

STUDY OF APPLICATION OF TITANIA CATALYSTS ON SOLAR PHOTOCATALYSIS: INFLUENCE OF TYPE OF POLLUTANTS AND WATER MATRICES

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ABSTRACT

A comparative analysis of photocatalytic efficiency has been carried out with both TiO₂ P25 and a home-made catalyst at a solar radiation pilot plant constituted by Compound Parabolic Collector (CPC) systems. The effect of the chemical nature of three different substrates (phenol, dichloroacetic acid and pyrimethanil) and the impact of inorganic ions in natural waters, on their final photo-efficiencies was also analyzed. Subsequently, this solar photocatalytic process was applied to the photodegradation of a mixture of emerging contaminants considering the separation and recovery of catalysts by sedimentation. Although TiO₂ P25 showed better results during phenol and dichloroacetic acid photodegradation, both photocatalysts presented similar photo-efficiencies in pyrimethanil mineralization and, specially, in the treatment of emerging pollutants. The presence of high concentrations of inorganic ions in natural waters constitutes a limiting factor for solar photocatalytic activity, but this process successfully photodegraded the mixture of micropollutants (carbamazepine, ibuprofen, sulfamethoxazole, ofloxacin, flumequine) in natural water matrix using both TiO₂ catalysts, at very short irradiation times ($t_{30w} < 35$ min). Therefore, solar assisted heterogeneous photocatalysis represents a very efficient, promising and competitive AOP to remove emerging contaminants like the pharmaceutical micropollutants studied here and frequently detected in Municipal Wastewater Treatment Plants.

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1. Introduction

Water is a natural resource needed for life, however, in the XXI, around 2000 million people will face severe shortages due to the loss of balance between the quantity and quality of available water and demand [1]. Therefore, the improvement of technologies for wastewater decontamination treatment is essential nowadays.

Heterogeneous photocatalysis is a promising Advanced Oxidation Catalytic Technology, whose efficiency in the treatment of poorly biodegradable substances is known, particularly when moderate to low concentrations of organic pollutants are abated [2,3]. The combination of nanostructured TiO₂ photocatalysis with solar technology (environmental friendly and sensitive light source) is a powerful tool to efficiently eliminate organic contamination in wastewater, because it conduces to total mineralization under mild conditions, resulting in energy savings [4].

Knowing that photocatalytic processes are governed by different parameters: pH, light intensity/wavelength, catalyst loading, surface area, surface charge, concentration and nature of substrate/pollutant, reactor geometry, etc [5], many efforts have been faced by the scientific community trying to correlate catalysts properties with photocatalytic activity, and the resulting outcomes always pointed out a mixed balance between certain surface, electronic and structural properties that seemed to be playing important roles on the overall photocatalytic behaviour, where, simultaneously, a very significant dependence on the photoreactor geometry and the corresponding operational conditions appeared to be also taking place. Therefore, the photocatalytic activity of every catalyst is essentially specific and related to the chemical nature of pollutant [5].

Titania based catalysts are useful and efficient photocatalysts for the abatement of organic microcontaminants solutions such as herbicides, pesticides, emerging contaminants (ECs), and others [6,7,8], where usually, relatively dilute multi-component solutions and fixed volumes are involved, that can be recycled to achieve complete mineralization of organic

carbon in the existing environment [9]. Pharmaceutical, drugs, personal-care products, steroid sex hormones and flame retardants among others, are introduced into the wastewater environment after being used in industry and household, given that conventional Municipal Wastewater Treatment Plants (MWTPs) are not able to totally degrade ECs at very low concentrations [10], with detection levels rarely exceeding $\mu\text{g}\cdot\text{ng}\cdot\text{L}^{-1}$ concentrations [11]. Nevertheless, these low concentrations could bring about harmful toxicology consequences in many aquatic ecosystems [12], since many types of microcontaminants have been documented in the effluents of MWTPs [7,8].

Nowadays, several researches are also studying the influence of inorganic ions and organic substances on TiO_2 photocatalysis [13,14], and seems to be a general consensus that inorganic ions affect the photocatalytic processes by their adsorption onto the TiO_2 surface and trapping positive holes and hydroxyl radicals during heterogeneous photocatalysis.

The aim of this work consisted in a comparative study of the catalytic photoefficiencies during the solar photodegradation of organic pollutants, between a home-made TiO_2 photocatalyst and the standard P-25 in different water matrices.

Firstly, the impact of the chemical nature of three organic pollutants (phenol, dichloroacetic acid (DCA) and pyrimethanil) on sunlight assisted photodegradation, with two titania (the commercial P25 and a home-made catalyst, TiEt-450) has been analyzed and compared. Furthermore, the effect on their photocatalytic efficiencies, of inorganic ions has been also studied when natural ground water matrix was employed. Secondly, the photodegradation of an emerging contaminants mixture as attractive and prominent advanced catalytic technology was also analyzed with these two TiO_2 catalysts.

The studied mixture of emerging contaminants consisted on five pharmaceutical microcontaminants: ofloxacin, sulfamethoxazole, carbamazepine, flumequine and ibuprofen, that were chosen due to their potential significant risk to the aquatic environment, and frequently present in the effluents of MWTPs or hospitals [15,16,17]. Again the influence of natural water was also analyzed for a comparative purpose.

Finally, given that catalyst efficiency and recovery are the key challenge that have limited the practical development of TiO₂ powder catalysts in wastewater applications, to determinate whether their photocatalytic efficiencies are enough good to assess the real application of solar heterogeneous photocatalysis to emerging contaminants removal, a lastly study of TiO₂ catalyst recovery by sedimentation was also carried out.

2. Experimental Section

2.1. Catalysts

A home-made TiO₂ catalyst (TiEt-450) was prepared by hydrolysis of titanium (IV) isopropoxide in ethanol under present KCl control [18]. Typically, 8.8 mL (0.030 mol) of titanium tetraisopropoxide was added to 200 mL of ethanol containing 0.8 mL of 0.01 M aqueous KCl (~pH 8.5) under vigorous stirring in ambient conditions. A white precipitate appeared immediately and moderate stirring was maintained for 6 hours. The powder was then recovered by filtration, washed several times with Milli-Q water and dried at 60°C for 12 hours. Finally the amorphous titania was heat-treated at 450°C for 2 hours under air atmosphere.

2.2. Characterization Studies

Structural characterization of the powder samples was analyzed with a polycrystalline X-ray diffractometer PANalytical X'Pert PRO operating at 40 kV and 40 mA, nickel-filtered Cu K α radiation and ultra-fast X'Celerator detector. The diffractograms were acquired between 4-90°, 0.02° step size and 50 s per point of accumulation time. Crystallite size was calculated employing the Scherrer equation [19], and the crystalline phases were identified by comparison with ICDD PDF database [20].

UV-Vis diffuse reflectance photocatalysts spectra were performed in a Varian (Agilent Technologies) UV-Vis-NIR Cary 5000 spectrophotometer. Band-gap energies were calculated using Tauc plots [21] from corresponding diffuse reflectance spectra.

Nitrogen adsorption-desorption isotherms were measured at 77 K in Micromeritics Tristar 3000 on previously outgassed samples overnight at 413 K and vacuum pressure ($<10^{-4}$ Pa). The specific surface areas were calculated according to the BET method [22].

