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Photocatalytic water treatment on TiO_2 thin layers

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ABSTRACT

Photocatalysis is generally applied as a suitable technique for water decontamination and/or purification, especially for decomposition of endocrine disruptors. Endocrine disruptors are commonly present not only in wastewater but also in natural water. Endocrine disruptors are persistent to degradation by common chemicals as well as biological and photolytic processes. Decomposition of three representative endocrine disruptors (17-ethynyl estradiol, bisphenol A, and 4-nonylphenol) was tested on previously prepared TiO_2 photocatalyst in two types of reactors; a batch reactor and a plug-flow reactor. TiO_2 thin layers deposited on three various substrates were prepared by a sol–gel process with employment of a dip-coating technique for subsequent application. Properties of the prepared layers were thoroughly characterized by XRD, SEM, AFM, UV–vis, and Raman spectroscopy. Photo-electrochemical properties were determined by linear voltammetry and amperometry to obtain photoinduced properties of the prepared TiO_2 photocatalyst which corresponded to the photocatalytic activity. Photocatalytic decomposition efficiency was evaluated with respect to individual compounds for both reactors together with values of toxicity and estrogenic activity during the photocatalytic decomposition process. Furthermore, resistance of individual compounds to the photocatalytic decomposition process was evaluated together with possible formation of intermediates or by-products.

Keywords: Water purification; Photocatalysis; Endocrine disruptor; TiO_2 layers

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1. Introduction

Environmental pollution is currently becoming an increasingly serious problem of our time. The rising amount of emerging group of environmental pollutants in wastewater, known as endocrine disrupting compounds (EDCs), starts to be alarming. EDCs are natural and synthetic chemicals having adverse effects on human beings and animals via influencing

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endocrine systems [1]. Due to their influence on hormonal balance of multicellular organisms, EDCs constitute a real threat in wastewater. Among EDCs, 17b-ethynylestradiol (EE2) excreted by animals and human beings at ng L^{-1} levels in surface waters was identified to have the highest endocrine disrupting activity. Similarly to EE2, other EDCs also resist degradation of typical sewage treatment operations and they are released into surface waters. With a particular concern for human health, EDCs must be treated before entering public drinking water systems [2].

An intensive effort has been focused on removal of single EDCs or their mixtures which belong to the group of environmental pollutants from polluted water by TiO_2 photocatalysis. Owing to that, conventional methods of water and sewage treatment are not completely effective in removing the EDCs; advanced oxidation processes have been intensively studied as suitable technologies for EDCs degradation [3–8].

TiO_2 in powder or a thin layer form has been a promising semiconductor widely used in the field of water or air purification. It is well established that titanium dioxide (TiO_2) in the presence of UV light can create very active species that are able to restore and preserve the environment clean by decomposition of harmful organics. TiO_2 has awakened a great interest due to its chemical stability, low toxicity, low cost, photoinduced ability, and other specific properties. It can be prepared as powder, in a thin layer form, fibers, or tubs [9–12]. TiO_2 is a *N*-type semiconductor due to oxygen vacancies and its conductivity is caused by the absorption of light with corresponding energy which evokes generation of charge carrier species (electron–hole pairs). The anatase structure presents excellent photoinduced properties caused by the ability of OH radical creation on the anatase surface. TiO_2 absorbs only in the UV area due to the width of energy band gap (3.20 eV for anatase, 3.02 eV for rutile); therefore, the UV lamp for activation has to be used [13]. This fact can greatly limit utilization of TiO_2 in some applications.

This metal oxide was initially used as white pigment utilized in paint, plastic, ceramics, glass, and paper production [14–16]. TiO_2 pigment is also used in food industry (dye E171) and in pharmaceutical industry (tooth paste, drugs, sunbathing cream). The main field of TiO_2 application is catalysis and photocatalysis. This oxide used to be applied as promotor, support, or catalyst (Fisher–Tropsch synthesis [17,18]). Concerning photocatalysis, it is used in selective reduction of NOx to N_2, VOC degradation, photocatalytical air or water purification [19–24]. Its antibacterial properties can be applied for destruction of biological organisms (self-cleaning application). It is important to note that these cleaning and antibacterial functions of TiO_2 are obtained without using any chemicals, it needs only light. This metal oxide has found its use in various applications and new ones are being created.

