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Glass fiber-supported TiO_2 photocatalyst: Efficient mineralization and removal of toxicity/estrogenicity of bisphenol A and its analogs

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ABSTRACT

Bisphenol A (BPA) and its analogs (BPF and BPAF) are a class of industrial chemicals that are proven to elicit endocrine disrupting effects, thus it is important to reduce their concentrations in effluent streams as much as possible. In this study, a simple and highly active glass fiber-supported TiO_2 photocatalyst was synthesized and applied in a UV-irradiated three-phase batch and continuous stirred-tank reactor (CSTR) for removal of toxicity and estrogenicity of water dissolved bisphenols. Bioassays of photocatalytically treated aqueous samples showed no estrogenic activity and complete removal of toxicity after 4 h of illumination, which was in accordance with high mineralization extent of bisphenols and their reaction derivatives. The photocatalytic examination of bisphenolic compounds revealed considerably higher stability of BPAF under UV light irradiation, due to two CF_3 groups attached to the central C atom. Moreover, these fluorinated groups were responsible for markedly higher toxicity of BPAF to crustaceans *Daphnia magna* in comparison to non-halogenated BPA and BPF, which manifested daphnids as excellent aquatic species for sensing fluorinated (halogenated) bisphenolic compounds. In addition, photocatalytic oxidation of bisphenol analogs in CSTR demonstrated feasibility of using the immobilized TiO_2 photocatalyst in continuous-flow light-assisted water purification systems. Detailed characterization of fresh and used photocatalysts confirmed substantial changes in active material structure. However, the corresponding impact on photocatalyst stability was found insignificant.

1. Introduction

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane), bisphenol F (BPF, bis(4-hydroxyphenyl) methane) and bisphenol AF (BPAF, 2,2-bis(4-hydroxyphenyl) hexafluoropropane) are a class of chemicals in which two phenolic rings are joined together through a bridging group that characterizes each particular compound. In BPA the bridging group is isopropylidene, while BPF differs from BPA only in virtue of its lack of two methyl groups on the central carbon atom. BPAF is a fluorinated analog of BPA, with two trifluoromethyl groups attached to the central carbon atom (Fig. 1) [1].

Bisphenols (BPs) have been extensively used in industry as intermediates in the production of polycarbonate, epoxy, and corrosion-resistant unsaturated polystyrene resins. The resins are fundamental components of high quality commercial polymer materials used in a wide range of essential applications from electronics to food protection [2]. As a result, large amount of bisphenols has been released into the environment and numerous studies have confirmed their presence in surface waters, municipal wastewaters, wastewater treatment plant (WWTP) effluents and sewage sludge [3–5].

Although bisphenols have been in use for more than a century, account has only recently been taken of human exposure or potential consequential health risks. BPA is regarded as an endocrine disrupting compound (EDC) that causes adverse effects on reproduction and development, neural networks, and cardiovascular, metabolic, and immune systems in humans [5]. BPA exhibits estrogenic activity even at concentrations below 1 ng/L, thus it is important to reduce its concentration in the environment as much as possible [6]. Comparable acute toxicity, genotoxicity and estrogenic activity were reported for BPF [7–10], while exposure to BPAF exhibits higher biological activities [8,11], including stronger estrogenic activity according to in vitro MVLN assay and in vivo vitellogenin assay [12], activation of the human pregnane X receptor, a nuclear receptor that functions as a regulator of xenobiotic

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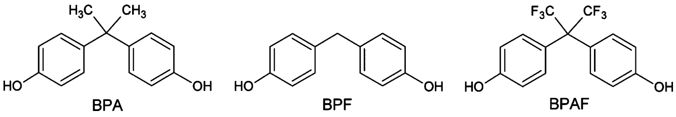

Fig. 1. Chemical structures of bisphenols used in this study as model pollutants.

[13] and testosterone reduction by directly affecting testis function in adult male rats [14].

Nowadays, the major sources of pollution with bisphenols are continuous emissions of wastewaters, e.g., landfill leachates and industrial effluents, which are usually sent to wastewater treatment plants and treated to the unsatisfactory extent [15]. As a consequence, various methods have been developed for more efficient removal of bisphenols from wastewaters, such as physical removal, biodegradation, and advanced oxidation processes (AOPs). Among these, AOPs are regarded as one of the most effective treatment technologies, due to in-situ generation of highly reactive radical species for degrading water contaminants. Among bisphenol analogs that are in commerce, BPA has been by far the most widely studied in versatile AOP systems, including photocatalytic oxidation, catalytic wet air oxidation (CWAO), ozonation, photo-Fenton oxidation, ultrasonic cavitation, UV/H_2O_2, etc., and fair to high efficiencies were reported [16–20]. On the other hand, only few attempts to eliminate either BPF or BPAF from aqueous solutions were reported so far. Liu et al. [21] examined UV-A light assisted photodegradation of BPAF and reported 78% conversions of TOC in the presence of acid-activated montmorillonite KSF. Moreover, MWCNTs as sorbent were used for separation of trace amount of BPAF from wastewater samples and 95% recoveries in ethanol were reported [22]. Lu et al. [23] suggested MnO_2-mediated oxidation as an effective treatment method for potential removal of BPF from wastes before their release into the environment. In addition, BPF was also effectively oxidized by horseradish peroxidase (HRP), especially, if the reaction was catalyzed in the presence of H_2O_2 and poly(ethylene glycol) [24].

