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Photocatalytic degradation of atenolol in aqueous suspension of new recyclable catalysts based on titanium dioxide

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ABSTRACT

Photocatalytic degradation of atenolol in aqueous suspensions using specifically synthetized mesoporous based TiO_2 materials as photocatalysts under UVC (254 nm) irradiation was investigated. A batch reactor and a UV lamp 16 W power were used to test the ATL removal with several initial concentrations of ATL (4.5 − 30 mg/L) and four synthetized TiO_2 photocatalysts, characterized by different BET surface areas and average pore sizes. Moreover, the effect of solution pH (4.8 − 9.0) and of the oxygen presence were investigated. The performances of the synthetized photocatalysts were compared with commercial Degussa P25. The atenolol degradation was studied using different concentration of catalyst (50 and 1000 mg/L) showing a maximum removal efficiency of 65%. Although the new catalysts showed a lower efficiency when compared to commercial P25, they can be easily recovered from water being in the form of micro-aggregate, and then reused without remarkable changes. The experimental data were fitted using a pseudo first order kinetic model.

1. Introduction

In recent years, several researches have paid their attention to the presence of PPCPs and EDCs in wastewater treatment plant effluents, surface, groundwater and drinking water [1–5]. Even if the amount of these substances in the aquatic environment is low, ranging from few (ng/L) to few (μg/L) (therefore, they are defined *micropollutants)*, their continuous release into the environment, together with their physical and chemical properties, constitutes a potential risk for aquatic and terrestrial organisms [6]. These compounds are also called *emerging pollutants* because, even if not yet included in routine monitoring programs, they may be regulated in the future for their ecotoxicity and persistence in the environment. The recent European directive 2013/39/UE updated the list of priority organic *micropollutants* in order to collect monitoring data and facilitate the determination of the appropriate measures to address the risks presented by such substances, some of which without setting limits on the maximum acceptable concentrations.

Referring to pharmaceuticals, after administration, the active substances are only partially metabolized. The unmetabolized active substances, together with a mixture of metabolites [7,8], are excreted largely in urine (generally 55–80% of the total substances [7]) and partially in feces, and thus they can enter the water cycle. ATL (4-[2-hydroxy-3-[(1-methyl)amino]propoxyl]benzeacemid), belongs to the group of β-blockers, a class of drugs used primarily in cardiovascular diseases; it is one of the pharmaceuticals released in large quantities in the environment through urban wastewater treatment plants' discharges [9–12]. Some studies showed that ATL could inhibit the growth of human embryonic cells and that it is ecotoxic to freshwater species [13]. Furthermore, ATL, such as other pharmaceuticals, is persistent against biological degradation and natural attenuation, therefore may remain in the environment for a long time [14]. In this way, ATL may reach natural water as groundwater and then drinking water [12].

Water treatment plants have an important role to reduce pharmaceuticals presence in the environment, since it is difficult to limit their use. Several researches have demonstrated that ordinary wastewater

Abbreviations: AOPs, Advanced Oxidation Processes; ATL, Atenolol; BJH, Barrett-Joyner-Halenda method; BET, Brunauer–Emmett–Teller method; EDCs, Endocrine disrupting compounds; HPLC, High Performance Liquid Chromatography; IC, Inorganic carbon; K_a, Dissociation constant; L-H, Langmuir-Hinshelwood; logKow, Octanol-water partition coefficient; PFO, pseudo-first order; PZC, Point of zero charge; PPCPs, pharmaceuticals and personal care products; TC, Total carbon; TOC, Total organic carbon; UV, Ultraviolet; UV–vis, Ultraviolet-visible; λ, Wavelength

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treatments such as activated sludge, granular activated carbon [15] and filtration cannot completely remove ATL [14,16,17]. In particular, the phase transfer technologies currently in use, such as adsorption and nanofiltration, do not lead to the destruction of this type of pollutants, but only to their transfer from one phase to another, leaving a problem for the removal of the transferred material [18].

AOPs are efficient methods for water and wastewater treatment [6,19,20] AOPs include heterogeneous and homogeneous photocatalysis based on near UV or solar visible irradiation, electrolysis, ozonation, Fenton's reagent, ultrasound and wet air oxidation; less conventional, but evolving, processes include ionizing radiation, microwaves, pulsed plasma and ferrate reagent [6]. On the other hand, these processes can lead to the formation of undesired by-products, that can be more hazardous than the parent compounds, and whose complete mineralization is difficult to be achieved [18].