This article deals with water treatment (removal of endocrine disruptors) by application of TiO_2 thin layers. Photocatalysis on TiO_2 seems to be a very promising technique for solving these environmental pollution problems. For these reasons, immobilized TiO_2 was applied for EDCs degradation. Degradation efficiency on TiO_2 thin layers was studied in batch and plug-flow reactors together with evaluation of toxicity and estrogenity of reaction products.

2. Experimental

2.1. Thin layer preparation

The templated sol–gel process was based on hydrolysis followed by polycondensation of metal precursor in organic matrix. The homogenous sol was prepared by addition of titanium alkoxide (TTIP, 99.999%, Sigma-Aldrich) used as Ti(IV) precursor into the inverse micellar solution. Reverse micelles were created by molecular templates Triton X 114 (non-ionic surfactant, Sigma-Aldrich) in the nonpolar environment of cyclohexane (Aldrich, 99.9%, HPLC grade). Sol–gel reactions took place in the core of a reverse micelle containing a small amount of water. The sol application was performed by a laboratory dip-coater (ID-Lab coater 4). Three supports were used for TiO_2 films deposition; glass beads with diameter 1.5 mm, glass tubes with inner diameter 4.5 mm, or indium tin oxide conductive glass (ITO, 5–15 X, Delta-Technologies Ltd). Three cycles of the dip-coating method with velocity 6 cm min^{-1} were applied. Among the single dip-coating cycles, samples were thermally treated by calcination at 450˚C for 4 h with the temperature ramp 1˚C min^{-1} during air flow in a muffle furnace. The same sol and treatment were also used for TiO_2 preparation in a powder form used for determination of TiO_2 texture characteristics.

2.2. Layer's characterizations

A crystallographic structure of prepared thin films was performed by X-ray diffraction (Panalytical-MRD laboratory diffractometer with the Cu anode) and Raman spectroscopy (Raman Dispersive Spectrometer Nicolet Almega XR, with wavelength 473 nm). Surface morphology was studied by a scanning electron microscope (Hitachi S4700) and AFM microscope (Thericroscopes). Layer thickness on the glass substrate was evaluated from the pictures made by SEM where the layer edge was depicted. Values of absorption edges of layers deposited on glass were obtained from UV–vis spectra (PerkinElmer Lambda 35 equipped with a Labsphere RSA-PE-20 integration sphere).

Textural properties of the prepared photocatalyst in a powder form were evaluated from N_2 physisorption performed on the volumetric instrument ASAP 2020 (Micromeritics, USA). Before the analysis, samples were dried at 105°C for 24 h at 0.1 Pa. Adsorption–desorption isotherms were measured by nitrogen at 77 K. The specific surface area (S_{BET}) was evaluated by the BET method; micropore volume and the mesopore surface area (S_{meso}) by the *t*-plot method with Lecloux–Pirard master isotherm; and pore-size distribution by the advanced BJH method [25].

2.3. Photocatalytic experiments

Two types of reactors, batch and plug-flow, were used for photocatalytic experiments. A batch reactor possesses the volume of reaction mixtures of 200 mL with 2.5 mg of TiO_2 supported on 5 g of beads. Experiments were performed under continuous shaking for 7 h. Four tubes with the length of 10 cm and inner diameter of 4.5 mm were applied as a plug-flow reactor with the volume 6.36 cm^3. 2.2 mg of TiO_2 covered the inner surface of tubes. Applied flow rates varied between 0.2 and 2 $cm^3\ min^{-1}$.

Three endocrine disruptors, EE2, bisphenol A (BPA), and 4-nonylphenol (4NP) with initial concentration of 10 ppm, were used for photocatalytic degradation tests in both reactors. For photocatalyst activation a UV lamp (Philips HOK 4/120 SE, 400 W medium pressure mercury lamp) with the wavelength of 250–420 nm was employed in the 20 cm-distance. Lamp intensities for individual UV light regions are shown in Table 1.