Electrophoretic migration measurements: the isoelectric point (IEP) of studied titania catalysts was determined by measuring the zeta-potential versus suspension pH. Experiments were carried out using 30 mg of $\approx 2 \mu\text{m}$ powdered samples suspended in 300 mL of 10^{-3} M KCl, adjusting the different pH values with 10^{-1} M KOH and HCl solutions.

The commercial TiO_2 P25, supplied by Evonik, was also analyzed for comparison study.

2.3. Photocatalytic activity studies

Photoreactors from the Plataforma Solar de Almería (PSA) were employed, based on compound parabolic collectors (CPCs). Photoreactor is constituted by a continuously stirred tank, a re-circulation pump and a solar collector that consists of two CPC modules (3.2 m^2 irradiated area) connected in series and 37° inclined to the horizontal plane (local latitude of PSA) [23]. Wastewater circulates inside CPC tubes under turbulent flow conditions, and the total volume treated per experiments was 35 L while the volume irradiated in the solar collector was 22 L. Weather conditions were evaluated to normalize the intensity of the solar irradiance; a broadband UV radiometer (285-400 nm) CUV3 Kipp&Zonen, located at the same orientation and inclination that CPC, was used to determine irradiance power (incident $\text{watts}\cdot\text{m}^{-2}$) in order to compare runs carried out in different days. Considering $30 \text{ W}_{\text{UV}}\cdot\text{m}^{-2}$ the average solar UV flux on a perfect sunny day, normalized illumination time, $t_{30\text{W}}$, was selected to standardize the solar irradiation [24].

Previously to photocatalytic activity evaluation, the catalyst was suspended in the pollutants dissolution and kept on stirring and recirculating for 30 minutes in darkness to determine the adsorption contribution. All runs were carried out at the following operating conditions: ambient temperature, atmospheric pressure, natural pH of each pollutant, total volume of 35 L and 22 L irradiated volume. Starting concentrations were: $20 \text{ mg}\cdot\text{L}^{-1}$ of initial phenol or pyrimethanil concentration, $200 \text{ mg}\cdot\text{L}^{-1}$ of P25 or $500 \text{ mg}\cdot\text{L}^{-1}$ of TiEt-450 catalysts

respectively. The initial concentration of DCA was $129 \text{ mg}\cdot\text{L}^{-1}$ to get the same initial TOC concentration in all cases.

Meanwhile, during photocatalytic degradation of five pharmaceutical emerging contaminants (EC): ofloxacin, sulfamethoxazole, carbamazepine, flumequine and ibuprofen, although 32 L of total volume were treated only 6.5 L was the irradiated volume to follow easily the concentration evolution of each EC with the irradiation time, where an initial concentration of $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ was used for each EC with a total organic concentration of emerging contaminants: $\sum[\text{CE}]_0 = 500 \text{ }\mu\text{g}\cdot\text{L}^{-1}$.

Total organic content (TOC) of aqueous samples was measured using Shimadzu TOC-5050A analyzer equipped with Shimadzu ASI-5000A autosampler. Phenol and pyrimethanil concentration was monitored by High Performance Liquid Chromatography (HPLC) Agilent technologies, employing Nucleosil C-18 column (LUNA® 5 μm , 3x150 mm at $0.5 \text{ mL}\cdot\text{min}^{-1}$). Phenol using water/methanol at 65/35 ratio as mobile phase at 228 nm and pyrimethanil using water/acetonitrile at 85/15 ratio as mobile phase at 210 nm.

The concentrations of DCA and chlorides were measured with a Dionex DX-600 ionic chromatograph, using a Dionex Ionpac AG11-HC Using $\text{H}_2\text{O}/\text{NaOH}$ 100 mM (80/20) as mobile phase at 1.5 mL/min.

Ultra-High Performance Liquid Chromatography (UPLC-UV Agilent Technologies) was employed to determine emerging contaminants concentrations using a C-18 (XDB-C-18) column. The starting conditions were 90% water with formic acid 25 mM (mobile phase A) and 10% ACN (mobile phase B) at 1.0 mL/min. A linear gradient progressed from 10% to 85% B in 13 min. Carbamazepine, Flumequine, Ibuprofen, Ofloxacin and Sulfamethoxazole were detected at 267, 248, 222, 295 and 267 nm, respectively.

Two different water matrixes were studied during the photocatalytic degradation of the treated pollutants, deionized water obtained from a PSA water purification system, designed as DW throughout the work, and natural ground water (NW) from PSA whose main physico-chemical properties are summarized in Table 1, where is noteworthy that some chemical parameters exceed the regular values of domestic waters. The very high conductivity

detected in this natural water ($2230 \mu\text{S}\cdot\text{cm}^{-1}$), the high concentrations of Ca^{2+} , Mg^{2+} , Cl^- and Na^+ ions, joined to a considerable higher carbonates concentration ($\text{CO}_3^{2-}/\text{HCO}_3^-$), with a residual TOC concentration $< 3 \text{ mg}\cdot\text{L}^{-1}$, and the important alkalinity level (7.8 pH) are indicative of a very hard degree for this natural ground water.

Due to the high content of carbonates (hydroxyl radical scavengers) in the used natural water, photodegradation studies (except for phenol) were carried out employing natural water previously treated with some little H_2SO_4 acidification ($\sim 50 \text{ mg}\cdot\text{L}^{-1}$). The final treated volume was recirculated in a 50 L tank during 12 h. Total carbonate concentration was determined by Total Inorganic Carbon (TIC) measurements, with TIC values lower than $5\text{-}10 \text{ mg}\cdot\text{L}^{-1}$, decreasing the initial pH value from 7.8 (natural ground water, NW) to $\sim 5.5\text{-}6.5$ (natural ground water with reduced carbonates, NW rC).

Finally, TiO_2 catalyst recovery was fulfilled by sedimentation [25] given that this methodology presented the most suitable recovery efficiency at the solar photocatalytic conditions studied here. Sedimentation of the catalyst suspensions were also followed by absorbance measurements in a UV-Vis Shimadzu spectrometer model 2100 at 800 nm.

Experimental errors associated to analytical techniques has been determined by repeated analysis or statistically and always were lower than $\pm 5\%$.

3. Results and discussion

3.1. Influence of the chemical nature of pollutants in different water matrices.

The two studied TiO_2 catalysts have different physico-chemical properties which can originate different photocatalytic performances. Whereas TiEt-450 catalyst presented a 100 % anatase crystal phase, titania P25 was integrated by a mix of anatase (85 %) and rutile (15 %) crystal phases.

Although very similar surface area values were observed comparing both titania catalysts (54 and $43 \text{ m}^2\cdot\text{g}^{-1}$ for P25 and TiEt-450 respectively), very noteworthy porosity differences can be concluded from their corresponding N_2 -isotherms (not shown here), whereas Evonik P25 showed a type II isotherms, typical of non-porous or macroporous materials [26], the home-

made TiEt-450 catalyst texture presented a type IV isotherm with a H2 hysteresis loop type [27], characteristic of many inorganic oxides, where its textural properties were fundamentally governed by mesoporosity. In contrast, no significant differences were found in their optical properties, with similar values for the estimated band gap (BG), 3.20 and 3.22 eV for P25 and TiEt-450 respectively.

