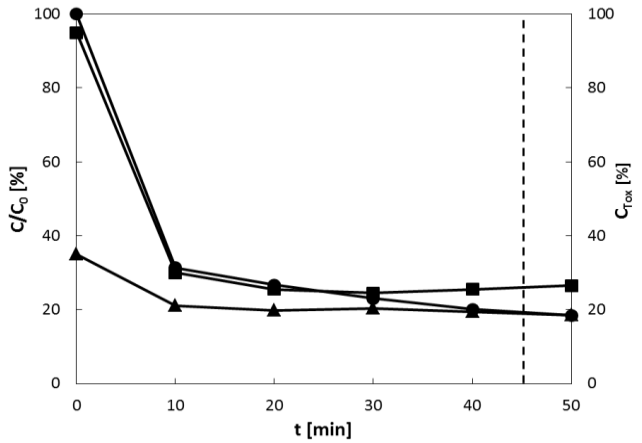

Fig. 6. *Estrogenity and toxicity of BPA during the photocatalytical experiment, ● – 5 L/h, ■ – Estrogenity, ▲ – Toxicity, -- 1 cycle (45 min)*

The results show a significant drop of BPA concentration in the solution during the first 10 minutes, which resulted in concentration and estrogenic activity reduction of 69 % resp. 70% and even the toxicity decreased from 35 % to 20 %. After this period, a slight decrease of BPA residual concentrations to 18.5 % was visible, which could be caused by variation in the flow rate.

These facts corroborate the original idea that during the photocatalytic process in the designed pilot plant unit not only the original compounds but also the intermediates and by-products can be successfully degraded.

D. Degradation of the real waste water

Accumulation of endocrine disruptors in nature has become a significant environmental problem in which municipal and industrial waste water is involved. Therefore, an industrial town with 67 thousand inhabitants was chosen as a source of real waste water. One of the small sewage plants employed for waste water treatment was selected for degradation experiments. The photocatalytic pilot plant reactor was placed as the last purification unit at that sewage plant. Besides the above mentioned contaminants (EE2, BPA, 4-NPH and IRG) were also monitored other common contaminants: estriol (E1), estron (E2) and estradiol (E3). It can be seen (Fig. 7) that concentrations of all contaminants varied in time, particularly concerning BPA and E1. Therefore, long-term photocatalytic experiments were also conducted. Fig. 8 shows the degradation process efficiency for water with a relatively high content of contaminants for the flow rate of 30 L/h with the residence time of 7 min.

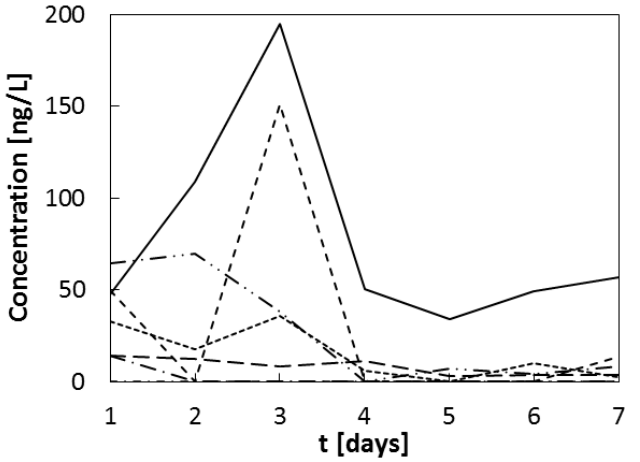

Fig. 7. *Concentration of EDCs during 7 consecutive days, −−− BPA, − − 4-NPH, - - -E1, −·−·E2, − · − E3, −··−··EE2, -----IRG*