Heterogeneous photocatalysis is a representative of AOPs and has proved to be of real interest as an efficient tool for degrading aquatic [25–27], atmospheric [28–30] and microbial [31] contaminants. The initial step in heterogeneous photocatalysis is generation of electron–hole pairs by light activation of semiconductor material. The photogenerated electron–hole pairs are requisite for the formation of reactive species, i.e., hydroxyl radicals ($^\bullet$OH), which facilitate the degradation of organic components. Ideally, during this process organic pollutants are mineralized to carbon dioxide, water and mineral acids [32]. Titania (TiO_2) is the most widely studied semiconductor photocatalyst in numerous environmental applications, due to its excellent photoactivity, physical and chemical stability, low cost and easy access. Usually, it is found in a powdered form and applied as a slurry catalyst, i.e., titanium dioxide powder suspended in polluted water. However, the post-treatment separation of TiO_2 powder from the treated water inevitably increases the cost of water purification process; therefore, immobilized photocatalysts appear to be more prosperous in light-assisted water treatment technologies, especially those that run around the clock [33]. In addition, the quantum yields of the two systems are comparable, which makes the immobilized systems even more attractive [34]. The overall performance of the latter is affected by various factors, such as synthesis conditions, immobilization procedures, and support type and shape [35].

In the present study, immobilized TiO_2 photocatalyst was synthesized by a routine preparation procedure, thoroughly characterized and subsequently applied in a UV irradiated three-phase batch and continuous stirred-tank reactor (CSTR) for removal of toxicity and estrogenicity of water dissolved BPs (bisphenol A, F and AF). Titania photocatalyst was supported by non-woven glass fibers (GF), which are flexible, offer high specific surface area and can sustain high calcination temperatures. The estrogenic activity (EA) of stock and treated samples was determined by yeast estrogen screen (YES) assay, which is based on human estrogen receptor-transfected yeast strain *Saccharomyces cerevisiae*. The toxicity tests were performed with marine bacteria *Vibrio fischeri* and water fleas *Daphnia magna*. Finally, the photocatalyst stability was examined in a continuous-flow UV irradiated reactor for 25 h on stream.

2. Experimental

2.1. Synthesis of immobilized TiO_2 photocatalyst

TiO_2 was immobilized by impregnating the non-woven glass fiber cloth (Sartorius^{TM}, grade MGA) with 0.3 M $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ (Sigma–Aldrich) solution. For this purpose, rectangular GF papers of dimensions 6 × 17 cm were cut and used as received in dip-coating preparation method. The substrate was immersed in the solution of the coating material and simultaneously withdrawn at a constant speed of 3 cm min^{-1} as depicted in the schematic drawing (Fig. S1). After wetting the filter paper, an excess liquid was drained from the surface. The as-prepared GF papers were dried at 60 °C, scrolled and placed in a calcination oven for 1 h at 500 °C. The dip-coating procedure was not repeated and fabricated immobilized photocatalysts were directly applied in photocatalytic oxidation process.

2.2. Characterization of immobilized TiO_2 photocatalyst

The textural, surface and morphological properties of fresh and used photocatalysts were investigated using SEM-EDX, XRD, UV–vis-DR, FTIR and N_2-physisorption. SEM-EDX analyses were performed by field-emission scanning electron microscope (FE-SEM SUPRA 35VP, Carl Zeiss), equipped with energy-dispersive detector (Inca 400, Oxford Instruments). The phase composition of immobilized TiO_2 was determined from the collected X-ray powder diffraction patterns. PANalytical X'pert PRO MPD diffractometer using Cu Kα1 radiation (1.54056 Å) in reflection geometry was applied for the measurement of Bragg diffractions. The data were collected in the range between 10 and 90° in steps of 0.034°. Crystalline phases were identified by comparison with PDF standards from the International Center for Diffraction Data (ICDD).

Diffuse reflectance UV–vis spectra of the bare support, and fresh and used supported TiO_2 were recorded at room temperature using a PerkinElmer Lambda 35 UV–vis spectrophotometer equipped with the RSA-PE-19 M Praying Mantis accessory, which is designed for diffuse reflectance measurements of horizontally positioned powder samples, pastes or rough surface samples. The white reflectance standard Spectralon® was used to perform the instrument background correction in the range of 200–900 nm. The ATR-FTIR spectra were recorded by FTIR analyzer model Frontier 100 (PerkinElmer), equipped with GladiATR VisionTM (PIKE Technologies) accessory that contained a diamond crystal. The obtained spectra were a result of 16 scans with a resolution of 2 cm^{-1} in the spectral range 4000–400 cm^{-1}.

Specific surface area measurements of the photocatalysts were determined from the adsorption isotherms of N_2 at −196 °C within the 0.06–0.30 P/P_0 range using a Micromeritics TriStar II 3020 instrument. This characterization was performed after degassing the samples under N_2 stream (purity 6.0) and programmed bi-level heating, starting with the first heating stage at 90 °C for 60 min and followed by the second heating stage at 180 °C for 240 min. The heating rate was set to 10 °C min^{-1} for both heating stages.

To measure the pH of the point of zero charge (pH_{PZC}), above which the surface is negatively charged, carefully weighed amounts