Electrophoretic mobility studies were performed to determine isoelectric points (IEP), which give a relevant indication about the charge and the acidic/basic character of TiO₂ surfaces. While a slightly acidic surface character was observed in P25, with a 6.8 IEP, a neutral surface seems to govern TiEt-450 catalyst (7.1). Finally, hydrodynamic particle size was determined by laser diffraction (LD) to understand the behavior of TiO₂ particles in water, given that aggregation of titania particles suspended in the aqueous media could have an important consequence on the final photoefficiency. TiO₂ P25 presented smaller hydrodynamic particle size (0.9 μm), what indicates higher dispersion in the aqueous media than TiEt-450 catalyst (3.0 μm), more aggregated, which will affect the final photoconversion. Titania catalysts are managed to mineralize almost any organic pollutant, but the photocatalytic activity depends on each pollutant type and nature [5,28], therefore, a complete analysis of catalyst photo-efficiency ought to include the photo-activity of different pollutants with varied chemical nature [29].

Consequently, in this work, the influence of the chemical nature of three organic compounds: phenol, a pollutant model studied in many wastewater treatments, dichloroacetic acid (DCA), a chlorinated organic compound used as anionic contaminant model; and the commercial pyrimethanil (Scala®, 40 % p/v), an aniline-pyrimidine compound, usually used as fungicide and selected as nitrogenated pesticide pollutant, have been studied. The optimal concentration in this solar CPC photoreactor for the two employed TiO₂ catalysts was defined in a previous study [30]. The selected initial concentration of DCA was 1 mM (≈ 129 mg·L⁻¹) to get the same value of initial TOC concentration for the three studied organic pollutants.

3.1.1 Phenol Photodegradation: effect of water matrix composition

In Fig. 1A is shown TOC, phenol and pH evolutions for P25 and TiEt-450 catalysts during phenol photodegradation in deionized (DW) and natural water (NW), respectively. Lines correspond to the consistent least square fittings from the experimental data that are given in symbols in the figure. Taking into account most of the authors agree that the rate of photo-mineralization with irradiated TiO_2 could be interpreted by the Langmuir-Hinshelwood law (L-H), being also accepted that both rate constant and order are only “*apparent*” [4], it could be reasonable to expect that when pollutant concentration is high enough to reach saturation level on titania catalyst surface, the reaction rate becomes constant and independent of the initial substrate concentration, being able to be simplified to a pseudo-zero-order kinetic equation for TOC, whereas a pseudo-first-order kinetic model could be considered to well-describe the original pollutant disappearance rate [4]. The calculated kinetic constants for phenol and TOC in deionized (DW) and natural water (NW) for the two studied catalysts are given in Table 2. For a comparison study in deionized water, it can be emphasized that both apparent constants obtained for phenol and TOC are much higher for P25 than for TiEt-450 titania catalyst, corroborating the better photodegradation performance of the commercial titania. The goodness of fit parameters found for both catalysts determines the correct fitting of the experimental values to pseudo-first kinetic model for phenol, and pseudo-zero-order for TOC respectively.

Phenol photodegradation proceeds through a complex scheme of successive steps that begins with the first hydroxylation products of phenol: hydroquinone and catechol, with the corresponding oxidized quinones, para- and ortho-benzoquinone, whereas the oxidation pathway converges to short-organic acids generation, such as maleic, malonic, acetic or oxalic among others, that finally undergoes to CO_2 and H_2O [31,32]. Then, values of pH progress during reaction can give valuable information about the photodegradation evolution such as degree of mineralization. The slightly decrease of initial pH for both titania catalysts (see Fig. 1A in pH (DW)) is pointing out the formation of some short-organic acids since the beginning of the photocatalytic reaction [33], but titania P25 photodegraded the phenol in

deionized water more efficiently arising complete phenol conversion at 140 minutes of irradiation time (t_{30w}), whereas TiEt-450 needed ≈ 240 minutes for total phenol removal.

The runs performed in natural water (see Fig. 1A in NW) showed that both phenol and TOC disappearance rates drastically decrease in each titania catalyst (see Table 2), and the irradiation time required to achieve total phenol conversion was increased four times respect to the t_{30w} values obtained with deionized water for both catalysts. Consequently, these attained results are consistent with the presence of ions in the treated wastewater matrix capable of scavenging photocatalyst-produced $\bullet\text{OH}$, as happens with $\text{CO}_3^{2-}/\text{HCO}_3^-$, NH_4^+ , SO_4^{2-} , NO_3^- or Cl^- in natural waters that powerfully inhibit the overall photodegradation process [34]. Besides, the inhibitory effect could be a consequence of competitive adsorption with pollutants on titania surface [35,36,37,38], to subsequently act as photo-generated holes (h^+) scavengers or directly reacting with the hydroxyl radicals ($\bullet\text{OH}$). Moreover the water matrix composition can also affect to the catalyst-pollutant interactions modifying the initial pH value and maybe, the titania particles aggregation in the reaction media [39].

All of that could explain the lower solar photoefficiency presented for the phenol photodegradation in natural water, and confirmed by the lowest apparent kinetic constants found in both catalysts for phenol and TOC disappearance rates.

3.1.2. DCA Photodegradation: Effect of water matrix composition

The degradation of DCA has been chosen as the reaction of an anionic contaminant model, due to its presence in the biological degradation pathway of a large number of chlorinated hydrocarbons and the important toxic effect as a consequence of being generated during water chlorination [29]. Moreover, the photocatalytic degradation of DCA has been extensively studied evincing that a single electron/hole pair is enough to reach its total removal [40,41].

The DCA photodegradation results for P25 and TiEt-450 catalysts in deionized and natural water with reduced carbonates are shown in Fig. 2A. In the case of deionized water, the measured chloride (Cl^-) concentration was proportional to DCA disappearance, arising the

maximum theoretical chloride value ($[Cl^-]_{max}$) at the same time that total DCA conversion was reached. The irradiation times (t_{30w}) to complete DCA removal was always lower than the corresponding to phenol photodegradation in both catalysts, which could be well related to the photodegradation pathway, characterized by no relevant formation of by-products along DCA photodegradation route [42]. pH values found during photocatalytic process were practically constant for both titania materials, and around 2.3-2.7.

In this conditions an important interaction between both titania catalysts, positively charged at the reaction conditions [42], and DCA, present as di-chloroacetate anion ($CHCl_2COO^-$) in dissolution ($pK_a = 1.26$) [28] could be expected in the reaction media, given that pH values were always significantly lower than the corresponding titania IEP ($pH < pI_{IEP}$) (6.8 and 7.1 for P25 and TiEt-450 respectively). All of that could be explained because the fundamental mechanism of DCA photodegradation takes place by direct attack of photo-generated holes (h^+) [28,43,44], instead of by indirect $\bullet OH$ attack as happens during phenol photodegradation (see Fig. 1B) [28]. Consequently, the photodegradation of DCA type pollutants is initiated by the direct hole transfer mechanism promoting photocatalytic decarboxylation as an outgrowth of a strong attractive electrostatic interactions between $CHCl_2COO^-$ anion and TiO_2 surface [5,43], as has been represented in Fig. 2B. On the contrary, phenol molecule is considered a non-ionic substrate, where a weak adsorption takes place on the TiO_2 catalyst surface and phenol photo-oxidation is usually linked to an indirect mechanism mainly mediated by $\bullet OH$ radical located close to surface-solution interlayers [36,37] (see Fig. 1B).

In order to analyse other aspects of the photocatalytic behaviour of the two studied titania catalysts, in Table 3 are also given the pseudo-kinetic constants for DCA and TOC, considering first-order kinetic model in both cases. Although total DCA removal was arisen in both catalysts at similar irradiation times, 100 and 125 minutes for P25 and TiEt-450 respectively, the corresponding pseudo-first-kinetic constants for DCA and TOC were slightly higher in the case of the commercial P25.

