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**Catalytic Wet-air Oxidation as an Efficient Treatment
Technique for Removal of Organic Pollutants and
Detoxification of Wastewaters**

Mirjana Bistan
Ph.D. student
National Institute of Chemistry
Slovenia

Dr. Tatjana Tišler
Senior Research Associate
National Institute of Chemistry
Slovenia

Dr. Boštjan Erjavec
Research Fellow
National Institute of Chemistry
Slovenia

Prof. Dr. Albin Pintar
Head of Laboratory
National Institute of Chemistry
Slovenia

Athens Institute for Education and Research
8 Valaoritou Street, Kolonaki, 10671 Athens, Greece
Tel: + 30 210 3634210 Fax: + 30 210 3634209
Email: info@atiner.gr URL: www.atiner.gr
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Mirjana Bistan
Ph.D. student
National Institute of Chemistry
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Dr. Tatjana Tišler
Senior Research Associate
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Dr. Boštjan Erjavec
Research Fellow
National Institute of Chemistry
Slovenia

Prof. Dr. Albin Pintar
Head of Laboratory
National Institute of Chemistry
Slovenia

Abstract

The ubiquitous presence of endocrine-disrupting compounds (EDCs) in environment is mainly the consequence of their incomplete removal in biological wastewater treatment plants. One of the promising options for EDCs removal is catalytic wet-air oxidation (CWAO), where pollutants are oxidized by activated O₂ species in the presence of a solid catalyst. 17β-estradiol (E2) and bisphenol A (BPA) were used in CWAO experiments conducted in a trickle-bed reactor up to 230° C over TiO₂ and Ru/TiO₂ solids. In the given range of operating conditions, E2 and BPA undergo noncatalytic and catalytic oxidation routes. The employed Ru(3.0 wt. %)/TiO₂ catalyst enabled complete and long lasting efficiency of E2 and BPA degradation as well as removal of toxicity and estrogenicity from the feed solution. No deactivation occurred and no carbonaceous deposits were accumulated on the catalyst surface.

Keywords: bisphenol A, catalytic wet-air oxidation, estrogen, 17β-estradiol, estrogenic activity, yeast estrogen screen (YES) assay, water treatment

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Contact Information of Corresponding author: Prof. Dr. Albin Pintar, Laboratory for Environmental Sciences and Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia; tel.: +386 1 47 60 237, fax: +386 1 47 60 460, e-mail address: albin.pintar@ki.si

The presence of biocides, pharmaceuticals, personal care products and endocrine-disrupting compounds (EDCs) in wastewater treatment plant (WWTP) effluents, receiving waters (*e.g.* rivers, lakes, oceans etc.), drinking water, and groundwater has become an issue of increasing international attention. Recently, concern about the ubiquitous presence of EDCs in environment has increased considerably due to the potential to elicit negative effects on the endocrine systems of humans and wildlife (Eggen *et al.*, 2003; Woodruff, 2011). EDCs are a large group of structurally diverse chemicals with different origins that interfere with the production, release, transport, metabolism, binding, action or elimination of natural hormones in the body. Estrogens such as estrone (E1), 17 β -estradiol (E2), estriol (E3) are primary female sex hormones, which are important in estrous cycle of mammals. They are excreted from human body into sewage (*i.e.* municipal) wastewaters and may exhibit significant estrogenic effects in aquatic organisms of receiving waters at concentrations as low as 0.1 ng/l (Sumpter, 2005). Natural and synthetic estrogens are considered to be the major source of estrogenic activity in municipal wastewaters (Körner *et al.*, 2000), whereas xenoestrogens (*e.g.* BPA) are frequently present in industrial wastewaters and landfill leachates (Coors *et al.*, 2003; Suzuki *et al.*, 2004). These compounds are considered to be incompletely removed from wastewaters by conventional biological processes in WWTPs and consequently tend to be discharged into receiving waters. However, the application of advanced oxidation processes (AOPs) such as catalytic wet-air oxidation, heterogeneous photocatalysis, ozone based technologies and ultrasound oxidation were found to be effective in removal of EDCs from aqueous samples (Araña *et al.*, 2002; Belgiorno *et al.*, 2007; Chiang *et al.*, 2004; Jiang *et al.*, 2005; Liu *et al.*, 2009; Ning *et al.*, 2007). The most common AOPs named above can be broadly defined as aqueous-phase oxidation methods, based primarily on the intermediacy of hydroxyl radicals and energy (*i.e.* heat) in the mechanisms leading to the destruction of the target compound, and can be used either separately or in various combinations. One of the most promising AOPs options to achieve significant extent of removal of organic compounds, such as EDCs, from industrial wastewaters is destruction of these contaminants by catalytic wet-air oxidation (CWAO), where the organic pollutants are oxidized by activated O₂ species in the presence of a solid catalyst, usually at temperatures of 130-250° C and pressures of 10-50 bar, into biodegradable intermediate products or mineralized into CO₂, water and associated inorganic salts (Kim & Ihm, 2011; Levec & Pintar, 2007). From the economical point