2.4. EDC, toxicity, and estrogenity analyses

EDC analyses were performed on Waters Alliance HPLC module equipped with a PDA detector, column thermostat, and Empower software. Identification was based on standard retention time and UV spectra by consensus (maximum 280 nm). The toxicity test is standardized as determination of the bioluminiscence inhibition of *Vibrio fischeri* bacteria strain. For this purpose, a gram 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 catalyzed with enzyme luciferase. The visible light was reduced at the contact of bacteria with the contaminant. Bioluminescence reduction was measured in 15 and 30 min intervals by a luminometer.

Estrogenity was tested on a *Saccharomyces cerevisiae* sp. strain with an integrated receptor for human estrogen and androgen compounds. Yeast cells in contact with hormonal active agents produce luciferase, which creates light measured by a luminometer, thanks to luciferin present in the medium.

Table 1
Lamp intensity for individual UV light regions

Type of light region	Intensity (W $m^{-2)}$
UV–vis	69
UVA	49
UVB	11
UVC	1

3. Results and discussion

3.1. Structural properties

Prepared photocatalysts in a thin layer form deposited by the dip-coating method on various substrates and calcined at 450°C possess the crystallographic structure of anatase. The crystalline form of the pure anatase was detected by data evaluation from XRD analyses and was confirmed by Raman spectroscopy. In Fig. 1(a), the main diffraction lines of anatase are depicted. Raman spectra (Fig. 1(b)) show attendance of characteristic vibration lines with 640, 525, 400, and 150 cm^{-1}, which confirms the pure anatase structure.

The layer morphology was studied by SEM and by AFM analyses (see Fig. 2(a) and (b)). The detailed view of the film surface made by SEM shows a smooth porous surface without any higher extent of surface defects. This fact is corroborated the results obtained by AFM analyses. Relative surface roughness expressed as an RMS factor (roots mean square values) is lower than 1, which indicates a very smooth surface of prepared layers.

Film thickness was evaluated from SEM images depicting the layer edge (Fig. 3). The thickness of 3 deposited layers was approximately 330 ± 10 nm. Moreover, clusters of TiO_2 particles were also easily detectable. Their size was about 20 nm and the particle size, which was evaluated from XRD diffraction lines, was 7 ± 1 nm. The absorption edge of prepared thin layers was determined from absorption spectra approximately at 355 nm. The prepared photocatalyst possessed a S_{BET} of about 82 $m^2\ g^{-1}$ formed mainly by the mesopore surface ($S_{\mathrm{meso}} = 62\ m^2\ g^{-1}$) with porosity of 48%.

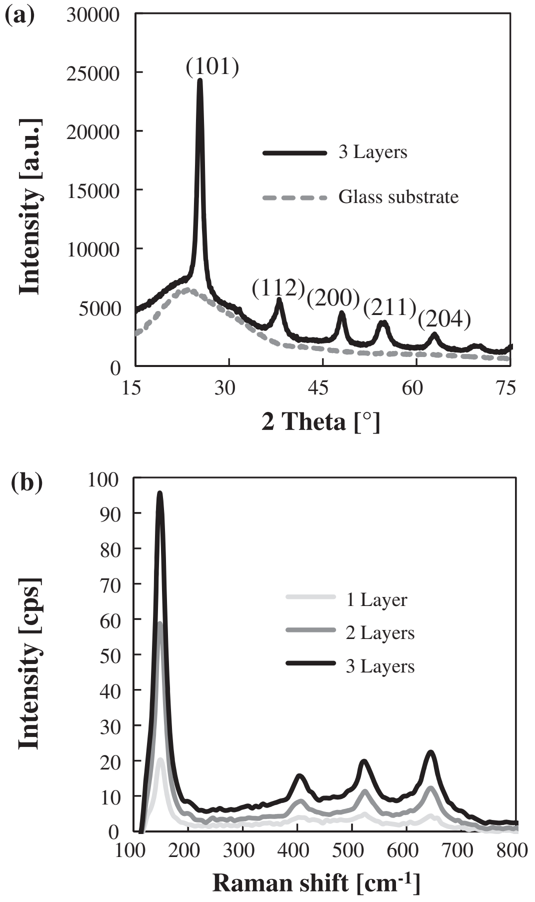

Fig. 1. XRD patterns (a), Raman spectrum (b).