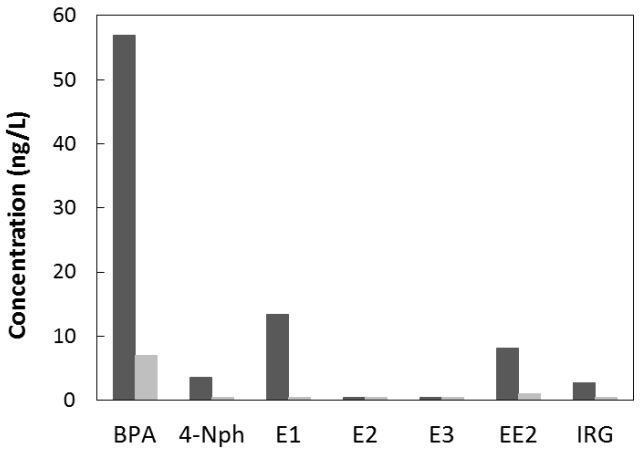

Fig. 8. *Endocrine disruptor degradation from real waste water in the pilot plant reactor (Flow rate 30 L/h; Residence time 7 min), ■ – Input, ■- Output*

Results show that decomposition of 4–Ph, E1 and IRG contaminants achieved more than 95 %, and EE2 and BPA decomposition reached 87 resp. 88 %. E2 and E3 compounds in this waste water sample occurred at minimal concentration only. Thus, a very good degradation efficiency of a pilot reactor was confirmed. High efficiency of the pilot plant reactor should be emphasized, particularly due to the fact that purification of water containing a huge number of mutually influenced contaminants is extremely complicated.

Not only concentration of contaminants but also toxicity and estrogenity determination, and water at the input and output of the photocatalytic pilot plant unit were characterized by the most important indicators of wastewater pollutions, namely TOC (total organic carbon) and COD_{Cr} (chemical oxygen demand). The obtained results are summarized in Table III.

TABLE III. VALUES OF WATER POLLUTION INDICATORS AT THE INPUT AND OUTPUT OF THE PHOTOCATALYTIC REACTOR (5 HOUR)

Water	pH	Conductivity [mS/m]	^{1}TOC [mg/L]	^{2}TIC [mg/L]	^{3}DOC [mg/L]	$^{4}COD_{Cr}$ [mg/L]	^{5}TSS [mg/L]
Input	7.5	127	9.8	38.9	8.5	62.7	3.8
Output	7.5	129	8.0	41.2	7.5	16.8	3.9

^{1}TOC – Total organic carbon, ^{2}TIC – Total inorganic carbon, ^{3}DOC – dissolved organic carbon, $^{4}COD_{Cr}$ – Chemical oxygen demand, ^{5}TSS – Total suspended solids

Generally, the process of photocatalytic oxidation (TiO_2/UV) reduced COD_{Cr} and TOC values. It is caused by the non-selective oxidation mechanism in which OH radicals oxidize the entire organic pollution. The value of TOC corresponded to the TOC normal background level in surface waters; therefore, no significant reduction of TOC value was detected. However, there was a significant decrease in COD_{Cr} indicator - almost to the normal background level. De facto, oxidation leads to mineralization of organic substances to targeted inorganic substances, which are CO_2 and H_2O and it causes the increase in TIC content (carbonates and free CO_2). Photocatalytic oxidation may also cause precipitation of certain inorganic materials, which is indicated by the increase in TSS values. In this case, a slight growth of both indicators TIC and TSS was detected, which corroborates the presumptions.

This study also drew attention to the increasing in flow rates and concentration of contaminants. Fig. 9 shows results of degradation process efficiency with a 10 times higher flow rate and 10 times higher concentration of endocrine disruptor pollutants. The same real waste water used for Fig. 8 experiments was spiked by individual contaminants to achieve their concentration between 480 – 550 ng/L. It is evident that even for such high concentrations of contaminants and flow rates 200 L/h or 325 L/h, degradation efficiency of the designed pilot plant reactor reached 93 %, or 88 %, resp.

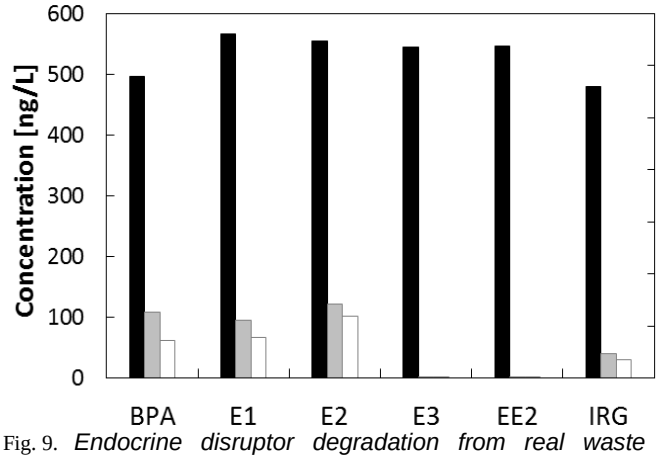

Fig. 9. *Endocrine disruptor degradation from real waste water in the pilot plant reactor (■ input, ■ output 325 L/h, □ output 200 L/h)*