of view, the CWAO process can be efficiently used for direct treatment of aqueous wastewaters containing high loading of organic compounds (typically presenting chemical oxygen demand (COD) values in the range of 10-100 g/l). However, for nano to micro levels, a preconcentration step would be needed in the process scheme. The CWAO of various organic compounds has been studied in the last decades over metal oxides, mixed metal oxide systems, cerium-based composite oxides and supported noble metal catalysts (Cybulski & Trawczyński, 2004). Titania and zirconia supported ruthenium catalysts have received much attention, because they exhibit high activity and chemical resistance in CWAO of different model pollutants (Kojima *et al.*, 2005; Perkas *et al.*, 2005) and industrial wastewaters (Pintar *et al.*, 2001). Recently, the performance of various Ru/TiO₂ catalysts to promote oxidation of aqueous solutions of formic acid, acetic acid and phenol was investigated in a continuous-flow trickle-bed reactor (Pintar *et al.*, 2008). Complete oxidation of formic acid was obtained at mild operating conditions (110° C), and no catalyst deactivation occurred that could be attributed to the dissolution of active ingredient material. Liquid-phase oxidation of recalcitrant acetic acid was found to be structure sensitive; the highest catalyst activity was obtained, when Ru phase on the catalyst surface prevailed in zero-valent state. The Ru/TiO₂ catalysts enabled complete removal of phenol as well as more than 99 % removal of total organic carbon (TOC) content at temperatures above 200° C. In the presence of a Ru/TiO₂ catalyst in the trickle-bed reactor, the acute toxicity to various aquatic organisms of the oxidized materials was greatly decreased; for example, acute toxicity of aqueous phenol solutions treated by the CWAO process was reduced by more than 98 %. Although CWAO have been employed for the destruction of several classes of aliphatic and aromatic organic pollutants in waters and wastewaters, relatively little information is available on the efficiency of this process to destroy EDCs, in particular degradation of (xeno)estrogens (Esplugas *et al.*, 2007; Klavarioti *et al.*, 2009). Further, secondary products can be formed during oxidation processes, which may have stronger biological effect than the original compound and are not eliminated significantly by the same process. For this reason, residual toxicity and estrogenicity of treated samples should be determined by using bioassays (Pintar *et al.*, 2008; Rizzo, 2011).

BPA is an organic pollutant, commonly used in the production of polycarbonate plastics and epoxy resins. It is toxic to aquatic organisms and estrogenic active. It thus belongs to the group of EDCs as the representative of xenoestrogens (Kang *et al.*, 2006). BPA is frequently present in industrial wastewaters, where concentrations as high as 1000 µg/l BPA can be expected (Suzuki *et al.*, 2004). Significantly higher concentrations, up to 17000 µg/l of BPA, can be found especially in landfill leachates via hydrolysis of BPA from plastics (Kang *et al.*, 2006).

In this study, CWAO runs were carried out to remove 17β-estradiol (E2), a natural estrogen hormone produced by human body, and bisphenol A (BPA) from aqueous samples. The experiments were conducted in a continuous-flow, three-phase trickle-bed reactor operating in a low-interaction (LIR) trickle-flow regime in order to investigate a potential of either bare TiO₂ support and Ru/TiO₂ catalyst for effective (*i.e.* long-term) removal of the parent molecule and intermediates from the liquid

phase. Estrogenic activity and/or toxicity of treated E2 and BPA aqueous samples was evaluated by means of a yeast estrogen screen assay (YES assay) (Routledge & Sumpter, 1996), acute toxicity tests and HPLC analysis, which was used for quantification of remaining E2 and BPA in aqueous solutions.

Experimental

Catalyst preparation

The catalyst sample containing 3.0 wt. % of Ru was prepared by incipient-wetness impregnation of TiO₂ extrudates (Degussa-Hüls AG, Aerolyst type, d_p: 1.4 mm, S_{BET}: 51 m²/g, V_{pore}: 0.36 cm³/g, d_{pore}: 28 nm) with an aqueous solution of RuCl₃×H₂O (Acros Organics), concentration of which was accurately determined by ICP-AES before impregnation. The TiO₂ support was dried at 100° C in an oven for 2 h and then impregnated at room temperature with an appropriate volume of solution containing the Ru salt to obtain 3.0 wt. % nominal Ru content. After the impregnation step, the catalyst precursor was dried (overnight at room temperature, then at 40° C for 5 h, and finally at 105° C for 2 h) and reduced directly in H₂ flow of 250 ml/min at 300° C for 1 h without previous calcination. The actual Ru loading in the synthesized Ru/TiO₂ catalyst, determined by using ICP-AES analysis, was found equal to 2.9 wt. %. Fresh and spent catalyst samples were characterized by means of N₂ sorption, H₂ chemisorption, XRD, SEM/EDX, XRF and CHNS techniques.

