

Article

Effect of Different Radiation Sources and Noble Metal Doped onto TiO₂ for Contaminants of Emerging Concern Removal

Rui C. Martins ¹, Eva Domingues ¹, Morgana Bosio ^{1,2}, Margarida J. Quina ¹,
Marta Gmurek ^{1,3}, Rosa M. Quinta-Ferreira ¹ and João Gomes ^{1,*}

- ¹ CIEPQPF—Chemical Engineering Processes and Forest Products Research Center, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Sílvio Lima, 3030-790 Coimbra, Portugal; martins@eq.uc.pt (R.C.M.); evadomingues@eq.uc.pt (E.D.); morganabosio@yahoo.com.br (M.B.); guida@eq.uc.pt (M.J.Q.); marta.gmurek@p.lodz.pl (M.G.); rosaqf@eq.uc.pt (R.M.Q.-F.)
- ² Centro de Tecnologia—Cidade Universitária—Bloco G—ala 115, COPPE—Chemical Engineering Program, Federal University of Rio de Janeiro, Rio de Janeiro 21941-909, Brazil
- ³ Department of Bioprocess Engineering, Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland
- * Correspondence: jgomes@eq.uc.pt; Tel.: +351-239-798-722

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Abstract: Water scarcity is a worldwide problem boosted by global warming and pollution of anthropogenic origin. The contaminants of emerging concern in water sources are increasing due to the inefficiency of conventional wastewater treatments, and these should be mitigated. Advanced oxidation processes appear as suitable solutions for decontamination. The photocatalytic oxidation of the mixture of sulfamethoxazole, carbamazepine and lorazepam was investigated. TiO₂ modified by Ag and TiO₂ modified by Pd were used as photocatalysts to improve photoactivity. The impact of light wavelengths was examined using UVA and visible radiation as well as natural sunlight. Visible light revealed the lowest ability for decontamination in 60 min of irradiation through Ag and Pd–TiO₂ photocatalytic oxidation. On the other hand, UVA and sunlight in the presence of photocatalysts were able to totally remove the contaminants. This can be related to the high production of reactive oxidative species at those conditions. The increase of the noble metal load promotes the improvement of the decontamination efficiency. The kinetic rate was analyzed for UVA and sunlight radiation for different photocatalytic conditions. The presence of a natural light source without energy costs leads to an increase in the pseudo-first-order kinetic constant. Sunlight radiation with a suitable photocatalyst can be a very good option for water decontamination.

Keywords: sunlight; UVA radiation; visible light; decontamination; photocatalytic oxidation; pharmaceuticals

1. Introduction

The stress level in population, the presence of more resistant bacteria and the number of people using high technology during childhood promote the rising consumption of anxiolytic, antibiotic and antiepileptic/anticonvulsant drugs, respectively [1]. The most common group of anxiolytic drugs are benzodiazepines, which are widely used by humans. Among them, alprazolam, lorazepam and diazepam can be considered as the most consumed. As antibiotic drugs, a wide range of different products can be considered as the most used such as amoxicillin, erythromycin and sulfamethoxazole. Carbamazepine is the most common antiepileptic or anticonvulsant drug. Thus, bearing in mind

these three groups of pharmaceutical products, sulfamethoxazole, lorazepam and carbamazepine are widely used by humans. According to the data from the Portuguese National Authority of Medicines and Health Products (Infarmed, IP) these compounds figure in the list of the 100 most consumed pharmaceuticals in Portugal. Moreover, some of them can be found in the European Legislation [2,3] as compounds that must be monitored in water sources by European Union (EU) Member States.

Conventional wastewater treatments reveal serious problems of removing recalcitrant compounds such as pharmaceutical and personal care products from municipal effluents [4–7]. Therefore, the concentration of these kinds of compounds is increasing in the natural waters, due to the continuous release of pharmaceutical industry and hospital effluents as well as human metabolic excretion in municipal wastewater treatment plants [8,9]. Considering that water reclamation is more necessary than ever due to water scarcity, it is important to find a suitable solution for the removal of these contaminants of emerging concern from wastewaters [10–12]. The advanced oxidation processes appear as good alternatives for the treatment of these compounds due to their capability of degrading a wide range of contaminants [11]. Heterogeneous photocatalysis seems to be a sustainable technology, since it can use natural sunlight as an energy source (it represents an example of sunlight photocatalysis). However, for the application of sunlight, a photoactive catalyst with this radiation source is required. The most used photocatalyst is titanium dioxide (TiO₂), which provides semiconductor characteristics and can be easily prepared. Moreover, it has a low cost and presents good chemical stability. The major drawback of TiO₂ is its high band gap. The typical band gap of TiO₂ (3.2 eV) requires the application of UV radiation ($\lambda < 388$ nm) so that photogenerated electron-holes are formed (Equation (1)) [13].