Finely, efficiency of the designed pilot plant reactor was also tested on the rinse water from pharmaceutical industry, which contained another EDCs compounds (Norethisteron, Danazol). Concentrations of both EDCs at the input and output of the photocatalytic reactor for two flow rates (20 L/h and 30 L/h) are summarized in Table IV. It can be seen that degradation efficiency was 90 – 100 % and mainly in all cases it was below the officially allowed limit 0.5 mg/L.

TABLE IV. CONCENTRATION OF NORETHISTERON AND DANAZOL AT THE INPUT AND OUTPUT OF THE PHOTOCATALYTIC REACTOR

	Input	Output	
	-	20 L/h	30 L/h
	c [mg/L]	**c** [mg/L]	**c** [mg/L]
Danazol	5.99	< 0.05	0.1
Norethisteron	4.82	0.106	0.45

IV. CONCLUSIONS

The pilot plant photocatalytic reactor with stainless steel annulets coated by TiO_2 thin layers with the active anatase crystalline structure was designed and successfully tested. For preliminary testing of the designed pilot plant reactor, 17α-ethynylestradiol and bisphenol A as representatives of endocrine disruptors in water solutions of concentration 10 ppm were employed. The photocatalytic degradation of EE2 and BPA was performed at various flow rates in the range of 5 – 14 L/h with efficiency between 78 - 95 % for EE2 and 44 – 80 % for BPA. During the decomposition process, the estrogenity of both simulated waters gradually decreased simultaneously with the degradation of contaminants. The same trend was found for toxicity of BPA solution, while EE2 revealed no toxicity during the whole degradation process. Based on this, it could be deduced that emerging products, intermediates or by-products revealing any estrogenic activity do not arise during the degradation process. These facts corroborate the original presumption that during the photocatalytic process in

this designed pilot plant unit not only the original compounds but also intermediates and by-products can be successfully degraded.

Regarding photocatalytic degradation experiments, the real waste water from an industrial town was chosen to guarantee the presence of various types of EDCs produced from households, hospitals and machinery. Seven main contaminants (EE2, E1, E2, E3, BPA, 4-NPH and IRG) were detected at the output of the sewage plant, which was used as the input into the pilot plant photocatalytic reactor. Long-term photocatalytic experiments were also conducted, due to the fact that concentrations of all contaminants significantly varied in time. The efficiency of the photocatalytic degradation process varied between 87 – 100 % for all photocatalytic experiments. These values of efficiency are significantly high, considering the difficulties connected with purification of water containing a huge number of the mutually influenced contaminants. Moreover, the highest applied flow rate (325 L/h) corresponds to volume of treated water at the smallest sewage plants.

To test the another possibilities of the photocatalytic pilot plant unit utilization, purification of the rinsed water from pharmaceutical industry containing other EDCs compounds (Norethisteron, Danazol) was also performed at two various flow rates; 20 and 30 L/h. Efficiency of the photocatalytic degradation process was 90 – 100 % and it should be emphasized here that the concentration of EDCs dropped down below the officially allowed limit 0.5 mg/L in all experiments.

Finally, it must be mentioned that all experiments were performed at the pilot plant reactor with the original TiO_2 layer, which refers to its enormous resistance and a long life time of the designed photocatalytic unit. It was proved that photocatalytic degradation of endocrine disruptors on TiO_2 layers is an efficient degradation method regarding both the pilot scale and the small real scale.

ACKNOWLEDGMENTS

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REFERENCES

[1] Endocrine Disruptor Screening Program (EDSP) Home Page. http://www.epa.gov/endo/index.htm (3.2. 2015).

[2] T. Colborn, F.S. vom Saal, A.M. Soto, Developmental effects of endocrine-disrupting chemicals in wildlife and humans. Environ. Health Perspect 101 (1993) 378–84.