When natural water matrix with reduced carbonates was used (see Fig. 2A), the results of DCA photodegradation showed an inhibition, pointing to qualitatively the same detrimental

effect observed for phenol photodegradation (see Fig. 1A), independently of the studied TiO₂ catalysts.

Trying to quantify and compare this inhibition effect, the ratio between phenol pseudo-constants in deionized water and natural water: $k_{\text{phenol}}(\text{DW})/k_{\text{phenol}}(\text{NW})$ was calculated, 4.6 and 6.6, for P25 and TiEt-450 respectively, whereas in the case of DCA photodegradation values with the same order of magnitude were found for both catalysts in deionized water and natural water with reduced carbonates, $k_{\text{DCA}}(\text{DW})/k_{\text{DCA}}(\text{NW rC})$: 4.3 and 4.8, for P25 and TiEt-450 respectively. The possible lower inhibition effect by the use of natural water with reduced carbonates can be considered almost neglected regarding TiO₂ P25, and little relevant in the home-made titania catalyst. All of that is probably indicative of the very significant inhibitory effect of other ions still present in this treated natural water. In this context, the noteworthy inhibition effect observed in DCA photodegradation with natural water with reduced carbonates could be more related to the chemical nature of the original pollutant and pH value in the reaction media, than to the presence of some ions in the aqueous medium. In this line, whereas in deionized water (see Fig. 2A DW) pH was almost constant, with values around 2.3-2.7 in both catalysts, in relation to natural water matrix with reduced carbonates (NW rC) the initial pH was considerably higher, 6-6.5, decreasing during organic matter photo-oxidation until arise acidic values, 3.5-4, at the end of photocatalytic process, presumably as a consequence of short-organic acids formation and HCl formation from chlorine of DCA (Fig. 2A). Therefore, whereas high substrate-catalyst interactions seem to be taking place at the lower pH found in deionized water, given that titania surface ($\text{pH} < \text{pH}_{\text{IEP}}$) is positively charged in both catalysts and DCA is dissociated, being the anion ($\text{CHCl}_2\text{COO}^-$) the main specie in solution ($\text{pK}_a = 1.26$), important reduction on adsorption degree between DCA and titania surfaces could reasonably be happening at the initial higher pH found as regards the natural water studied here, leading to a detrimental effect on solar photodegradation of DCA [45,46,47].

3.1.3. Pyrimethanil Photodegradation: Effect of water matrix composition

Pyrimethanil, TOC and pH evolutions with irradiation time, for P25 and TiEt-450 catalysts, in deionized (DW) and natural water with reduced carbonates (NW rC) are shown in Fig. 3. Meanwhile, in Table 4 are given the pseudo-kinetic constants for pyrimethanil and TOC, calculated considering pseudo-first and zero order-model respectively. Now, the ratio between the pyrimethanil pseudo-constants in deionized water and natural water with reduced carbonates: $k_{\text{pyrimethanil}}(\text{DW})/k_{\text{pyrimethanil}}(\text{NW rC})$ was 1.1 for the two studied titania catalysts, whereas in the case of TOC were, $k_{\text{TOC}}(\text{DW})/k_{\text{TOC}}(\text{NW rC})$: 1.1 and 1.2, for P25 and TiEt-450, respectively; very similar photo-efficiencies have been found with the two water matrices exhibiting opposite behaviour than phenol and DCA photodegradation in natural waters.

Therefore, in relation to pyrimethanil photodegradation the presence of ions in the natural water have not led to a detrimental effect; at the contrary, similar performances have been found in both titania catalysts at the operating conditions studied here. Nevertheless, the important inhibitory effect of photocatalytic process in natural waters with higher hardness seems to have been reduced in this case by acidification of the studied natural water and consecutive $\text{CO}_3^{2-}/\text{HCO}_3^-$ species removal, reducing the competitive adsorption with the target substrates for the active sites on the TiO_2 surface. Some studies have related the presence of chloride with an enhanced or detrimental effect during photocatalytic degradation, depending on its concentration, the target pollutant and reaction mechanism [48,49]. In this sense, chlorine radicals could induce selectivity on AOPs, while $\cdot\text{OH}$ radicals attack unselectively to the organic matter, chlorine radicals prefer the electron rich molecules, consequently electron donors group substituents could be preferably degraded [50].

Regarding to the photocatalytic behavior of the two titania catalysts, it can be concluded that the commercial P25 exhibited significant higher rate in phenol photodegradation. Some authors correlate the optimal photocatalytic properties of TiO_2 P25 with the photogenerated charges (species) in the anatase-rutile interface [51] whereas other authors attributed it principally to the excellent electronic and structural properties of titania crystal phases [52]. In

spite of that, both titania catalysts studied in this work arise very close efficiencies during pyrimethanil and DCA mineralization.

3.2. Photocatalytic degradation of emerging contaminants in different water matrices.

The concentration evolution of each microcontaminant in deionized water joined to their total concentration ($\Sigma[CE]$), are shown in Fig. 4. Although the photodegradation rate of the pharmaceutical microcontaminants was very similar for both titania catalysts, some differences can be deduced while comparing the photodegradation rate of each microcontaminant (see Table 5 where the pseudo-kinetic constants for the five microcontaminants are given, which have been calculated considering pseudo-first order-model). Whereas ofloxacin, flumequine, and ibuprofen reached total photo-oxidation at an irradiation time less than 5 and \approx 5-7 minutes respectively, sulfamethoxazole and carbamazepine presented the lowest photodegradation rate, and need around 20-30 minutes of irradiation time to reduce its concentration to the detection limit. Therefore, it can be assumed that the photodegradation sequence for the five microcontaminants studied here is the following:

Ofloxacin \approx Flumequine > Ibuprofen \gg Sulfamethoxazole \approx Carbamazepine

In order to compare both photocatalysts the pseudo-kinetic constants (Table 5) have been calculated considering pseudo-first order-model for the five microcontaminants. It could be observed that the apparent kinetic constants obtained for TiEt-450 were slightly lower than for P25. The irradiation time to achieve total removal of all the pharmaceutical microcontaminants ($\Sigma[CE]$) was 22 and 28 minutes, for P25 and TiEt-450 respectively. Consequently, both titania catalysts have evidenced that solar assisted heterogeneous photocatalysis is a potential AOPs to treat a mixture of $500 \mu\text{g}\cdot\text{L}^{-1}$ of emerging contaminants such as the five pharmaceutical microcontaminants studied here and frequently detected in Municipal Wastewater Treatment Plants (MWTP).

Given that these types of microcontaminants can be found in different wastewater effluents from hospitals, MWTP or domestic, among others, it is perfectly expected that these emerging

contaminants could happen in solution joined to different inorganic ions in natural waters. To analyze this effect, a photodegradation study of this mixture of pharmaceutical microcontaminants was carried out in the matrix of natural water with reduced carbonates (NW rC) used before and whose characteristics are given in Table 1. In Fig. 5 was represented the evolution of each emerging contaminant concentration and total Emerging Contaminants concentration ($\sum[CE]$) during photocatalytic degradation with P25 and TiEt-450 catalysts in natural water with reduced carbonates; and the corresponding values of the apparent pseudo-first order kinetic constants are depicted in Table 5. Some important differences can be seen in contrast with the obtained results in the case of deionized water. Firstly, a significant decrease in the apparent kinetic constants for both TiO_2 was observed when natural water was employed. However, not all the studied microcontaminants were affected in the same extension by the presence of inorganic ions in the water matrix. Whereas a significantly lower photodegradation rate was observed for ofloxacin, flumequine and ibuprofen, the degradation of carbamazepine and especially sulfamethoxazole a very low inhibition was detected during their photodegradation process in the natural water.