CWAO experiments

CWAO experiments were carried out in a Microactivity-Reference unit (PID Eng&Tech, Spain), which is an automated and computer-controlled, continuous-flow trickle-bed reactor for catalytic microactivity tests. The apparatus is described in detail elsewhere (Pintar *et al.*, 2008). The properties of the catalyst bed and operating conditions are listed in Table 1. Concentration of E2 (min. 99 %, Aldrich) in the feed aqueous solution prepared daily by using ultrapure water was 0.272 mg/l, while the feed concentration of BPA (min. 99 %, Aldrich) was equal to 20.0 mg/l. It should be noted that in the case of CWAO of E2 representative liquid-phase samples of about 250 ml were collected at the reactor outlet in intervals of at least 8 hours, which was required in order to obtain a sufficient volume of samples subjected to further preconcentration.

Analysis of end-product solutions (HPLC, TOC)

In the case of E2 oxidation, all samples were extracted and concentrated using solid-phase extraction (SPE) technique by being passed through the Oasis® HLB 6cc (500 mg) SPE cartridges (Milford, Massachusetts, USA). Conditioning of cartridges was performed with 4 ml of methanol, followed by 4 ml of distilled water. After loading

samples, the cartridges were washed with 4 ml methanol (5 v/v %), dried under a gentle stream of nitrogen (N₂) and eluted with 4 ml of methanol. Eluted samples were collected in test tubes and concentrated under a gentle stream of N₂ to the volume of 0.5 ml.

HPLC analyses to determine residual E2 and BPA content were performed in the isocratic analytical mode using a 250 mm × 4.6 mm Phenomenex Luna C18 5 μ column thermostated at 30° C (UV detection at λ=210 nm with a mobile phase of methanol (75 %) and ultrapure water (25 %) at a flow rate of 0.8 ml/min).

The total amount of organic substances in withdrawn aqueous-phase samples was determined by measuring the total organic carbon (TOC). TOC content was determined applying a high-temperature catalytic oxidation (HTCO) method carried out at 750° C by using an advanced TOC analyzer (Teledyne Tekmar, model Torch) equipped with a high-pressure NDIR detector, by subtracting measured inorganic carbon (IC) content from measured total carbon (TC) content. In all analyses, 3–4 repeated measurements were taken for each liquid-phase sample, and the average value of TOC concentration was reported. The error of analysis was never greater than ± 0.5 %.

YES assay and toxicity tests

Estrogenic activity of initial and treated samples was evaluated by “Yeast Estrogen Screen Assay” (YES assay) using recombinant yeast strain *Saccharomyces cerevisiae* BJ1991, developed at Glaxo Corporation. Yeast hosts an integrated gene coding for human estrogen receptor (hER) in its genome and expression plasmids carrying the reporter gene *lac-Z*, which encodes the enzyme β-galactosidase. Following the activation of *lac-Z* gene in the presence of estrogenic active compounds, β-galactosidase degrades substrate β-D-galactopyranoside (CPRG), which changes its color from yellow to red. On each microtiter plate a positive, negative and blank controls were used. 17β-estradiol (E2) was used as a positive control (in concentration 27.2 μg/l) and progesterone (P) as natural human androgen hormone, without the ability of binding to the human estrogen receptor, was used as a negative control (in concentration 31.4 μg/l). As a blank control (B), yeasts exposed to the growth medium with CPRG were used in order to detect whether yeasts themselves, without exposing to estrogen active compound, could degrade CPRG. For determining estrogenic activity (EA), the absorbance measurements at 575 and 620 nm were carried out on the microtiter plate reader PowerWave XS (BioTek, USA). The values of EA were expressed as the activity of enzyme β-galactosidase, calculated by using an equation adopted by Fent *et al.* (2006). The relative estrogenic activity (REA) was calculated regarding estrogenic activity of initial samples.

Besides the measurements of estrogenicity, standardized acute/chronic toxicity tests were carried out using marine bacteria *Vibrio fischeri*, unicellular green algae *Desmodesmus subspicatus*, water fleas *Daphnia magna* and zebrafish embryos *Danio rerio* described elsewhere.