[3] R.J. Kavlock, G.P. Daston, C. DeRosa, P. Fenner-Crisp, Research needs for the risk assessment of health and environmental effects of endocrine disruptors: a report of the U.S. EPA-sponsored workshop. Environ. Health Perspect. 104 (1996) 715 – 740.

[4] W. Kloas, I. Lutz, R. Einspanier, Amphibians as a model to study endocrine disruptors: II. Estrogenic activity of environmental chemicals in vitro and in vivo. Sci. Total Environ. 225 (1999) 59 – 68.

[5] E. Alleva, J. Brock, A. Brouwer, T. Colborn, Statement from the work session on environmental endocrine-disrupting chemicals: neural, endocrine, and behavioral effects. Toxicol. Ind. Health 14 (1998) 1–8.

[6] J. Bantle, W.W. Bowerman, C. Carey, T. Colborn, Statement from the Work Session on Environmentally induced Alterations in Development: A Focus on Wildlife. Environ. Health Perspect 103 (1995) 3–5.

[7] Z.H. Liu, M. Ito, Y. Kanjo, A. Yamamoto, Profile and removal of endocrine disrupting chemicals by using an ER/AR competitive ligand binding assay and chemical analyses. J. Environ. Sci. 21 (2009) 900 – 906.

[8] H.M. Coleman, M.I. Abdullah, B.R. Eggins, F.L. Palmer, Photocatalytic degradation of 17 beta-oestradiol, oestriol and 17 alpha-ethynyloestradiol in water monitored using fluorescence spectroscopy, Appl. Catal. B-Environ. 55 (2005) 23-30.

[9] J.X. Mai, W.L. Sun, L. Xiong, Y. Liu, J.R. Ni, Titanium dioxide mediated photocatalytic degradation of 17 beta-estradiol in aqueous solution, Chemosphere 73 (2008) 600-603.

[10] Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, Degradation of bisphenol A in water by TiO_2 photocatalyst, Environ. Sci. Technol. 35 (2001) 2365-2368.

[11] Y. Ohko, K.I. Iuchi, C. Niwa, T. Tatsuma, T. Nakashima, T. Iguchi, Y. Kubota, A. Fujishima, 17 beta-estrodial degradation by TiO_2 photocatalysis as means of reducing estrogenic activity, Environ. Sci. Technol. 36 (2002) 4175-4181.

[12] P. Muller, P. Klan, V. Cirkva, The electrodeless discharge lamp: a prospective tool for photochemistry - Part 4. Temperature - and envelope material - dependent emission characteristics, J. Photochem. Photobiol. A-Chem. 158 (2003) 1-5.

[13] I. Gultekin, N.H. Ince, Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes, J. Environ. Manage. 85 (2007) 816-832.

[14] E.J. Rosenfeldt, K.G. Linden, Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes, Environ. Sci. Technol. 38 (2004) 5476-5483.

[15] H.M. Coleman, K. Chiang, R. Amal, Effects of Ag and Pt on photocatalytic degradation of endocrine

disrupting chemicals in water, Chem. Eng. J. 113 (2005) 65-72.

[16] T.E. Doll, F.H. Frimmel, Removal of selected persistent organic pollutants by heterogeneous photocatalysis in water, Catal. Today 101 (2005) 195-202.

[17] K. Nomiyama, T. Tanizaki, T. Koga, K. Arizono, R. Shinohara, Oxidative degradation of BPA using TiO_2 in water, and transition of estrogenic activity in the degradation pathways, Arch. Environ. Contam. Toxicol. 52 (2007) 8-15.

[18] J.G. Yu, H.G. Yu, C.H. Ao, S.C. Lee, J.C. Yu, W.K. Ho, Preparation, characterization and photocatalytic activity of in situ Fe-doped TiO_2 thin films, Thin Solid Films 496 (2006) 273-280.

[19] T. Nakashima, Y. Ohko, D.A. Tryk, A. Fujishima, Decomposition of endocrine-disrupting chemicals in water by use of TiO_2 photocatalysts immobilized on polytetrafluoroethylene mesh sheets, J. Photochem. Photobiol. A-Chem. 151 (2002) 207-212.

[20] M. Kositzi, I. Poulios, S. Malato, J. Caceres, A. Campos, Solar photocatalytic treatment of synthetic municipal wastewater, Water Res. 38 (2004) 1147-1154.

