

# Immobilized TiO<sub>2</sub>-based photocatalyst for efficient removal of estrogenicity of bisphenol analogues (BPA, BPF, BPAF)

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## Introduction

Bisphenol A (BPA) and its analogues (BPF and BPAF) are a class of chemicals that are proven to elicit endocrine disrupting effects [1]. There are currently increasing concerns about bisphenols (BPs) as a result of their widespread distribution in various environmental compartments and potential adverse effects to biota and humans.

Heterogeneous photocatalytic oxidation is one of the most promising methods for degradation of such chemicals, due to its high mineralization efficiency, low toxicity, ideally producing carbon dioxide, water and inorganic mineral ions as end products [2]. Among the photocatalysts used, titanium dioxide (TiO<sub>2</sub>) is considered as a very efficient one because of its photoactivity, physical and chemical stability, low cost and easy access.

In the present study, immobilized TiO<sub>2</sub> photocatalyst was synthesized by a novel preparation procedure, thoroughly characterized and subsequently applied in a UV irradiated batch reactor for removal of estrogenicity of water dissolved BPs.

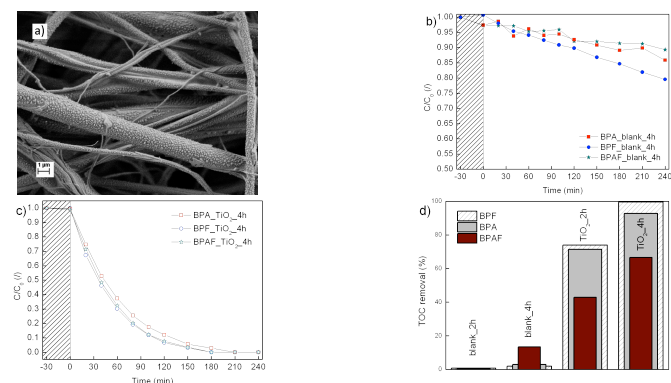
## Materials and Methods

TiO<sub>2</sub> was immobilized by impregnating the glass fiber (GF) cloth with titanium oxysulfate solution, followed by drying and annealing at 500 °C. The textural, surface and morphological properties of newly developed photocatalyst were investigated using SEM-EDX, XRD, UV-Vis-DR, FTIR, etc. analytical techniques. Photolytic/photocatalytic degradation runs (t = 2 and 4 h) of solutions containing BPs (C<sub>0</sub> = 44 µM) were carried out in a 250 mL batch reactor under irradiation of UV high-pressure mercury lamp. The continuously collected particle-free samples were further analyzed for residual BPs and total organic carbon (TOC) content, using HPLC, UV-Vis and TOC analyzer. The estrogenic activity (EA) of feed and treated samples were determined by yeast estrogen screen (YES) assay, which is based on human estrogen receptor-transfected yeast strain *Saccharomyces cerevisiae* BJ1991 [3].

## Results and Discussion

The N<sub>2</sub> physisorption measurements confirmed the loading of TiO<sub>2</sub> on the GF surface, since the BET specific surface area increased from 3 to 6 m<sup>2</sup>/g, due to increased surface roughness of GFs. On contrary, the BET specific surface area of bare GFs decreased to 2 m<sup>2</sup>/g as a consequence of sintering process. The XRD pattern of immobilized TiO<sub>2</sub> photocatalyst coincided with the anatase phase as the predominant crystalline structure of the photocatalyst. In addition, the UV-Vis-DR spectrum resembled a response of a typical TiO<sub>2</sub> based material, exhibiting a strong cut off at 383 nm, which corresponded to the band gap energy of 3.24 eV. Finally, the existence of loaded TiO<sub>2</sub> was also confirmed by SEM (Figure 1a) and EDX spectroscopy. SEM micrographs revealed a uniform distribution of TiO<sub>2</sub> particles over the GFs (0.93 mg of TiO<sub>2</sub> per 1 cm<sup>2</sup> of GFs), which was in accordance with SEM-EDX mapping.

The photolytic experiments (Figure 1b) demonstrated that BPF showed the least photo-resistant character among examined BF analogues. BPF differs from BPA only in virtue of its lack of two methyl groups on the central carbon atom. On contrary, BPAF with two trifluoromethyl groups attached to the central carbon atom was the most stable under UV light irradiation. However, the photocatalytic oxidation runs (Figure 1c) showed similar behavior; after 3.5 h more than 99% of initial pollutant concentration was degraded. This could be attributed to similar adsorption behavior of parent molecules on the catalyst surface, thus initiating the same active centre of examined BPs. Analyses of photocatalytically treated solutions using TOC analyzer demonstrated that complete mineralization of BPF was achieved after 4 h of irradiation. Slightly less TOC was removed in BPA solution, while the mineralization of BPAF was the least efficient, but still almost 70 %. The most plausible explanation, why BPAF and its derivatives are less prone to photocatalytic degradation, is due to restricted cleavage of strong C-F bonds. Nevertheless, after 4 h of photocatalytic treatment of BP solutions, the estrogenic activity (EA) of all three analogue solutions dropped to zero, considering wide range of concentrations (concentration factor from 0.1 to 10). The only exception represented BPAF at the highest concentration factors (from 5 to 10), where EA could not be determined, due to toxic effects towards yeasts and, therefore, inhibited activity.



**Figure 1.** a) SEM micrograph of TiO<sub>2</sub> supported on glass fibers. b) Photolytic degradation of bisphenol analogues. c) Photocatalytic degradation of bisphenol analogues. d) TOC removal as a function of BP analogue and time of photo(catalytic) oxidation.

## Significance

Immobilized TiO<sub>2</sub>-based photocatalyst was synthesized and its physicochemical properties were thoroughly investigated. The photocatalyst demonstrated excellent conversions of estrogen disrupting BPs (BPA, BPF, BPAF), resulting in complete removal of estrogenicity.

## References

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