



# Effect of water matrix on photocatalytic degradation and general kinetic modeling



Nerea Rioja<sup>a,b</sup>, Saioa Zorita<sup>b</sup>, Francisco J. Peñas<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Soil Science, University of Navarra, 31008 Pamplona, Spain

<sup>b</sup> Tecnalia-Energy and Environment Division, c/ Geldo, Parque Tecnológico de Bizkaia, Edificio 700, 48160 Derio, Spain

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## ABSTRACT

Photocatalysis employing TiO<sub>2</sub> nanoparticles was studied to assess the effect of aqueous matrix nature in the degradation of clofibric acid (CFA) under UV-A radiation. Aeroxide TiO<sub>2</sub>-P25 at 0.50 g/L was the most effective catalyst among those tested, with a CFA degradation of 98.5% after 15 min. The CFA photodegradation in environmental waters (tap, mineral, river and recycled wastewater) and in the presence of inorganic (NaCl, FeCl<sub>3</sub>, FeCl<sub>2</sub>, AlCl<sub>3</sub>, CaCl<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>) and organic compounds (humic acids, and a surfactant) commonly found in real waters was compared to that obtained in pure water. In general, the removal efficiency decreased with inorganic salts, especially with sulfates and carbonates (>70% deactivation), and also in environmental waters (>90%). A general kinetic model has been developed to describe the CFA photodegradation depending on the type and concentration of substances present in water. The first-order kinetic constants were estimated by defining a characteristic parameter for each ion species tested in the aqueous matrix. High correlation ( $R^2 > 0.99$  in most cases) was observed between experimental CFA concentrations and those predicted by the model.

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## 1. Introduction

In the last couple of decades the advances in water quality analytical techniques has led to an increased focus on water micropollutants and emerging contaminants such as pharmaceuticals [1–5]. The presence of therapeutic drugs in the aquatic environment is becoming widespread [5–8], mainly because actual wastewater treatment plants (WWTP) fail on a quantitative removal of many of these pollutants [9–11]. Furthermore, due to the expected scarcity of freshwater resources, there is an increasing need on high quality recycled water.

On the other hand, despite the fact that heterogeneous photocatalysis has been studied for some years now, it is still considered a promising treatment technology for eliminating organic micropollutants from water [12–14]. Its attractiveness relies on its ability to degrade organic chemicals into innocuous end products. Among the organic compounds that have been degraded in water by heterogeneous photocatalysis, dyes, pharmaceuticals, phenols plus many other pollutants are found [15–18]. However, one of the major limitations is that actual catalysts lack of high quantum yields mainly due to the fast recombination of the photogenerated electrons and

holes after excitation [19]. In fact, typical quantum yields are often below 10%, although a maximum of 40% has been reported [19,20]. This decrease in degradation efficiency is generally due to intrinsic and extrinsic factors [21]. The first ones are related to the system design and catalyst type while the others are linked to the aqueous matrix (i.e. pH, structure and concentration of pollutant, ionic composition, and presence of impurities) [15,19].

Although the photocatalytic technology is aimed for environmental applications, most of the studies are conducted in pure water, and little is known about its performance using real matrices (such as tap, river, or recycled water). Some studies found that inorganic ions can significantly diminish the photocatalytic efficiency [22,23], being this effect primarily attributed to the adsorption of ions on TiO<sub>2</sub> surface [24]. The effect of wastewater matrices on photocatalytic degradation of pollutants has been little studied, showing lower removal rates than those with pure water [25–29]. This efficiency decrease has been largely attributed to the quenching of radicals by salts and organic matter [25]. However, for the further development of this technology, more studies on how water components affect photocatalysis are required.

This work addresses the effect of water matrix nature on photocatalytic degradation of emerging contaminants in water, using clofibric acid (CFA) as the target pollutant. The kinetics of CFA photocatalytic oxidation in various environmental waters (mineral, tap, river, and recycled water) has been determined for several

\* Corresponding author. Fax: +34 948 425600.

**Table 1**  
Main features of the commercial photocatalysts.

	Kertak TiO <sub>2</sub> -nanofibres	Aeroxide TiO <sub>2</sub> P25	Aeroxide TiO <sub>2</sub> P90	Microsphere photospheres
Diameter or length (μm) <sup>a</sup>	0.295 ± 0.070	0.021–0.025	0.014	45
Surface area (m <sup>2</sup> /g) <sup>a</sup>	98.7	50	90–100	–
Crystallinity <sup>a</sup>	100% Anatase	80% Anatase, 20% Rutile	90% Anatase, 10% Rutile	–

<sup>a</sup> Information provided by the manufacturers.

catalyst types (Aeroxide TiO<sub>2</sub> powder P25 and P90, Photospheres, Kertak TiO<sub>2</sub> nanofibres, and TiO<sub>2</sub>-SiO<sub>2</sub> composite), and for different concentrations of organic (sodium *n*-octyl-sulfate, and humic acid) and inorganic (NaCl, FeCl<sub>3</sub>, FeCl<sub>2</sub>, AlCl<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and CaCl<sub>2</sub>) compounds. A new kinetic model for predicting the photodegradation efficiency of CFA in different water samples has been developed by introducing a parameter characteristic of each substance used to form the respective aqueous matrix.