Thus, the photodegradation rate when natural water with reduced carbonates was used was the following: Ofloxacin >> Flumequine \approx Sulfamethoxazole > Carbamazepine \approx Ibuprofen. Although apparently, the carbonates partial removal has allowed a reduction of the inhibition effect caused when natural water matrix was employed, the order of photodegradation was modified, probably due to changes on selectivity induced by the presence of some inorganic ions [50].

Lastly, photo-oxidation of a mixture of five pharmaceutical microcontaminants ($500 \mu\text{g}\cdot\text{L}^{-1}$) can be efficiently treated by solar assisted heterogeneous photocatalysis in a natural water with an important presence of inorganic ions, given that photocatalytic process at pilot plant totally remove all the studied microcontaminants until values close to the detection limit at very short irradiation times ($t_{30w} < 35$ minutes) with both titania catalysts studied.

On the other side, the use of powder catalysts in aqueous suspensions constrains to go through a final step of catalyst recovery. Many times, this is an important challenge to assess

the competitiveness of the real application of photocatalytic water treatments. The efficiency of catalyst recovery has been evaluated by the sedimentation procedure described by [25] as an interesting alternative to other procedures, such as ultrafiltration or microfiltration with important operational and energy cost, being very easy and applicable to solar scale with low cost.

The global process efficiency of both catalysts in the photocatalytic degradation of emerging contaminants is given in Fig. 6, where the operation time has been evaluated considering the grade of photodegradation and recovery efficiency. In this context, sedimentation time has been defined as the necessary time to decrease an 80 % the titania concentration in the aqueous suspension after adjusting pH at values close to photocatalyst IEP, whereas the step of photodegradation was described as the irradiation time where a 90 % of all microcontaminants concentration was photodegraded. It should be appreciated that although no important differences were found during the photodegradation process, the recovery step was the stage that limits the overall photocatalytic process, where a very short-recovery time was necessary with TiEt-450 catalyst. Therefore, this home-made titania catalyst has presented the best global photoefficiency (photo-oxidation step + catalyst recovery step) in solar photocatalytic removal of emerging contaminants.

4. Conclusions

From the comparison study of the solar photocatalytic performance carried out with the two titania catalysts (comercial P25 Evonik-Degussa and laboratory synthesized TiEt-450) studied here can be concluded that:

First, though P25 catalyst showed better results during phenol and dichloroacetic acid photodegradation, both photocatalysts presented similar photo-efficiencies in pyrimethanil mineralization and, specially, in the treatment of emerging microcontaminants mixture.

Whereas an important inhibition effect happened in phenol and dichloroacetic acid photodegradation when a natural water matrix with or with reduced carbonates was used, in

the case of pyrimethanil the presence of ions have not led to a detrimental effect, perhaps due to the coexistence of other species (like chloride) capable to generate radicals.

A mixture of five pharmaceutical microcontaminants could be efficiently treated by solar assisted heterogeneous photocatalysis in natural water with important presence of inorganic ions, given that total removal of all the studied microcontaminants was reached at very short irradiation times ($t_{30w} < 35$ minutes) with both titania catalysts. The global evaluation of the photocatalytic process, considering also the operational aspects related to the separation and recovery of the TiO_2 catalysts, showed that the best results were arisen with TiEt-450 catalyst, what suppose an improved behavior in the application of solar photocatalysis on real wastewaters containing emerging contaminants.

Acknowledgments

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Table 1 - Physico-chemical parameters of deionized (DW) and natural ground water (NW)

Parameters	DW	NW
pH	5.9	7.8
TOC (mg·L⁻¹)	< 1	0-3
Conductivity at 20°C (μS·cm⁻¹)	< 10	2230
HCO₃⁻/CO₃²⁻ (mg·L⁻¹)	< 2.5 *	~880*
Ca²⁺ (mg·L⁻¹)	n.d.	120
Mg²⁺ (mg·L⁻¹)	n.d.	72
K⁺ (mg·L⁻¹)	n.d.	8.2
Na⁺ (mg·L⁻¹)	n.d.	460
Cl⁻ (mg·L⁻¹)	0.2-0.3	340
NO₃⁻ (mg·L⁻¹)	< 0.2	24
SO₄²⁻ (mg·L⁻¹)	n.d.	250

* Calculated from Inorganic Carbon (IC)

n.d.: Not detected

Table 2 - Pseudo kinetic constants for phenol and TOC photodegradation in deionized water (DW) and natural water (NW)

Catalyst	Aqueous Matrix	Phenol		TOC	
		k_{Phenol} (min^{-1})	r^2	$r_{0,\text{TOC}} \approx k_{\text{TOC}}$ ($\text{mmolC}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$)	r^2
P25	DW	0.0213	0.985	0.0063	0.998
P25	NW	0.0046	0.993	0.0017	0.976
TiEt-450	DW	0.0119	0.977	0.0031	0.984
TiEt-450	NW	0.0018	0.997	0.0008	0.918

Table 3 - Pseudo first order kinetic constants for DCA and TOC photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC)

Catalyst	Aqueous Matrix	DCA		TOC	
		k_{DCA} (min ⁻¹)	r^2	k_{TOC} (min ⁻¹)	r^2
P25	DW	0.0363	0.990	0.0245	0.999
P25	NW rC	0.0085	0.981	0.0067	0.991
TiEt-450	DW	0.0237	0.972	0.0179	0.981
TiEt-450	NW rC	0.0049	0.992	0.0047	0.994

Table 4 - Pseudo kinetic constants for pyrimethanil and TOC photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC)

Catalyst	Aqueous Matrix	Pyrimethanil		TOC	
		$k_{\text{Pyrimethanil}}$ (min^{-1})	r^2	$r_{0,\text{TOC}} \approx k_{\text{TOC}}$ ($\text{mmolC}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$)	r^2
P25	DW	0.0837	0.997	0.0040	0.979
P25	NW rC	0.0812	0.992	0.0036	0.968
TiEt	DW	0.0415	0.992	0.0036	0.982
TiEt	NW rC	0.0369	0.989	0.0032	0.982

Table 5 - Pseudo first order kinetic constants for emerging contaminants (EC) photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC)

EC	DW				NW rC			
	P25		TiEt		P25		TiEt	
	k (min ⁻¹)	r ²						
Ofloxacin	*	-	*	-	0.519	0.985	0.210	0.999
Sulfamethoxazole	0.170	0.995	0.095	0.994	0.185	0.984	0.061	0.997
Carbamazepine	0.124	0.992	0.077	0.995	0.089	0.971	0.043	0.999
Flumequine	*	-	*	-	0.171	0.965	0.081	0.990
Ibuprofen	0.355	0.976	0.321	0.998	0.081	0.995	0.040	0.985

* t_{30w} < 5 min: irradiation time to complete pollutant photodegradation.