Results and discussion

Catalyst characterization

Specific surface area, total pore volume and average pore width of TiO₂ in the form of extrudates and fresh Ru(3.0 wt. %)/TiO₂ catalyst (S_{BET} : 50 m²/g, V_{pore} : 0.34 cm³/g, d_{pore} : 27 nm) showed that the deposition of Ru did not significantly modify the textural properties and the corresponding XRD powder patterns. The XRD pattern of titania supports, which contain more than 99.5 % TiO₂ as determined by XRF analysis, revealed the presence of anatase (Titanium oxide, PDF 03-065-5714) and rutile (Titanium oxide, PDF 00-004-0551) phases, and that anatase is the prevailing crystallographic form. The XRD pattern is not affected by the deposition of Ru, as the diffraction peaks of metallic Ru (Ruthenium, syn, PDF 06-0663: $2\theta=38.39$, 42.15 and 44.01°) were not observed. It was further found out that the accessibility of Ru is poor on Ru(3.0 wt. %)/TiO₂ catalyst. The presence of rather large and discrete Ru particles on the surface of synthesized catalyst, as determined by H₂ chemisorption measurements (25 nm) is supported by SEM examination, which reveals the presence of Ru clusters in the range of 14-34 nm.

XRD, N₂ adsorption-desorption isotherms (at -196° C) and ICP-AES analyses were performed on catalysts before and after the CWAO runs (used catalyst samples were thoroughly washed with distilled water and dried prior to analysis). A comparison of X-ray powder diffraction pattern of spent Ru(3.0 wt. %)/TiO₂ catalyst to that of the fresh one reveals that no peak characteristic of metallic Ru, ruthenium oxide phases or other phases (*i.e.* Fe, Fe-oxides, carbon) was identified; the reflections correspond to those of the TiO₂ support. Furthermore, the measurements of textural properties of used catalysts revealed no differences in total pore volume and average pore width, while a small drop of specific surface area at an extent of about 5 % was observed in comparison to fresh solids. In the light of these findings, Ru dispersion in spent Ru(3.0 wt. %)/TiO₂ catalyst was found to be equal to 5.3 %. This is very similar to the value reported above, which confirms that in the applied range of CWAO operating conditions ($T=200-230^\circ\text{C}$, $p(\text{O}_2)=10.0\text{ bar}$) sintering of Ru particles does not occur to a measurable extent. The above described facts demonstrate great chemical stability of the employed Ru/TiO₂ catalyst for promoting reactions in hydrothermal conditions.

CWAO runs

E2 conversions as a function of time on stream obtained in consecutive CWAO runs performed at different reaction temperatures (200 and 230° C, respectively) in the presence of inert SiC (average particle diameter of approx. 0.5 mm, BET specific surface area below 0.1 m²/g), bare TiO₂ support or Ru(3.0 wt. %)/TiO₂ catalyst are shown in Fig. 1. The effect of temperature was investigated in this range, because it was observed in our previous study (Pintar *et al.*, 2008; Taboada *et al.*, 2009) that CWAO of phenol carried out over titania- and CNF-supported catalysts at

temperatures below 200° C resulted in catalyst deactivation due to strong adsorption of partially oxidized C-6 intermediates (such as benzoquinones and hydroquinones) on the catalyst surface. Accordingly, gradual decrease of E2 conversions was noted in the reactor outlet when the reaction was carried out over Ru/TiO₂ particles at 160 and 180° C, respectively. When conducting the process in the presence of solid particles (either SiC, TiO₂ or Ru/TiO₂) under He, there was no removal of organic carbon from the liquid phase; thus, the E2 conversion is only a result of oxidation pathways. In any of runs, only carbon dioxide was detected in the off-gas stream. Moderate E2 conversions were obtained when the reactor was filled with SiC (Fig. 1), even at short residence time of the liquid phase calculated to be about 0.24 min. Since it was verified that the measured E2 conversions are not influenced by adsorption effects, these observations confirm that in the given range of operating conditions E2 oxidation undergoes both noncatalytic as well catalytic oxidative routes. The E2 removal over the bare TiO₂ support was significantly improved as compared to runs conducted in the presence of SiC (Fig. 1). As titania extrudates are more than 99 % pure (XRF analysis), it is obvious that the observed activity for E2 oxidation is solely caused by TiO₂ itself, which is attributed to the nonstoichiometric nature of this solid. Furthermore, complete conversion of E2 was attained in the presence of Ru(3.0 wt. %)/TiO₂ catalyst, and no measurable drop of activity was observed in the investigated time period of about 80 h. No leaching of either titanium or ruthenium (to the detection limit of 0.01 mg/l) was detected in the experiments performed in the presence of these solids. This confirms that the examined solids are not susceptible to anodic decomposition. Finally, examination of spent catalysts after reaction by means of CHNS elemental analysis showed that carbonaceous deposits, which could be produced by oxidative coupling reactions, were not accumulated on the surface of these solids during the CWAQ of E2 (Table 2).