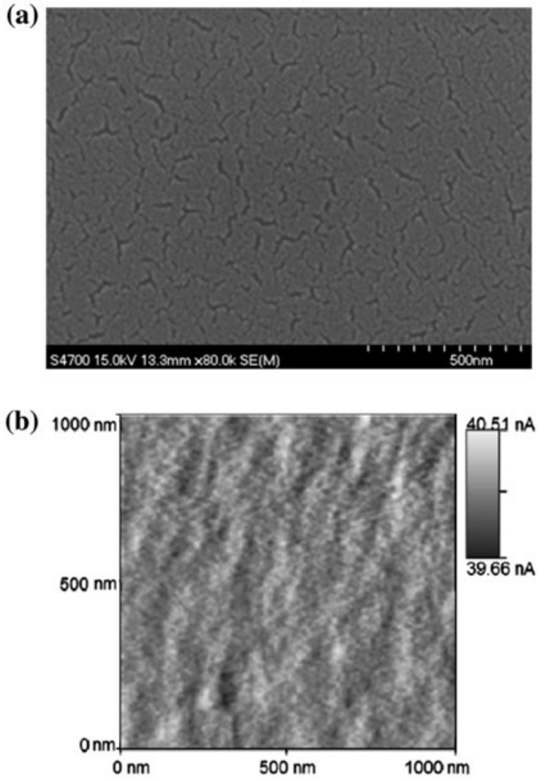

Fig. 2. Layer surface made by SEM (a), AFM analyses of the layer morphology (b).

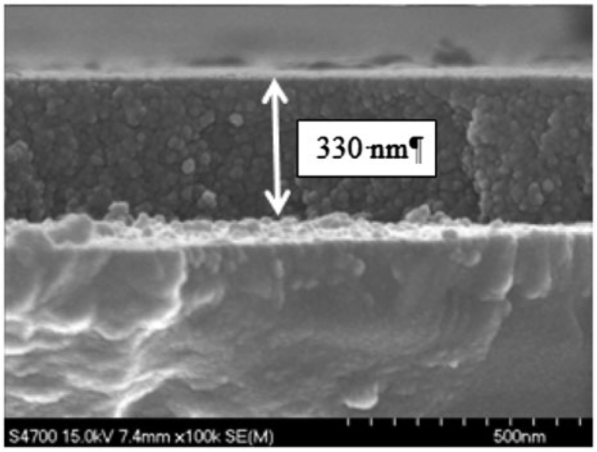

Fig. 3. Layer thickness.

3.2. Photocatalytic experiments

Degradation of EDCs in water solution was studied on prepared TiO_2 layers in two types of reactors; a batch reactor and a plug-flow reactor. Three representative endocrine disruptors were selected for testing: EE2, which represents a pharmaceutical substance of hormonal contraception; BPA, which is released e.g., from food packages to water; and 4-NPh, which belongs to biodegradation products of detergents and antioxidants. It is necessary to emphasize that only photocatalysis (no photolysis) takes part in degradation processes. Lamp intensities for individual UV light regions are obvious from Table 1. Obtained results for all three EDCs in the bath reactor during 7 h experiments are depicted in Fig. 4. It is evident that total decomposition of EE2 was achieved even after 5 h with excellent reproducibility. 4-NPh and BPA revealed higher resistance to the photocatalytic degradation process compared with EE2. 30% of 4-NPh and only 10% of BPA were decomposed after 7 h. Nevertheless, reproducibility of 4-NPh and BPA experiments corresponded to EE2 reproducibility with standard deviation (SD) lower than 3%.

