



Degradation of the drugs Gemfibrozil and Tamoxifen in pressurized and de-pressurized membrane photoreactors using suspended polycrystalline TiO₂ as catalyst

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ABSTRACT

The performance of two configurations of catalytic membrane photoreactors (pressurized and de-pressurized) in batch and continuous systems for the degradation of two pharmaceuticals (Gemfibrozil and Tamoxifen), using suspended TiO₂ as catalyst, was investigated. The effects of parameters such as pH of the aqueous TiO₂ suspensions, pump flow rate and membrane clean-up, on the efficiency of the membrane photoreactor, were studied. In the batch pressurized photoreactor, catalyst and drugs rejections presented interesting values but a small or no-rejection to degradation products of both the drugs was evidenced. A good operating stability (steady-state maintained for more than 1.5 h) was observed in the continuous systems, reaching a steady state in ca. 120 min and a complete abatement of the Gemfibrozil together a constant retentate mineralization of 60%. A TOC rejection of about 62% in the pressurized photoreactor was obtained, while the no TOC rejection in the de-pressurized (submerged membrane) system, showed the necessity to identify a membrane selective to intermediate products. However, in both systems one common benefit was the retention of the suspended catalyst in the reaction ambient and the possibility to run continuous operations. The permeate flux (65.1 L h⁻¹ m⁻²) was higher in the submerged membrane photoreactor showing it interesting for application purposes.

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1. Introduction

Pharmaceutically active compounds (PhACs) are an important group of toxic organic contaminants that recently has attracted much attention to the international scientific community because of their presence in the aquatic environment [1]. These compounds reach the aquatic environment as refusals of the hospital structures, pharmaceutical industries, municipal sewage treatment plants, as well as residues of their use in agriculture and breeding [2]. Several investigations [3,4] have shown evidence that some substances of pharmaceutical origin, and their active metabolites, are not completely removed during conventional wastewater treatments and are not biodegraded; therefore, they are detectable in the environment with concentration levels up to the μg L⁻¹ [5–8]. Despite such values are lower than maximum concentrations found for other industrial contaminants, the problem of their toxicological chronic effects, due to the continuous exposure to pharmaceutical pollutants, appears to be of great importance. Indeed, they are considered among the pollutants which cause greater health risks

for humans and members of terrestrial and aquatic ecosystems [9].

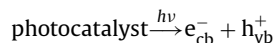
On this basis the demand to develop efficient systems, alternative to the traditional purification methods, for removing these compounds from waters, has assumed a great research interest. Hybrid processes coupling membranes and photocatalysis could represent a useful solution to these problems. Membranes could play the role of confining the photocatalyst and, if a suitable membrane is used, of selective barrier for the species to be degraded [10]. Photocatalysis is a technology which has been used to carry out a large variety of reactions such as partial or total oxidations, dehydrogenation, hydrogen transfer, water detoxification, metal deposition, gaseous pollutant removal, etc. [11].

Photocatalytic processes have been studied in the mineralization of toxic organic compounds [12,13], herbicides [14–16], pesticides [17,18], hormones [19], dyes [10,20], pharmaceuticals [1,21], etc. As reported by Augugliaro et al. [22], in order to improve the performance of the photoprocess, heterogeneous photocatalysis has been combined with physical or chemical operations, such as ozonation [23,24], ultrasonic irradiation, electrochemical treatment, biological treatment [25,26], membrane reactor [1,27], etc., with an increase of the efficiency of the photocatalytic process

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or/and of the overall process. Some studies have been also carried out with the aim of understanding the fundamental processes and enhancing photocatalytic efficiencies [28]. An interesting perspective is the possibility to use photocatalysis exploiting the solar light as energy source [21,29–31], with significant energetic savings.

These processes are based on the electronic excitation of a catalyst (semiconductor) by UV or UV–vis light with generation of highly reactive and oxidizing hydroxyl radical. When the catalyst is illuminated with photons whose energy is equal to or greater than its band-gap energy E_G ($h\nu \geq E_G$), electrons are promoted from the valence band to the conduction band (e_{cb}^-) with the creation of electron–hole pairs (h_{vb}^+):



The hole oxidizes a donor molecule (water or hydroxyl ions) to hydroxyl radicals which initiate a chain of reactions leading to the oxidation of organic compounds.

Concerning the location of the catalyst in membrane photoreactors, two operating modes have been widely studied: catalyst suspended and catalyst immobilized on a support. The system with the suspended catalyst has been found more efficient [20,32,33] due to the greater available active surface area of the catalyst compared to the immobilized system.

In addition to the configuration where the catalyst is suspended and recirculated in the pressurized side of the membrane, another configuration, where the catalyst is suspended outside the membrane immersed in the batch reactor and the permeate is sucked by a de-pressurization, has been also studied. Both these systems permit to work in continuous, but the immersed membrane photoreactor should be more interesting on the application point of view.