Fig. 2 shows BPA conversion as a function of time on stream in consecutive CWAQ runs performed at different reaction temperatures (200 and 230° C, respectively) in the presence of inert SiC, bare TiO₂ support or Ru(3.0 wt. %)/TiO₂ catalyst. Observations very similar to the ones obtained during the CWAQ of E2, were noted. These measurements further demonstrate good chemical stability of examined solids (no drop of activity was observed in the investigated time period), good reproducibility of data and confirm that the material of construction (either stainless steel or Hastelloy C-276) exhibits no measurable effect on BPA conversion. It can be seen in Fig. 2 that at T=200° C slight increase of BPA conversion as a function of time on stream was observed in the presence of TiO₂ support. This is attributed to the nonstoichiometric nature of TiO₂ and consequently establishment of gas-liquid-solid equilibrium during the initial stage of reaction course. TOC conversions in end-product solutions derived from corresponding BPA oxidation runs are depicted in Fig. 3. Rather moderate TOC conversions were obtained in the presence of SiC or TiO₂ support. Comparing further TOC conversions obtained on the TiO₂ oxide and on the corresponding supported ruthenium catalyst (41 vs. 96 % at T=200° C), one may note that addition of ruthenium increased drastically the overall oxidative transformation of BPA to carbon dioxide. This is attributed to the fact that ruthenium exhibits an ability

to oxidize small organic compounds, such as acetic acid, that are resistant and not easily degraded by oxides. In the end-product solution obtained after the CWAO of BPA carried out in the presence of Ru(3.0 wt. %)/TiO₂ catalyst, only acetic acid was identified, as determined by ion chromatography. Furthermore, CHNS examination of SiC, TiO₂ support and Ru(3.0 wt. %)/TiO₂ catalyst after reaction under oxidative conditions showed that no coke was accumulated on the surface of these solids during the CWAO of BPA (Table 2).

The oxidation promoted by TiO₂ based solids can be interpreted by their redox properties via a free-radical mechanism. The TiO₂ surface may first interact with oxygen to produce O₂^{•-} and HO₂[•] radicals. These species are able to initiate a radical mechanism by abstracting H[•] radicals from the adsorbed organic components. The ability of oxides to activate oxygen derives from the ease with which they deviate from the stoichiometric composition resulting in an oxygen deficient surface. The activity enhancement with ruthenium is very likely due to the possibility of this metal to undergo a redox cycle between two oxidation states and thus to activate oxygen.

Estrogenicity and toxicity

The results presented in Table 3 list the average values of conversion and estrogenicity (presented as relative estrogenic activity - REA) of E2 aqueous samples treated by means of CWAO process. High conversions of E2 (above 70 %) were achieved at all conditions used in the CWAO process. Due to remaining E2 in samples 1a (81.6 µg/l), 1b (27.2 µg/l) and 2a (19.0 µg/l), and correspondingly high sensitivity of the YES assay, estrogenic activity was still detected in these end-product solutions (Fig. 4). Importantly, in other treated samples (2b, 3a, 3b) neither E2 nor estrogenic activity was detected, which leads us to the conclusion that E2 was completely degraded. Further, E2 is moderately toxic to aquatic organisms after acute exposure; *e.g.*, the reported 48h EC50 value for *Daphnia magna* is 2.97 mg/l (Hirano *et al.*, 2004). In the light of this fact, no toxicity of feed solution and treated samples was determined, which is due to very low E2 feed concentration. Finally, due to high activity of Ru/TiO₂ catalyst to promote C-C bond cleavage, negligible amounts of short-chain carboxylic acids were observed in the reactor outlet.

Results of toxicity and estrogenicity tests of the initial BPA sample (feed solutions) and samples treated by means of CWAO process in the continuous-flow trickle-bed reactor are presented in Table 4. It is clearly seen that BPA conversions increased by the operating temperature and the use of catalysts. The same trend is also seen from the results of luminescence inhibition of marine bacteria *V. fischeri* and from the results of growth rate inhibition of green algae *D. subspicatus*, where at higher temperature used in the CWAO process (*i.e.* 230° C) the luminescence inhibition and the algal growth rate inhibition was for up to 30 % lower. However, the results of mortality of zebrafish embryos *D. rerio* did not follow the same trend; the mortality of zebrafish embryos increased by higher operating temperature. Since TOC conversion increased with an increase of reaction temperature (Fig. 3), this cannot be attributed to higher accumulation of intermediates in the liquid phase. Higher mortality of

zebrafish embryos observed when conducting CWAO of BPA at 230° C (sample 7b) is probably due to enhanced leaching of metallic parts of the reactor set-up; however, this remains to be investigated. A significant drop of toxicity for zebrafish embryos was noticeable only when using Ru(3.0 wt. %)/TiO₂ at the operating temperature of 200° C (sample 7a), where only 10 % of embryos revealed lethal effects. As for the estrogenicity, the REA remarkably drops to 0 % in all treated samples with either bare TiO₂ (runs #6a and #6b) or Ru-containing catalyst (runs #7a and #7b), independent of the reaction temperature. Overall, the CWAO process seems to be most effective for BPA treatment when Ru(3.0 wt. %)/TiO₂ catalyst was used at the operating temperature equal to 230° C. Under those conditions, the conversion of BPA was 100 %, accompanied with TOC conversion higher than 97 %, and there was no toxicity measured for *V. fischeri* and *D. subspicatus* as well as no estrogenicity (REA) detected. On the other hand, zebrafish embryos *D. rerio* were more sensitive, since in 60 % of embryos the lethal effects were detected. Nevertheless, these observations are in very good agreement with the results of our previous investigation (Pintar *et al.*, 2008) in which great potential of Ru/TiO₂ catalysts for the detoxification of aqueous solutions of formic acid, acetic acid and phenol by means of CWAO was reported.