[21] L.A. Perez-Estrada, M.I. Maldonado, W. Gernjak, A. Aguera, A.R. Fernandez-Alba, M.M. Ballesteros, S. Malato, Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale, Catal. Today 101 (2005) 219-226.

[22] A.R. Fernandez-Alba, D. Hernando, A. Aguera, J. Caceres, S. Malato, Toxicity assays: a way for evaluating AOPs efficiency, Water Res. 36 (2002) 4255-4262.

[23] T.E. Doll, F.H. Frimmel, Cross-flow microfiltration with periodical back-washing for photocatalytic degradation of pharmaceutical and diagnostic residues-evaluation of the long-term stability of the photocatalytic activity of TiO_2, Water Res. 39 (2005) 847-854.

[24] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-plant scale: an overview, Appl. Catal. B 37 (2002) 1-15.

[25] S. Malato, J. Blanco, A. Vidal, P. Fernandez, J. Caceres, P. Trincado, J.C. Oliveira, M. Vincent, New large solar photocatalytic plant: set-up and preliminary results, Chemosphere 47 (2002) 235-240.

[26] V. Augugliaro, E. Garcia-Lopez, V. Loddo, S. Malato-Rodriguez, I. Maldonado, G. Marci, R. Molinari, L. Palmisano, Degradation of lincomycin in aqueous medium: Coupling of solar photocatalysis and membrane separation, Sol. Energy 79 (2005) 402-408.

[27] P. Le-Clech, E.K. Lee, V. Chen, Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters, Water Res. 40 (2006) 323-330.

[28] M. Morozova, P. Kluson, J. Krysa, M. Zlamal, O. Solcova, Role of the template molecular structure on the photo-electrochemical functionality of the sol-gel titania thin films, J. Sol-Gel Sci. Technol. 52 (2009) 398-407.

[29] M.D. Hernando, S. Vettori, M.J.M. Bueno, A.R. Fernandez-Alba, Toxicity evaluation with Vibrio fischeri test of organic chemicals used in aquaculture, Chemosphere 68 (2007) 724-730.

[30] O. Solcova, L. Spacilova, Y. Maleterova, M. Morozova, M. Ezechias, Z. Kresinova; Photocatalytic water treatment on TiO_2 thin layers; Desalination and Water Treatment, (2015) 1–8, doi: 10.1080/19443994.2015.1049964

[31] ÚCHP AV ČR, v.v.i. - Dekonta a.s. *Device for Photo-Catalytic Decontamination of Water Containing Organic Compounds, Especially Endocrine Disruptors*. Kastanek F., Solcova O., Maleterova Y., Spacilova L., Maternova H., Masin P., Zebrak R.; patent no.: *304681,* 17.07. 2014

[32] M. Morozova, P. Kluson, P. Dzik, M. Vesely, M. Baudys, J. Krysa, O. Solcova, The influence of various deposition techniques on the photoelectrochemical properties of the titanium dioxide thin film, J. Sol-Gel Sci. Technol. 65 (2013) 452-458

[33] M. Sanchez-Polo, M.M. Abdel daiem, R. Ocampo-Perez, J. Rivera-Utrilla, A.J. Mota, Sci. Total Environ., Comparative study of the photodegradation of Bisphenol A by $HO^{\cdot}$, $SO_4^{\cdot-}$ and $CO_3^{\cdot-}/HCO_3^{\cdot}$ radicals in aqueous phase, 463-464 (2013) 423-431.

[34] Y.F. Huang, Y.H. Huang, Identification of produced powerful radicals involved in the mineralization of Bisphenol A using a novel UV-$Na_2S_2O_8/H_2O_2$-Fe(II,III) two-stage oxidation process, J. Hazard. Mater. 162 (2009) 1211-1216.

[35] E. Unosson, K. Welch, C. Persson, H. Engqvist, Stability and prospect of UV/H_2O_2 activated titania films for biomedical use, Appl. Surf. Sci., 285 (2013) 317-323.

[36] J. Sharma, I.M. Mishra, V. Kumar, Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H_2O_2 and $UV/S_2O_8^{2-}$ oxidation systems, J. Environ. Manage., 156 (2015) 266-275.