During photocatalytic decomposition experiments, some new intermediates or by-products are usually created and these compounds can possess higher estrogenity and toxicity than the original contaminants. Therefore, estrogenity and toxicity of EDC

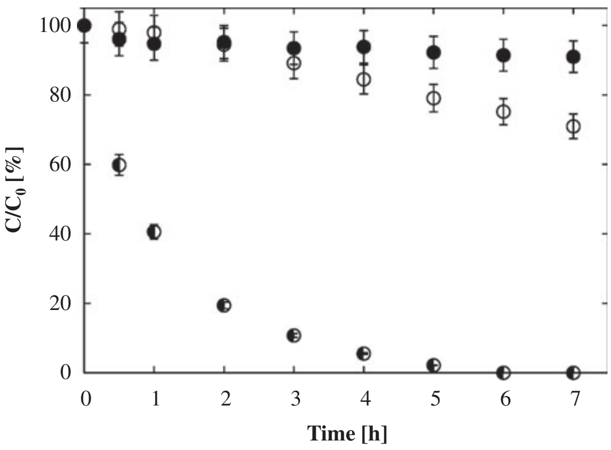

Fig. 4. Decomposition course of 4-NPh ◐, EE2 ○, and BPA ● in batch reactor.

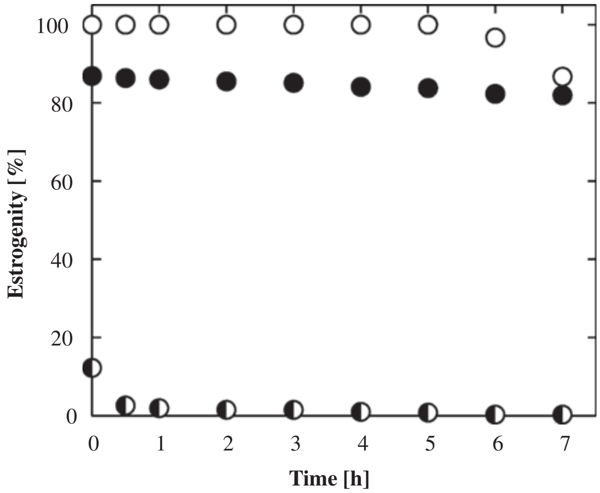

Fig. 5. Estrogenity course of 4-NPh ◐, EE2 ○, and BPA ● in batch reactor.

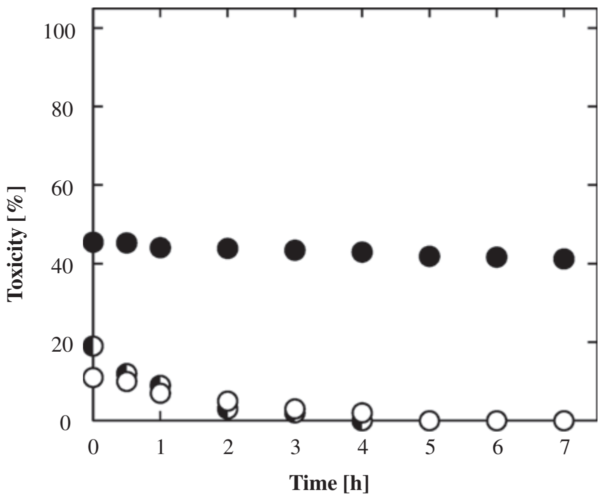

Fig. 6. Toxicity course of 4-NPh ◐, EE2 ○, and BPA ● in batch reactor.

decomposition were determined. Obtained data for all three contaminants are summarized in Figs. 5 and 6. It is obvious that efficiency of photocatalytic process on estrogenity and toxicity values significantly varied for three tested compounds. Residual estrogenity decreased in the range of EE2, BPA, 4-NPh and toxicity in the range of BPA, 4-NPh, EE2. However, both estrogenity and toxicity of all compounds decreased during experiments. Thus, no emerging products, intermediates, or by-products revealing higher estrogenic activity and toxicity than original compounds were created.