Conclusions

The CWAO process when carried out in the trickle-bed reactor filled with the Ru/TiO₂ catalyst seems to be very effective for E2 and BPA removal from aqueous samples, as complete degradation and removal of estrogenicity was obviously achieved, even at very short residence time of liquid phase in the catalytic bed. These findings are in very good agreement with the results of our previous investigations (Pintar *et al.*, 2008), in which great potential of Ru/TiO₂ catalysts for the detoxification of aqueous solutions of aliphatic and aromatic compounds was reported. This makes the Ru/TiO₂ catalyst a universal solid for treating a variety of organic pollutants in effluents.

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Table 1. Experimental conditions of the CWAO of E2 ($c_{\text{feed}}=0.272$ mg/l) and BPA ($c_{\text{feed}}=20.0$ mg/l) carried out in a continuous-flow trickle-bed reactor

Mass of catalyst in bed, g	3.0
Bed density, g/cm ³	0.94
Bed porosity, /	0.41
Equivalent catalyst particle diameter, mm	1.42
Catalyst particle density, g/cm ³	1.59
Reaction temperature, ° C	200, 230
Total operating pressure, bar	25.5, ^a 38.0
Oxygen partial pressure, bar	10.0
Gas flow rate, ml/min	60
Superficial gas flow rate (G), kg m ⁻² s ⁻¹	0.357, ^a 0.500
Liquid flow rate, ml/min	0.5
Superficial liquid flow rate (L), kg m ⁻² s ⁻¹	0.134, ^a 0.132
$t_{\text{res,L}}$, min	0.24, ^a 0.23

^aT=230° C.

Table 2. Carbon content (measured by means of CHNS elemental analysis) on the surface of fresh and spent catalyst samples used in the CWAO of E2 aqueous solution. $c(\text{E2})_{\text{feed}}: 0.272$ mg/l, $c(\text{BPA})_{\text{feed}}: 20.0$ mg/l

Catalyst sample		^a Carbon content, wt. %	
		E2	BPA
SiC	fresh	0.03	0.03
	spent ^b	0.02	0.02
TiO ₂	fresh	0.13	0.11
	spent	0.14	0.09
Ru(3.0 wt. %)/TiO ₂	fresh	0.07	0.07
	spent	0.05	0.04

^aLimit of detection: 0.01 wt. %.

^bAfter CWAO of E2 (or BPA) carried out at both 200 and 230° C.

Table 3. Conversion and estrogenicity (REA) of 17 β -estradiol (E2) aqueous samples treated by means of CWAO process in the presence of various solids

Sample	Conversion,	Remained E2,	REA,
	%	$\mu\text{g/l}$	%
E2, feed solution	/	272	100
blank (ultrapure water)	/	/	0
1a: E2, SiC, T=200° C	70.0 \pm 6.0	81.6	95.2 \pm 2.5
1b: E2, SiC, T=230° C	90.0 \pm 5.6	27.2	90.4 \pm 3.5
2a: E2, TiO ₂ , T=200° C	93.0 \pm 2.2	19.0	100
2b: E2, TiO ₂ , T=230° C	100	0	0
3a: E2, Ru(3.0 wt. %)/TiO ₂ , T=200° C	100	0	0

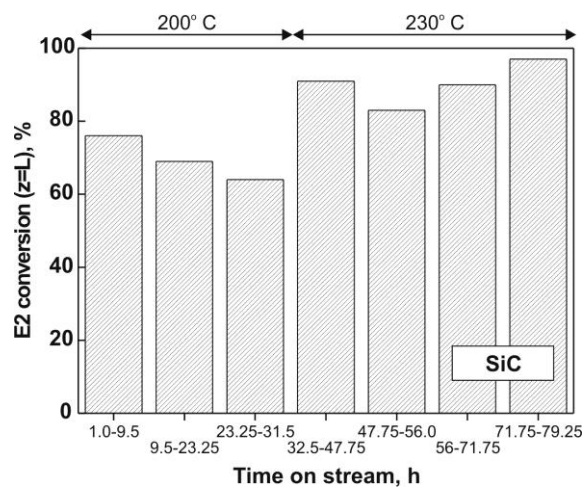
3b: E2, Ru(3.0 wt. %)/TiO₂, T=230° C 100 0 0

Table 4. Toxicity and estrogenicity of BPA samples treated by means of CWAO process. c(BPA)_{feed}: 20.0 mg/l