In recent years, heterogeneous photocatalysis showed to be one of the most promising among AOPs, able to couple low-energy ultraviolet light with semiconductors particles as photocatalysts. It is no-toxic and low in cost thanks to the possible reuse of the catalyst; titanium dioxide (TiO_2) for the abatement of organic compounds either in reactors as suspended photocatalyst or as immobilized photocatalysts on supporting materials [21,22]. The use of TiO_2 particles suspended in contaminated water provides large surface area. In fact, the TiO_2 catalyst in nano-size dimensions has a large surface area-to-volume ratio and can promote the efficient charge separation and trapping at the physical surface [23,24]. On the other hand, fixed-bed configurations eliminate the need of catalyst filtration and centrifugation but present lower removal efficiencies. In particular, a reduction of 60–70% in performance is reported in aqueous systems for immobilized TiO_2 compared to the suspended catalyst [25]. To date, the most widely applied titania photocatalyst for water treatment is the nanopowder Degussa P25. The powder nanoscale TiO_2 gives an enhanced oxidation capability but their particle size and morphology represents the main problem in the scale-up of water treatment process [26].

In this study, the photocatalytic activity of mesoporous based TiO_2 powders, *ad hoc* synthesized according to previous studies [27], in aqueous ATL solutions, under UVC (254 nm) irradiation was investigated. These photocatalysts were chosen also for their easy post-separation process, in fact the recovered catalyst performance was also investigated. The performances of the synthetized photocatalysts were compared with commercial Degussa P25. The effects of various process parameters such as initial concentration of ATL and concentration of suspended catalysts, dissolved oxygen, pH and irradiation time were studied. Finally, experimental data were fitted by a model.

2. Materials and methods

2.1. Atenolol

ATL (4-[2-hydroxy-3-[(1-methyl) amino] propoxyl] benzeacemide) belongs to the group of β-blockers, a class of drugs used primarily in cardiovascular diseases. In human body the drug is minimally metabolized by the hepatic glands. Approximately 50 − 85% is excreted through the renal system within 24 h. The fact that human body metabolizes only a minimum percentage of this drug causes a continuous release in the environment.

In this work, ATL was supplied by Sigma-Aldrich as 99% pure for calibration curves and as 98% pure like contaminant for the experiments.

ATL is not very soluble in the water and has a weakly acidic character. One of the most important characteristics is the octanol-water partition coefficient, $\log K_{ow}$ which is a measure of its hydrophilicity or hydrophobicity. Its low octanol/water partition coefficient means that ATL is more likely to accumulate in aqueous compartments such as blood serum.

The main characteristics of the molecule are listed in Table A (Supporting information).

All aqueous solutions were prepared with pure water (18 MΩ resistivity) taken from Millipore system. The abatement of ATL was studied at initial concentrations varying from 4.5 to 30 (mg/L). Although these concentrations are some order of magnitude higher than that present in different water bodies, they are used in order to get more precise measurement throughout the experimental tests [28].

2.2. Catalysts

Four mesoporous samples of titania (T1, T2, T3, T4) were used for the photo-catalytic removal of ATL. Comparative studies were also performed with the commercial Degussa P25 (Sigma-Aldrich).

All the mesoporous aggregates of ZrO_2-containing (5 mol%) TiO_2 were synthesized without the surfactant templating technologies. They have been prepared by co-hydrolysis of mixtures of titanium tetraethoxide, $(Ti(OC_2H_5)_4)$,and zirconium tetraisopropoxide, $(Zr(OC_3H_7)_4)$ (R.G Aldrich), changing parameters of synthesis such as: hydrolysis temperature (25° or 140 °C), hydrolysis time (1 or 48 h), the nature (NH_4Cl or NH_4OH) and the concentration (0.072 or 1.0 M) of the catalysing agent. All the resulting products were calcined at 450 °C for 2 h. The detailed experimental conditions for the synthesis have been carried out according to the procedures mentioned in a previous paper [29] and are reported in Table 1 together with the characteristics of both P25 and of the resulting mesoporous products.

The samples T1, T2, T3 and T4 resulted well crystallized as anatase while P25 contains an anatase-rutile mixture. The samples T1 and T3 were synthesized by forced hydrolysis at 140 °C in the presence of

Table 1
Titania characteristics and operating conditions for the syntheses. $T_{1\text{-}4}$ synthetized photocatalyst.

Sample					
Properties	P25	T1	T2	T3	T4
Temperature/time of the hydrolysis treatment (°C/h)	–	140/48	25/1	140/48	25/1
Alcoholic medium	–	Ethanol			
Catalyst agent/catalyst concentration (mol/L)	–	NH_4Cl/0.072/0.	NH_4OH/0.072	NH_4OH/0.0720.	NH_4OH/1.0
Calcination Temperature/time of calcination treatment (°C/h)		450/2			
Crystallinity/Crystalline Form	Full crystallized/Anatase (80%) − Rutile (20%)	Full crystallized/ Anatase (100%)			
Pore structure	Mesoporous				
BET surface area [m^2/g]	56	106	74	87	123
Average crystallite size [nm]	21	14.6	17.1	16.3	12.9
Average pore diameter [nm]	6.2	7.4	8.9	16.1	7.3