## 2. Experimental

### 2.1. Photocatalytic materials and water matrices

Titanium dioxide Aeroxide P25 and P90 were acquired from Evonik (Germany), Photospheres from Microsphere Technology (Ireland), and TiO<sub>2</sub> nanofibres from Kertak Nanotechnology (Czech Republic). A batch of TiO<sub>2</sub>-SiO<sub>2</sub> particles were prepared according to the method of Jafry et al. [30]. The available features of the four commercial photocatalysts assayed are given in Table 1.

Deionized water was obtained from a purification system (Millipore Milli-Q, USA). Bottled mineral water (pH 7.5, conductivity 521 μS/cm, TOC <0.2 mg/L) was purchased at a local supermarket. Tap water (pH 7.9, conductivity 232 μS/cm, TOC 2.2 mg/L) was obtained from the local drinking water supply. The river water matrix (pH 8.13, conductivity 509 μS/cm, TOC 4.7 mg/L) was collected from the Asua river (Spain). The recycled wastewater matrix consisted of the filtrate (Whatman GF/F 0.7 μm, Germany) of treated sewage water (pH 7.54, conductivity 818 μS/cm, TOC 27.1 mg/L) collected from the Zumaia WWTP effluent (Spain).

### 2.2. Photocatalytic experiments

Batch experiments were carried out in 150-mL reaction cells under UV-A light irradiation (365 nm, 0.89 mW/cm<sup>2</sup>). An UV-A lamp (GE Lighting, F20T12/BL 20W, USA), with a spectral peak of 367 nm, was used as the source light. The scheme of the experimental setup is shown in the supplementary material (Fig. A.1). The radiation intensity was measured inside of the reactor using a UV-A radiometer (Lutron, Taiwan) located at the bottom of the vessel. In each assay, an enough amount of the corresponding photocatalytic material to typically give 50 mg of TiO<sub>2</sub> was suspended in 100-mL of pure water (i.e. 500 mg-TiO<sub>2</sub>/L) and spiked with the target drug (clofibrac acid, 1.00 μg/mL) and other compounds when necessary. Some environmental waters were used as aqueous matrix in other experimental series. Each test was conducted in triplicate, keeping the first 60 min in darkness for adsorption and then the next 15 min for photocatalytic degradation. The previous essays carried out in darkness showed a low CFA adsorption within 60 min (5.7 ± 0.9%). Aliquots of 0.6 mL were periodically sampled from reaction cells, and then centrifuged at 4500 rpm for 30 min (Sigma Laborzentrifugen, 4–15, Germany) to remove the photocatalyst particles before analysis.

### 2.3. Analytical methods

The concentration of clofibrac acid was measured in triplicate by HPLC. More details can be found elsewhere [29]. A conductivity meter (Hanna Instruments, HI9835, Spain) was employed to determine the conductivity and NaCl content of the samples. A portable instrument (Mettler-Toledo, SevenGo SG2, Switzerland) was used to measure and control pH in samples. Particle size and zeta potential were measured by electrophoretic light scattering (Malvern Instruments, Zetasizer Nano-ZS, UK), at 25 °C, and using a high-concentration cell (Malvern Instruments, ZEN1010, UK). For each water matrix, suspensions of the photocatalytic particles (0.50 g-TiO<sub>2</sub>/L unless otherwise stated) were stirred at 700 rpm for at least 2 min prior to taking the samples for measurements. All of the non-linear regression parameters were obtained by minimizing the sum of the squared difference between the experimental and calculated data using the Solver add-in (Microsoft, Excel 2010, USA).

### 2.4. Reagents

Clofibrac acid, iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, aluminium chloride hexahydrate, sodium sulfate, sodium carbonate, sodium bicarbonate, humic acid sodium salt [CAS 68131-04-4], hydrochloric acid (37%), sodium hydroxide, and sodium phosphate monobasic were obtained from Sigma-Aldrich (Germany). Sodium chloride, iron(III) sulphate hydrate (75%), aluminium sulfate octadecahydrate, and acetonitrile were purchased from Panreac (Spain). Sodium *n*-octylsulfate was supplied by Alfa Aesar (Germany). All reagents were used as received.

## 3. Results and discussion

### 3.1. Effect of photocatalyst type and dosage

Since activity of heterogeneous catalysts depends, among others, on particle size and crystalline structure, preliminary experiments were conducted with five TiO<sub>2</sub> catalysts in order to find the most suitable form for maximal performance. The CFA degradation profiles obtained (*C/C*<sub>0</sub> vs *t*) are depicted in Fig. 1. The error bars are the standard deviation of the mean for 3 batches. The photocatalytic degradation of CFA was well described by a pseudo-first-order kinetics, being this pattern also observed in the remaining experiments. As clearly shown, Aeroxide P25 and P90 were found to be highly active for CFA degradation (more than 95% after 15 min) in comparison with titania-P25/silica particles (51%), whereas the removal efficiencies were less than 10% for both Kertak nanofibres and Photospheres. Thus, as Aeroxide TiO<sub>2</sub>-P25 showed the best performance in CFA removal, this nanoparticle photocatalyst was employed henceforth.

In general, photodegradation rate increases with catalyst loading until a maximum beyond which efficiency drops off because of the higher turbidity reduces the penetration of light through water. Therefore, additional experiments were conducted with TiO<sub>2</sub>-P25 to determine the optimal catalyst loading for CFA degradation. As observed in Fig. 2a, loads of 500 and 1000 mg-TiO<sub>2</sub>/L yielded virtually the same degradation profiles, whilst the CFA removal rate was significantly lower at 200 mg-TiO<sub>2</sub>/L. The kinetic constant obtained

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