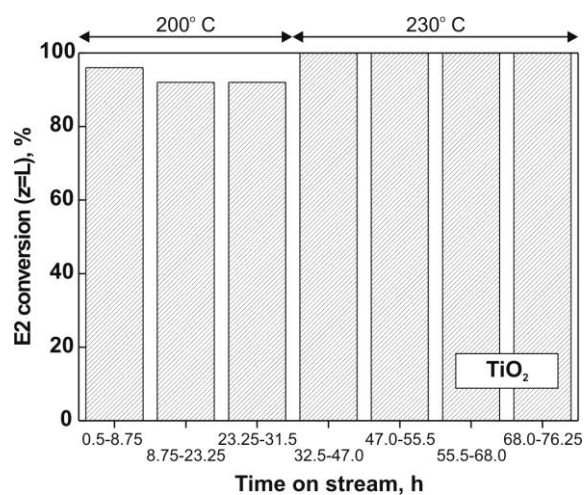
Sample	Conversion (%)	<i>V. fischeri</i> Luminiscence inh. (%)	<i>D. subsp.</i> Growth inh. (%)	<i>D. rerio</i> Mortality (%)	REA (%)
4 BPA, feed solution	/	72	51	100	100
5a BPA, SiC, T=200° C	38.5	42	31	100	100
5b BPA, SiC, T=230° C	58.5	11	0	90	100
6a BPA, TiO ₂ , T=200° C	87.5	34	28	80	0
6b BPA, TiO ₂ , T=230° C	96.2	0	0	90	0
7a BPA, 3% Ru/TiO ₂ , T=200° C	100	27	22	10	0
7b BPA, 3% Ru/TiO ₂ , T=230° C	100	0	0	60	0

Figure 1. E2 conversion as a function of time on stream obtained over inert SiC (a), TiO₂ extrudates (b) and Ru(3.0 wt. %)/TiO₂ catalyst (c) at 200 and 230° C. $c(E2)_{\text{feed}}$: 0.272 mg/l

a



b



c

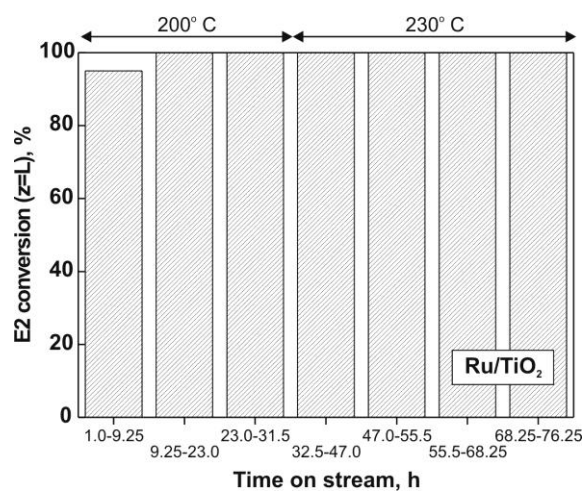
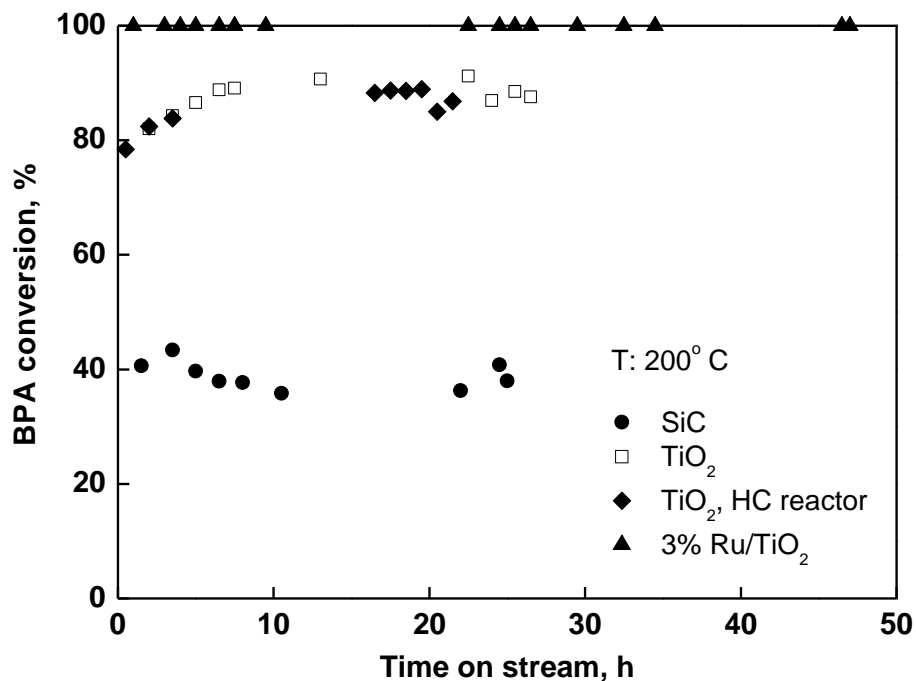