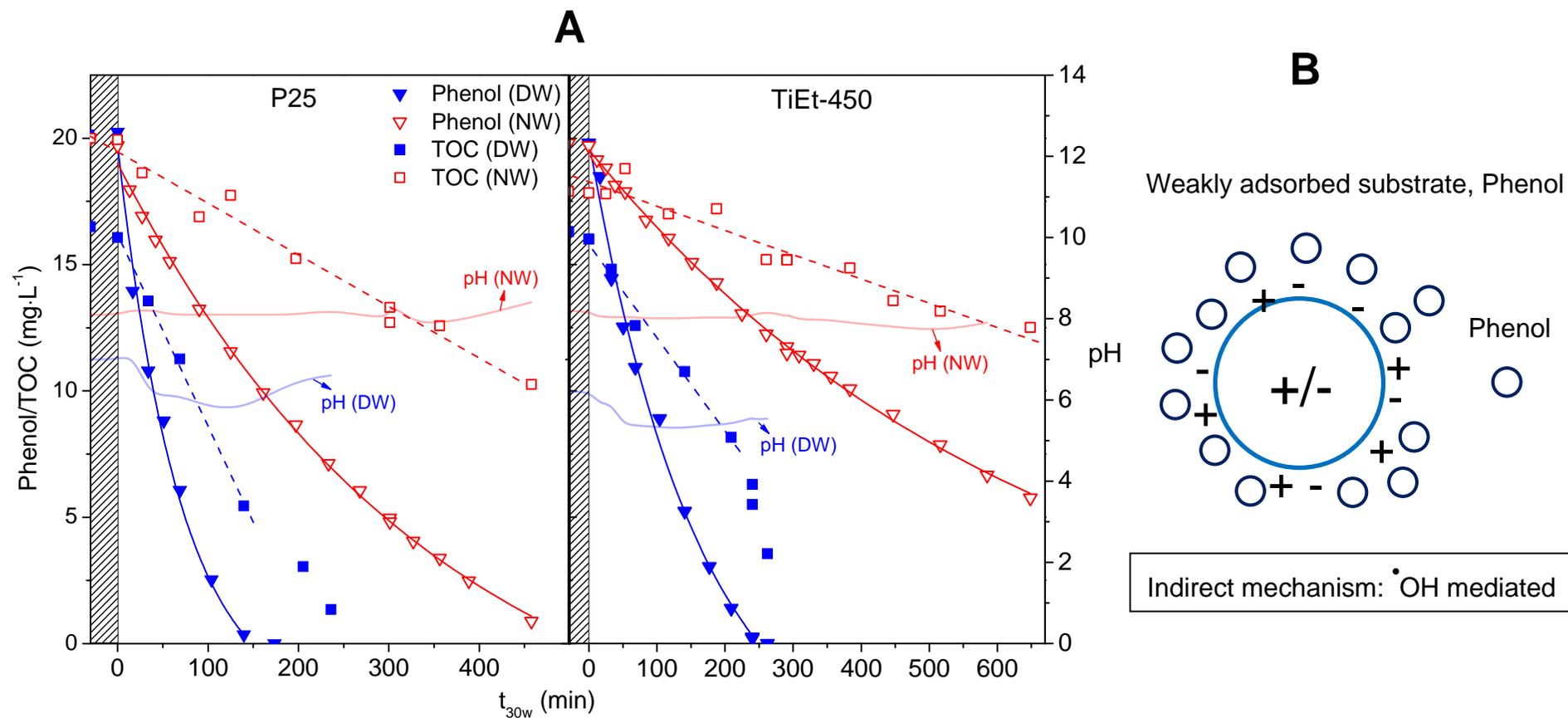


Fig. 1 - (A) TOC, phenol and pH evolution for P25 and TiEt-450 catalysts during phenol photodegradation in deionized water (DW) and natural water (NW, respectively); (lines correspond to least square fittings from experimental data). (B) Scheme of photodegradation indirect mechanism.

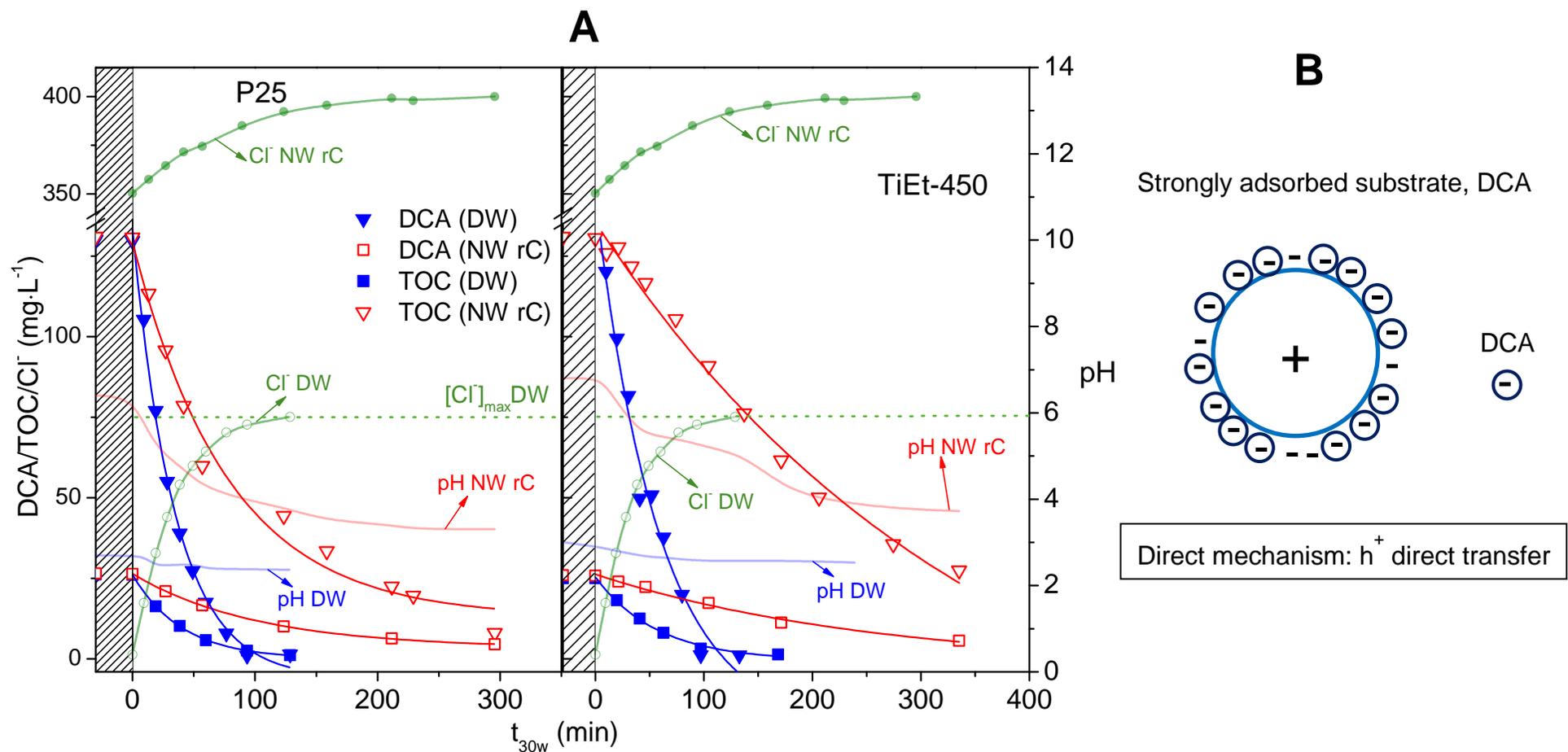


Fig. 2 - (A) TOC, DCA and pH evolution for P25 and TiEt-450 catalysts during DCA photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC), respectively; (lines correspond to least square fittings from experimental data). (B) Scheme of photodegradation direct mechanism.

