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Short Communication

Ru/TiO_2 catalyst for efficient removal of estrogens from aqueous samples by means of wet-air oxidation

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ABSTRACT

The ubiquitous presence of endocrine-disrupting compounds (EDCs) in the environment is mainly the consequence of their incomplete removal from biological wastewater treatment plants. One of the promising options for EDC removal is catalytic wet-air oxidation (CWAO), where pollutants are oxidized by activated O_2 species in the presence of a solid catalyst. 17β-estradiol (E2) was used in CWAO experiments conducted in a trickle-bed reactor up to 230 °C over TiO_2 and Ru/TiO_2 solids. In the given range of operating conditions, E2 undergoes noncatalytic and catalytic oxidation routes. The employed Ru(3.0 wt.%)/TiO_2 catalyst enabled complete and long lasting efficiency of E2 degradation as well as removal of estrogenicity from the feed solution. No deactivation occurred and no carbonaceous deposits were accumulated on the catalyst surface.

1. Introduction

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 the environment has increased considerably due to the potential to elicit negative effects on the endocrine systems of humans and wildlife [1,2]. 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), 17β-estradiol (E2), and 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 [3]. Natural and synthetic estrogens are considered to be the major source of estrogenic activity in municipal wastewaters [4], whereas xenoestrogens (e.g. BPA) are frequently present in industrial wastewaters and landfill leachates [5,6]. 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 the removal of EDCs from aqueous samples [7–12]. 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 AOP 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 O_2 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 CO_2, water and associated inorganic salts [13,14]. 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 [15]. Titania and zirconia supported ruthenium catalysts have received much attention, because they exhibit high activity and chemical resistance in CWAO of different model pollutants [16,17] and industrial wastewaters [18]. Recently, the performance of various Ru/TiO_2 catalysts to promote oxidation of aqueous solutions of formic acid, acetic acid and phenol was investigated in a

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continuous-flow trickle-bed reactor [19]. 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/TiO_2 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/TiO_2 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 has 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 [20,21]. 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 [19,22].

In this study, CWAO runs were carried out to remove 17β-estradiol (E2), a natural estrogen hormone produced by the human body, 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 TiO_2 support and Ru/TiO_2 catalyst for effective (i.e. long-term) removal of the parent molecule and intermediates from the liquid phase. Estrogenic activity of treated E2 aqueous samples was evaluated by means of a yeast estrogen screen assay (YES assay) [23] and by HPLC analysis, which was used for quantification of remaining E2 in aqueous solutions.

2. Experimental

2.1. Catalyst preparation

The catalyst sample containing 3.0 wt.% of Ru was prepared by incipient-wetness impregnation of TiO_2 extrudates (Degussa-Hüls AG, Aerolyst type, d_p: 1.4 mm, S_{BET}: 51 m^2/g, V_{pore}: 0.36 cm^3/g, d_{pore}: 28 nm) with an aqueous solution of $RuCl_3 \cdot xH_2O$ (Acros Organics), concentration of which was accurately determined by ICP-AES before impregnation. The TiO_2 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 H_2 flow of 250 ml/min at 300 °C for 1 h without previous calcination. The actual Ru loading in the synthesized Ru/TiO_2 catalyst, determined by using ICP-AES analysis, was found to be equal to 2.9 wt.%. Fresh and spent catalyst samples were characterized by means of N_2 sorption, H_2 chemisorption, XRD, SEM/EDX, XRF and CHNS techniques.

2.2. 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 [19]. 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. It should be noted that representative liquid-phase samples of about 250 ml were collected at the reactor outlet in intervals of at least 8 h, which was required in order to obtain a sufficient volume of samples subjected to further preconcentration.

Table 1
Experimental conditions of the CWAO of E2 (c_{feed} = 0.272 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
$t_{res,L}$, min	0.24, [a]0.23

[a] T = 230 °C.

2.3. Analysis of end-product solutions (HPLC)

All samples were extracted and concentrated using solid-phase extraction (SPE) technique by being passed through the Oasis® HLB 6 cm^3 (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 (N_2) and eluted with 4 ml of methanol. Eluted samples were collected in test tubes and concentrated under a gentle stream of N_2 to the volume of 0.5 ml.

HPLC analyses to determine residual E2 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).

2.4. YES assay

Estrogenic activity of initial and treated samples was evaluated by "Yeast Estrogen Screen Assay" (YES assay) using recombinant yeast strain *Saccharomyces cerevisiae* BJ1991, developed in the Genetics Department at Glaxo Corporation under the guidance of Professor John P. Sumpter. 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 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. [24]. The relative estrogenic