The electrons reduce the adsorbed oxygen on the photocatalyst surface to promote the production of superoxide radicals (Equation (2)). On the other hand, the adsorbed water is oxidized in the photogenerated holes to produce hydroxyl radicals. These reactive oxidative species can be helpful to enhance the degradation of contaminants of emerging concern (CEC) [14]. However, to achieve the production of this species, it is necessary to break the band gap of pure TiO₂. Normally, this band gap can be reduced with the presence of dopants which can be non-metals or noble metals. Noble metals such as Pd and Ag present a good performance in terms of narrowing the band gap due to surface plasmon resonance, which allows photocatalytic activity at a higher wavelength [15–19].

Gomes et al. [14] used Pd and Ag (0.5 wt.%) doped onto TiO₂ and verified an excellent performance with UVA radiation over the degradation of a mixture of five parabens as compared to pure TiO₂. On the other hand, sunlight radiation using TiO₂ in a solar pilot plant greatly contributed to lorazepam degradation [20]. The visible light was also tested with these photocatalysts to promote the degradation of different compounds such as phenol and a mixture of parabens [18,19].

Noble metals can also trap electrons and reduce the recombination phenomenon [21]. However, the metal load must be carefully selected since noble metals in excess can work as active site scavengers, reducing the efficiency of photocatalytic oxidation [18,22,23].

The aim of this work was to evaluate the effect of two different loads of Pd and Ag (0.5 and 1 wt.%) onto TiO₂ for the photocatalytic oxidation of a mixture of CECs: sulfamethoxazole (SMX), carbamazepine (CBZ) and lorazepam (LRZ). The impact of light wavelengths was addressed using simulated sunlight (ultraviolet A (UVA) and visible (Vis)) as well as natural sunlight.

2. Materials and Methods

2.1. Photocatalysts Preparation and Chemicals

Noble metal-doped TiO₂ catalysts were prepared by a photodeposition method [24]. TiO₂ was previously prepared by the sol-gel method, where aging occurred at 45 °C for 24 h. AgNO₃ (0.5 and 1 wt.%) and PdCl₂ (0.5 and 1 wt.%) were used as Ag and Pd precursors, respectively. These precursors were mixed with a TiO₂ suspension in ethanol for Ag and isopropanol for Pd, and then photoirradiated. The radiation source used in photodeposition was UV-Vis light (1000 W Xe lamp) over 100 min for Ag and 6 h for Pd. The main characterization of catalysts was carried out previously [14,24–26]. Four catalysts were tested: 0.5%Ag–TiO₂, 1%Ag–TiO₂, 0.5%Pd–TiO₂ and 1%Pd–TiO₂. The optical properties of some samples were obtained through UV-Vis diffuse reflectance (DRS) in an Evolution 220 spectrophotometer (thermo scientific, Warsaw, Poland). The band gap was determined using the Tauc plot method.

Sulfamethoxazole (SMX), carbamazepine (CBZ) and lorazepam (LRZ) were purchased from Sigma-Aldrich, and the molecular structures are presented in Figure 1. Each compound was used in a concentration of 1 mg/L in ultrapure water (Millipore system).

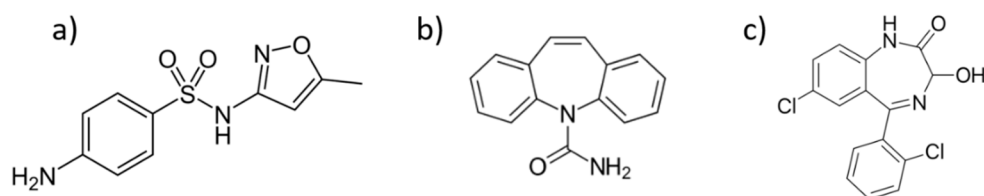


Figure 1. Molecular structure of (a) sulfamethoxazole, (b) carbamazepine and (c) lorazepam.

2.2. Experimental Methodology

Photocatalytic oxidations through sunlight and visible light radiation were carried out in a cylindrical borosilicate reactor (500 mL) equipped with a compound parabolic concentrator (CPC) collector (Figure 2a). A porous stone axially placed inside the reactor was used to promote the air bubbling and guarantee the homogeneity of the reaction mixture. Aluminium foil was used to cover the reactor during the adsorption experiments. During the experiments with sunlight radiation, the irradiance was measured with an Oceans Optics USB 4000 fiber optic spectrometer (Ocean Optics, Winter Park, FL, USA) with a resolution of 0.4 nm. This equipment also allows the radiation spectrum analysis. The solar experiments were performed on the rooftop of the Department of Chemical Engineering from the University of Coimbra (N 40.1865243°, E 8.41797950°). In the experiments with visible light radiation, a high-pressure sodium lamp (LUMATEK 600 W, LUMATEK, London, UK) was used.