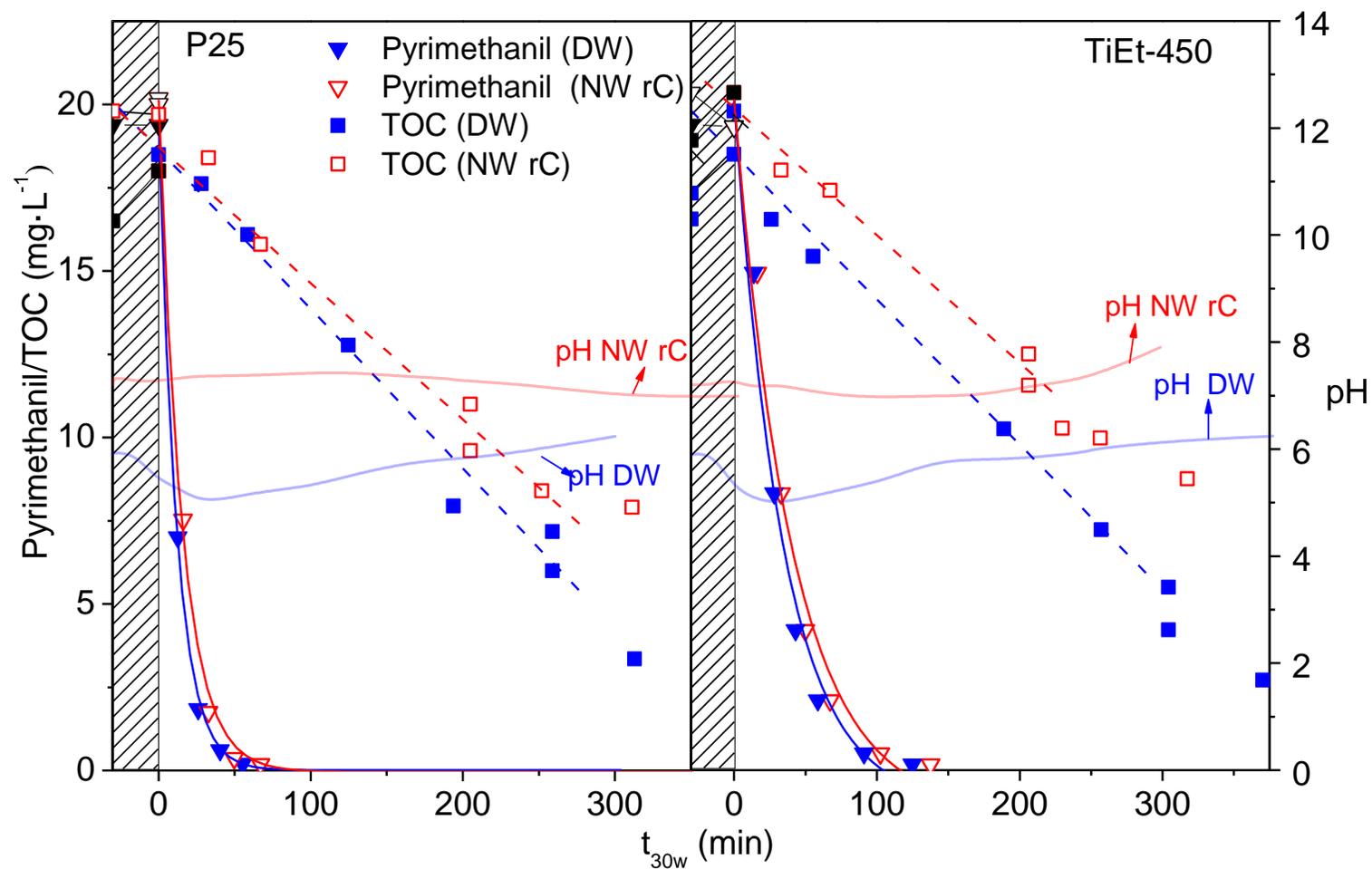


Fig. 3 - TOC, Pyrimethanil and pH evolution for P25 and TiEt-450 catalysts along pyrimethanil photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC), respectively. (Lines correspond to fittings from experimental data).

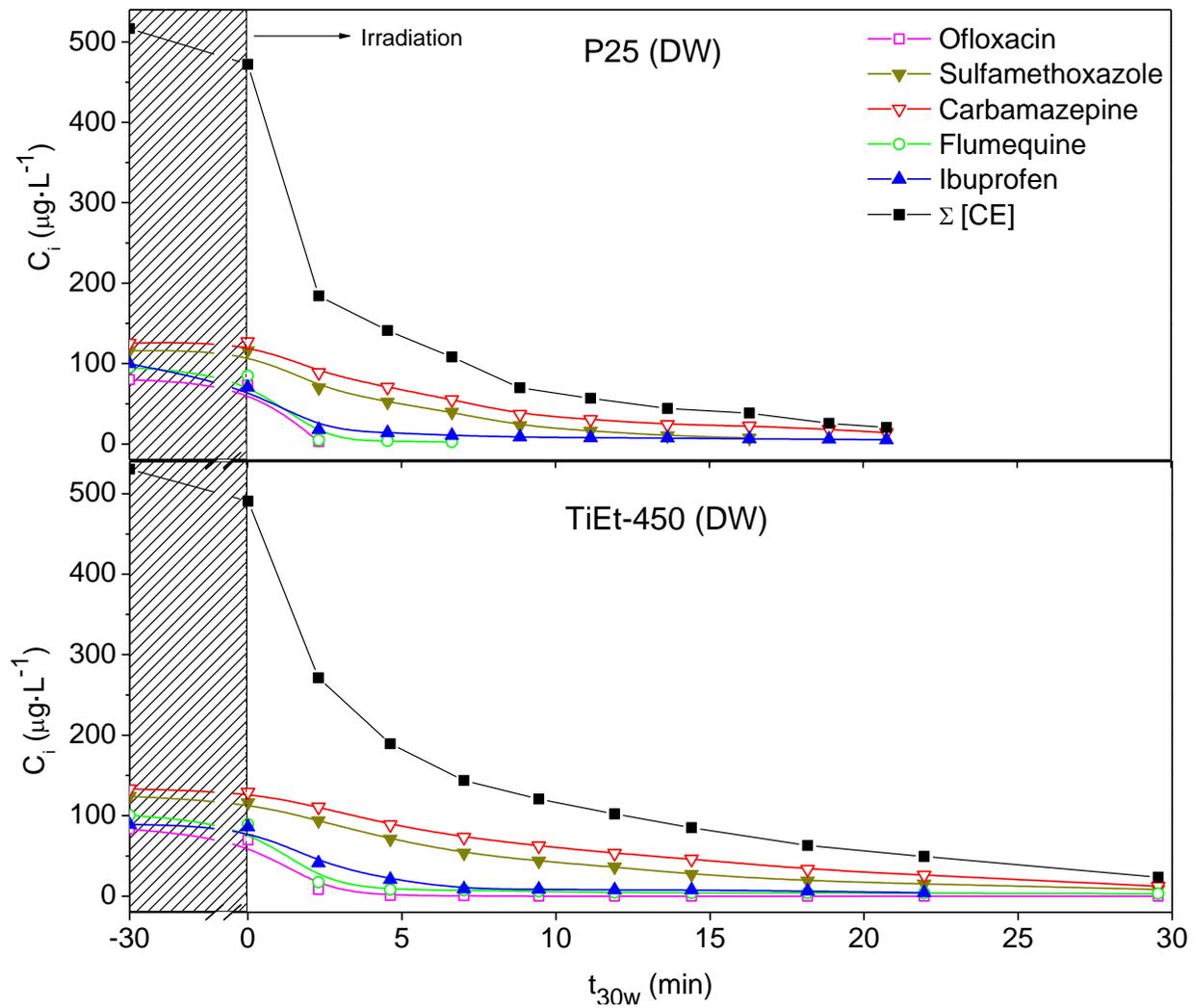


Fig. 4 - Evolution of emerging contaminants concentration during photocatalytic degradation over P25 and TiEt-450 catalysts in deionized water (DW). (Σ [CE]) corresponds to total concentration of Emerging Contaminants)