It can be summarized that the slow gradual decrease of BPA estrogenity and toxicity corresponds to its decomposition rate. On the contrary, 4-NPh revealed no estrogenity and toxicity after 2 h similarly to EE2 toxicity. However, values of EE2 estrogenic activity decreased slowly (10% after 7 h) with respect to quick decomposition. This fact points to the formation of more stable degradation intermediates, whose decomposition is slower.

The photocatalytic activity of TiO_2 layers deposited on an inner surface of plug-flow reactor tubes was also tested on decomposition of EE2, BPA, and 4-NPh in water solution. Obtained results for two various flow rates, 0.5 and 0.2 $cm^3\ min^{-1}$, are shown in Fig. 7. It is evident that decomposition of individual compounds corresponds to the data obtained in a batch reactor and depends on retention time. The best results were obtained for 4-NPh. At flow rates 0.5,

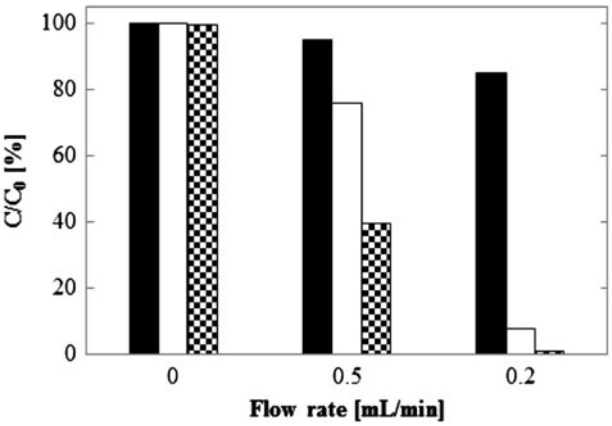

Fig. 7. Decomposition of ■ BPA, □ EE2, ⊡ 4-NPh at flow rates 0.5 and 0.2 $cm^3\ min^{-1}$.

Table 2
Decomposition of 4-NPh at flow rate 0.5 cm^3 min^{-1}

Experiment	1 (mg/L)	2 (mg/L)	3 (mg/L)	4 (mg/L)	$C_{average}$ (mg/L)	D_{max} (%)	SD (mg/L)
C_{output}	4.928	4.768	4.826	4.850	4.843	1.75	0.0663

60% efficiency and at 0.2 cm^3 min^{-1} even 99% efficiency of degradation process was achieved. Slightly worse results were obtained for EE2. Efficiency at flow rates 0.5 and 0.2 cm^3 min^{-1} was 24 and 92%. The most resistant compound was again BPA with maximal 15% efficiency of the photocatalytic process. Photocatalytic degradation of all compounds for individual flow rates was measured repeatedly to guarantee reproducibility of experiments. Obtained results for 4-NPh and flow rate 0.5 cm^3 min^{-1} are summarized in Table 2. It is evident that reproducibility of results is excellent with maximal deviation (D_{max}) 1.75% and SD 1.3%.

Decomposition of EE2 for four different flow rates is shown in Fig. 8, where obtained conversions on retention time are depicted. It is obvious that linear dependence was obtained with the correlation coefficient of 0.99. Thus, in agreement with literature [26], the first reaction order was evaluated.

Estrogenity and toxicity values of individual compounds decrease during the decomposition process and correspond to the values obtained for the batch reactor. Results for 4-NPh at flow rate 0.5 cm^3 min^{-1} are shown in Fig. 9, where the vertical line stands for retention time of the reactor 12.8 min. It can be seen that during the photocatalytic degradation experiment, values of toxicity and estrogenic activity copied the decreasing trend of 4-NPh concentration; which means that they corresponded to the degradation process.