This study reports the photodegradation process of the drugs Gemfibrozil and Tamoxifen, not studied before in membrane photoreactors, by using TiO_2 as the catalyst. Aim of this work was to understand the effects of some parameters on the efficiency of membrane photoreactors. Particularly, the influence of the pH of aqueous TiO_2 suspensions on the passage of the catalyst through the membrane pores was investigated in order to minimize its presence in the permeate. Particular attention was addressed to some aspects that affect the behaviour of the membranes in terms of rejection, flux and fouling, such as recirculation flow rate and membrane clean-up. These results were then used to perform the photodegradation experiments in the batch and in the continuous membrane photoreactors (with pressurized and sucked (submerged) membranes) to study the catalytic efficiency of the photodegradation process. In particular, the submerged membrane, differently from the configurations reported in literature, is placed in a permeation cell located separately from the irradiation zone.

2. Experimental

2.1. Materials

Gemfibrozil (GEM) is the 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (is a fibrate hypolipidemic agent) (Fig. 1a), $\text{C}_{15}\text{H}_{22}\text{O}_3$, MW = 250.35 g mol⁻¹, from Sigma. Gemfibrozil solutions were prepared by dissolving 10 mg of the drug in 1 L of ultrapure water (Elix 5, Millipore).

Tamoxifen (TAM) is the 2-[4-(1,2-diphenylbut-1-enyl)phenoxy]-N,N-dimethyl-ethanamine (an antineoplastic agent used for the treatment of breast cancer) (Fig. 1b), $\text{C}_{26}\text{H}_{29}\text{NO}$, MW = 371.53 g mol⁻¹, from Sigma. Tamoxifen solutions were prepared by dissolving 8 mg of the drug in 1 L of ultrapure water (Elix 5, Millipore) and adding hydrochloric acid or citric acid.

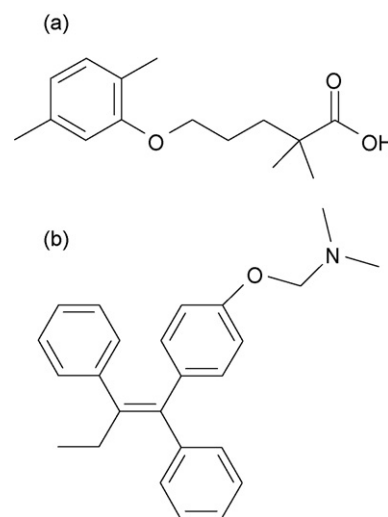


Fig. 1. Chemical structures of Gemfibrozil (a) and Tamoxifen (b).

Sodium hydroxide (NaOH , MW = 40.00 g mol⁻¹, purity = 98%) from Sigma, hydrochloric acid 37% (w/w) (HCl , MW = 36.46 g mol⁻¹) from Riedel-de Haen and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, MW = 210.14 g mol⁻¹, purity = 99.8%) were used to correct the pH of aqueous phases.

In every test, the photocatalyst was TiO_2 , Degussa P25 type (specific surface area = 44 m² g⁻¹, crystallographic phase ca. 80% anatase and 20% rutile, band gap 3.2 eV).

Commercial flat sheet nanofiltration membranes NTR 7410 (Nitto Denko, Tokyo) were used in the rejection and photocatalytic tests in the configuration where the catalyst was recirculated in the pressurized side of the membrane. They were made of sulfonate polyethersulfone polymer with 600/800 Da cut-off (rejection 10% with 0.2% NaCl at 4.9 bar, 25 °C, pH 6.5). After each run, the membranes were regenerated by immersion in an aqueous solution containing 0.2% (w/w) of an enzymatic detergent (Ultrasil 50 by Henkel).

Commercial capillary membranes made by hydrophilic polyethersulfone (PES) (X-Flow, Norit), 2.9/1.9 mm outside/inside diameter and 0.05–0.1 μm average pore size were used in the configuration with immersed membrane.

2.2. Methods

Gemfibrozil and Tamoxifen concentration and the relative area of peaks of their degradation products were detected by high performance liquid chromatography (HPLC, Agilent 1100 Series instrument) using a Phenomenex Synergi 4u Fusion-RP 80A (4.60 mm × 250 mm, 4 μm) column by UV readings at 220 nm and 235 nm wavelength for GEM and TAM, respectively. The mobile phase consisted of an acetonitrile/phosphate buffer at pH 3.1 solution 70/30 (v/v) fed to a flow rate of 1.0 mL min⁻¹. The column pressure was 82 bar and the injection volume was 20 μL.

Gemfibrozil and Tamoxifen mineralization was evaluated by dissolved organic carbon (DOC) measurements, performed by using a TOC-VCSN from Shimadzu.

All the samples used were filtered by means of a low-adsorbing membrane (mean pore size 0.2 μm) before carrying out the analyses.

The properties of TiO_2 suspensions, at different pH and concentrations, filtered with 0.2 μm membranes, were determined by light scattering analyses, using the 90-Plus particle size analyzer (Brookhaven Instruments).

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