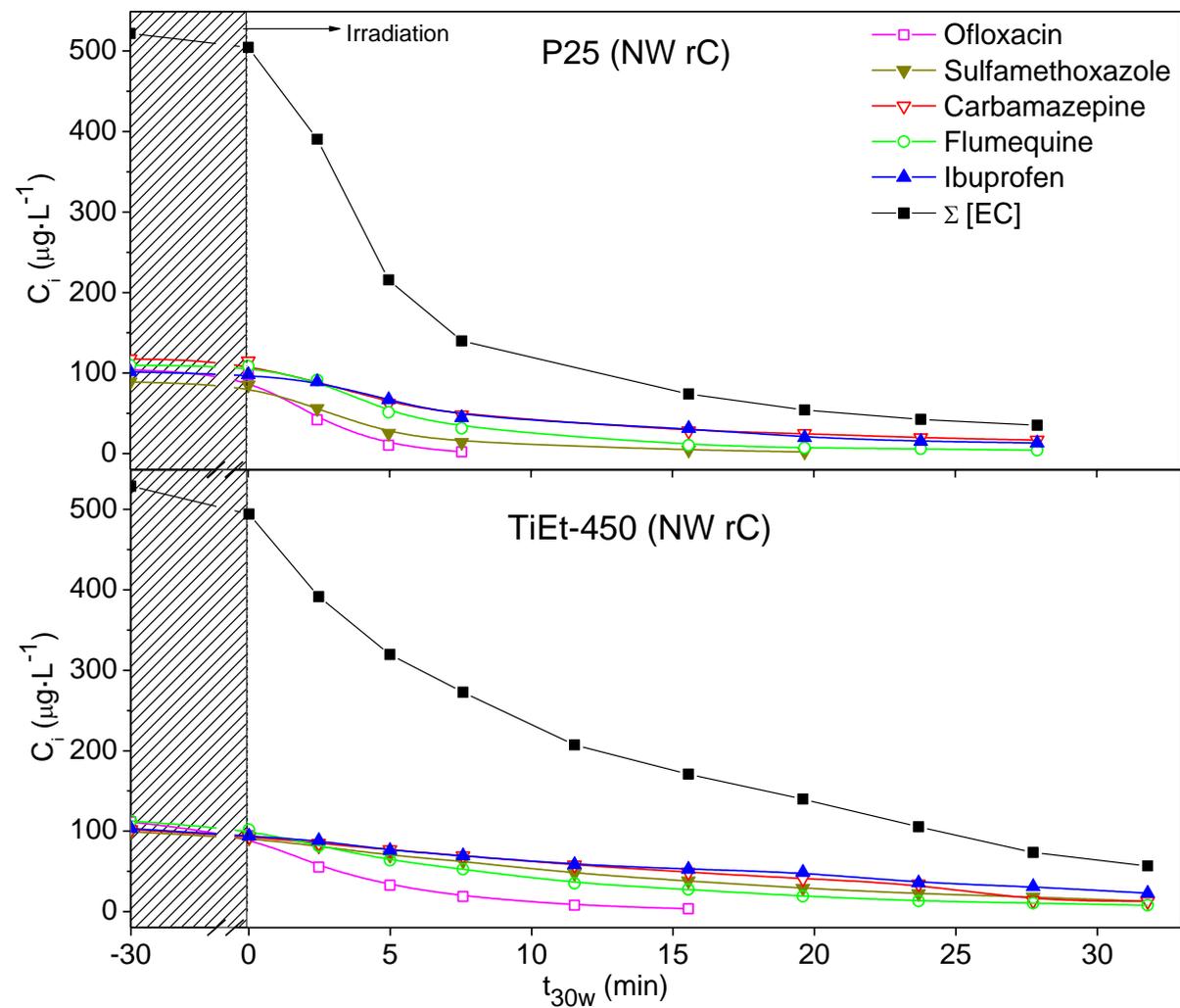


Fig. 5 - Evolution of emerging contaminants concentration during photocatalytic degradation over P25 and TiEt-450 catalysts in natural water with reduced carbonates (NW rC). (Σ [CE]) corresponds to total concentration of Emerging Contaminants)

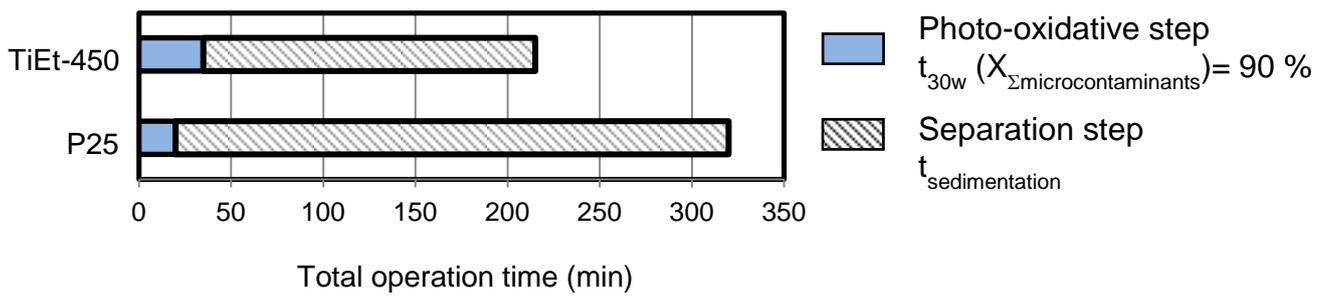


Fig. 6 - Comparison study of the global photocatalytic efficiency in emerging contaminants removal: Photodegradation Step + Catalyst Recovery Step with the two studied TiO_2 catalysts.

Figures captions:

Fig. 1 - (A) TOC, phenol and pH evolution for P25 and TiEt-450 catalysts during phenol photodegradation in deionized water (DW) and natural water (NW, respectively); (lines correspond to least square fittings from experimental data). (B) Scheme of photodegradation indirect mechanism.

Fig. 2 - (A) TOC, DCA and pH evolution for P25 and TiEt-450 catalysts during DCA photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC), respectively; (lines correspond to least square fittings from experimental data). (B) Scheme of photodegradation direct mechanism.

Fig. 3 - TOC, Pyrimethanil and pH evolution for P25 and TiEt-450 catalysts along pyrimethanil photodegradation in deionized water (DW) and natural water with reduced carbonates (NW rC), respectively. (Lines correspond to fittings from experimental data).

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