Figure 2. BPA conversion as a function of time on stream obtained over various catalysts at (a) 200 and (b) 230° C. $c(\text{BPA})_{\text{feed}}$: 20.0 mg/l

a



b

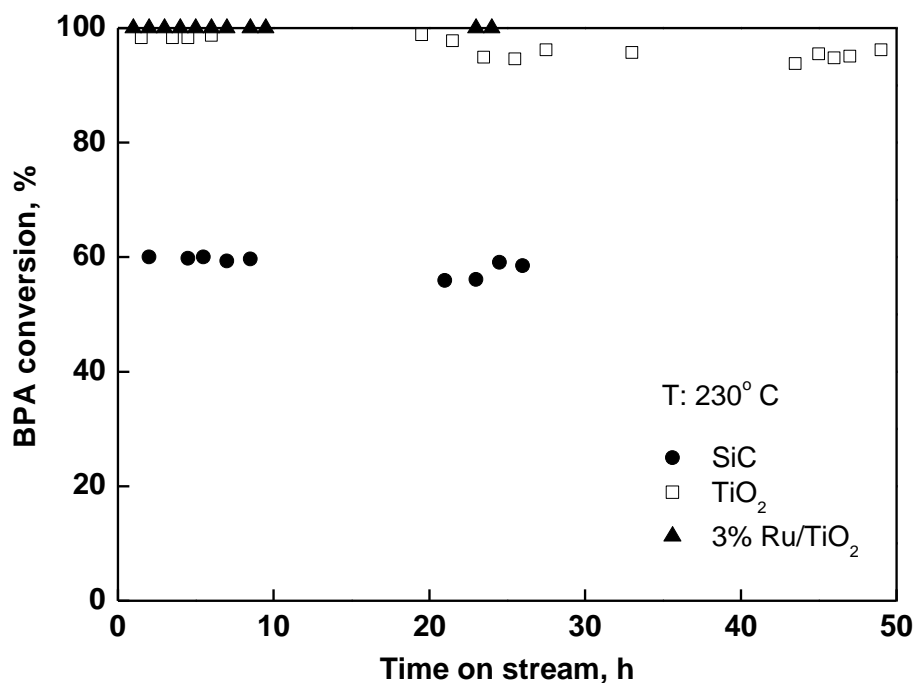


Figure 3. TOC conversion as a function of temperature obtained over various catalysts during CWAO of BPA. $c(\text{BPA})_{\text{feed}}: 20.0 \text{ mg/l}$

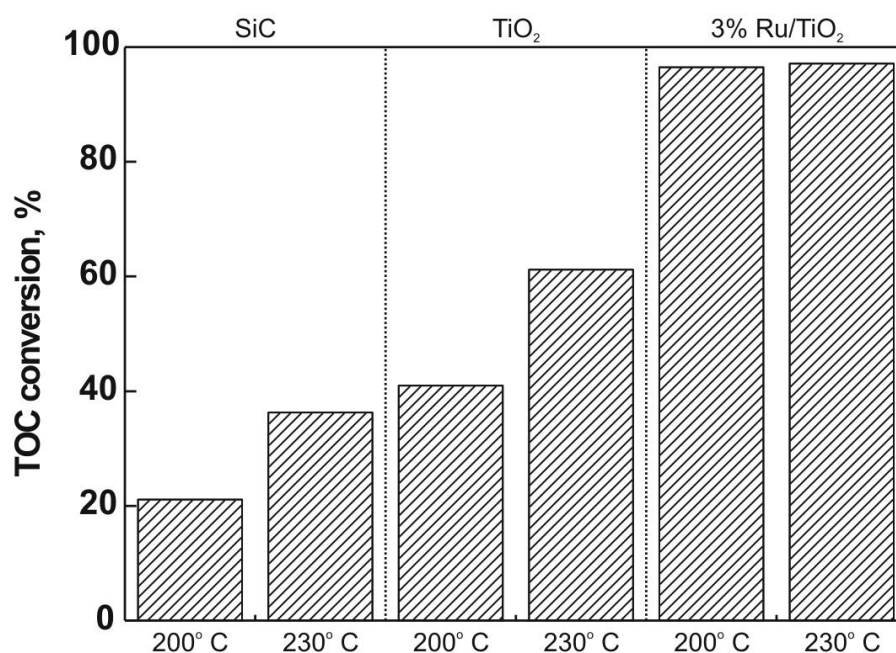


Figure 4. Results of YES test demonstrating the efficiency of Ru(3.0 wt. %)/TiO₂ catalyst to completely remove the estrogenicity of E2 dissolved in water. Refer to Table 3 for sample labels.