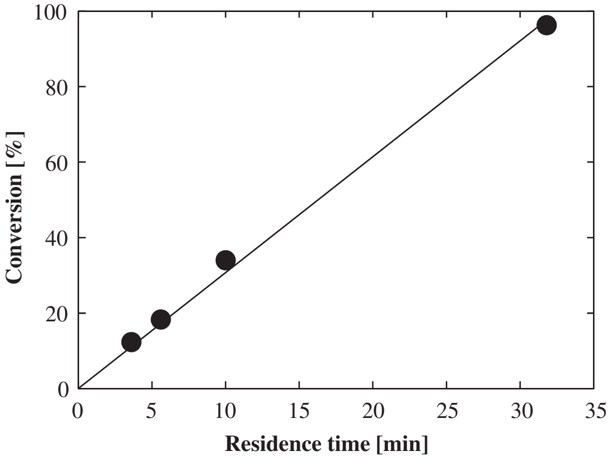

Fig. 8. Dependence of EE2 conversion on residence time for EE2, points—experimental, line—calculated ($y = 3.0712x$, $R^2 = 0.9965$).

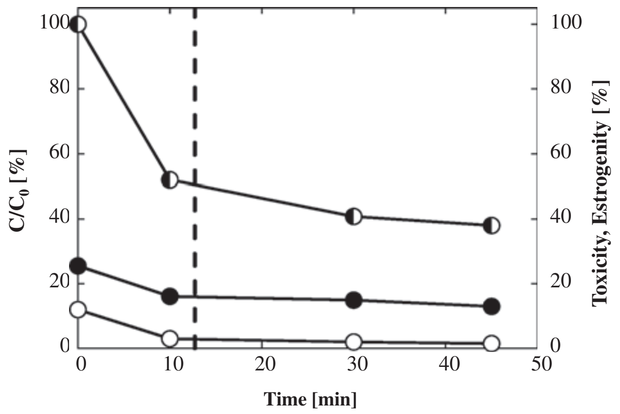

Fig. 9. Dependence of 4-NPh concentration ◐, 4-NPh toxicity ●, and 4-NPh estrogenity ○ on time, retention time of reactor.

4. Conclusions

Decomposition of three representative endocrine disruptors (EE2, BPA, and 4-NPh) on TiO_2 layers as a photocatalyst was tested in two types of reactors, a batch reactor and a plug-flow reactor. The glass beads covered by a thin layer of TiO_2 were applied as a photocatalyst in the batch reactor. In the plug-flow reactor, the thin layer of TiO_2 was supported on the inner reactor walls.

Based on minimally three times repeated experiments, it was verified that the total decomposition of 4-NPh was achieved after 5 h. However, 4-NPh and BPA revealed higher resistance to the photocatalytic degradation process compared with EE2. 30% of 4-NPh and even only 10% of BPA were decomposed after 7 h. Nevertheless, higher efficiency was obtained for the plug-flow reactor with TiO_2 photocatalyst deposited on the inner surface of tubes. The degradation process in plug-flow reactor provided even 98% efficiency to 4-NPh and 95% efficiency to EE2 at flow rates 0.2 cm^3 min^{-1}. Similarly to the batch reactor, the most resistant compound was again BPA with maximal 15% efficiency of the photocatalytic process at the same flow rate. It is necessary to stress that the excellent reproducibility was achieved for all experiments in both reactors.

Values of toxicity and estrogenic activities during the photocatalytic decomposition process significantly varied for three tested EDC without any influence of the reactor type. The slow gradual decrease of BPA estrogenity and toxicity corresponds to its decomposition rate and corroborates its high resistance to the photocatalytic decomposition process. On the contrary, the estrogenic activity and toxicity of 4-NPh rapidly decreased similarly to its concentration. The most interesting are the values of EE2 estrogenic activity. Estrogenity decreased really slowly regarding the quick decomposition of EE2. This fact points to the formation of more stable degradation intermediates. However, both estrogenity and toxicity of all compounds substantially decreased during experiments; thus, no emerging products, intermediates, or by-products revealing any higher estrogenic activity or toxicity than original compounds were created during the decomposition process.

Based on these results, it can be summarized that photocatalytic decomposition of endocrine disruptors on TiO_2 layers, especially in a plug-flow reactor, seems to be an efficient degradation method and a promising technique for final water purification as the last part of sewage treatment plant.

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