Photocatalytic oxidation under UVA radiation experiments was carried out in a 2 L glass reactor equipped with 3 Philips TL 6W BLB (tube diameter of 16 mm) lamps with the maximum emission peak at 365 nm (Figure 2b). The photon flux ($E_0 = 5.75 \times 10^{-7}$ Einstein/Ls) was determined using a ferrioxalate actinometer [27], as described in a previous work [14]. These experiments occurred at a controlled temperature (25 ± 1 °C) over 60 min with a stirring speed was 700 rpm. These conditions were previously optimized to ensure the chemical regime [28]. During photocatalytic oxidation under UVA radiation experiments, the reactor was fed with a pure oxygen stream. Moreover, the reactor was covered with aluminium foil to minimize the interference of external radiation.

In all experiments, the concentration of the photocatalyst in the reactor was 70 mg/L and the photocatalyst was placed in contact with the solution for 10 min before turning on the light, to test the catalyst adsorption capacity without irradiation. Then the solution taken for analysis was filtrated by an acetate cellulose syringe filter with a pore size of 0.45 µm (CHROMAFIL Xtra, CA 45/25, Mancherey-Nagel, Düren, Germany).

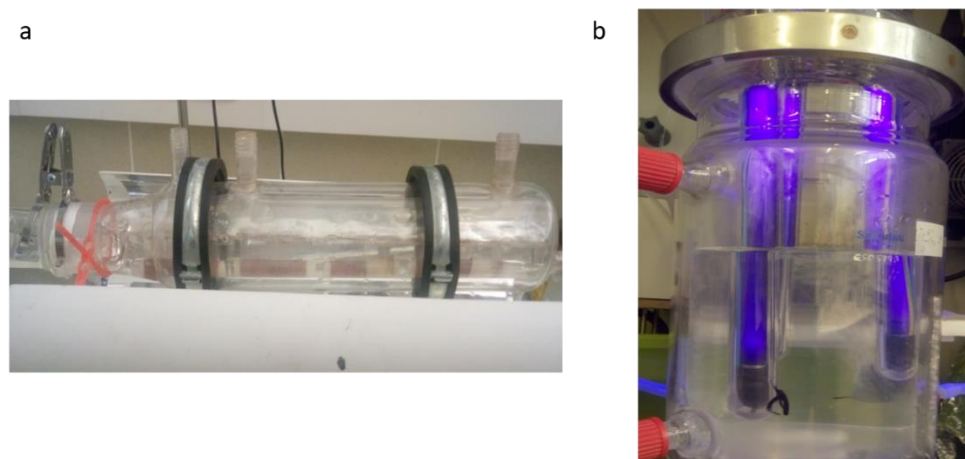


Figure 2. (a) Sunlight photoreactor and (b) UVA reactor.

Kinetic studies were made for the degradation rate of contaminants assuming pseudo-first-order kinetics [29,30],

$$-\frac{dC}{dt} = k' \cdot C \quad (4)$$

where C is the concentration of the contaminant (mg/L) and k' is the pseudo-first-order degradation rate constant (min^{-1}).

2.3. Analytical Methods

SMX, LRZ and CBZ were quantified by high-performance liquid chromatography, equipped with a diode array detector (HPLC-DAD, UFLC, Shimadzu, Duisburg, Germany). The analysis was performed using a SiliaChrom C-18 column by applying isocratic flow conditions at a temperature of 30 °C. Acetonitrile and 1.4 g/L of NaH_2PO_4 in ultrapure water, at the volumetric ratio 40/60, was applied as the mobile phase at a flow rate of 1 mL/min. The injection volume was 100 μL . The contaminants were quantified at the 255 nm wavelength.

3. Results

3.1. Effect of Noble Metals Doping on Photocatalytic Oxidation

Figure 3 reveals the absorption spectrum of the mixture of 1 mg/L of each compound. That data allowed the identification of the maximum absorption wavelength, enabling us to draw conclusions about the mixture potential for degradation through photolysis.

Absorption spectra for each individual compound can be found in the literature [20,31]. The absorption profiles of SMX and CBZ are similar, with the maximum absorption at 250 nm. LRZ has a significant peak absorption near to the same wavelength [20]. Moreover, as it can be seen in Figure 3, the mixture light absorption initiates near the UVA radiation range for wavelengths below 365 nm. However, it significantly increases in the UVB range. Therefore, UVB radiation present on sunlight radiation can have some impact on mixture degradation.

Photolysis under sunlight radiation was compared with photocatalytic oxidation using undoped and doped titanium dioxide catalysts (0.5 wt.% Ag and Pd- TiO_2) on the abatement of the pharmaceutical mixture. These experiments were performed in the summer (June 2018) under the same conditions, so that the irradiation flux was almost the same ($428 \pm 12 \text{ W/m}^2$). The abatement of the pollutants along the treatment time is reported in Figure 4 (a—SMX, b—CBZ and c—LRZ).

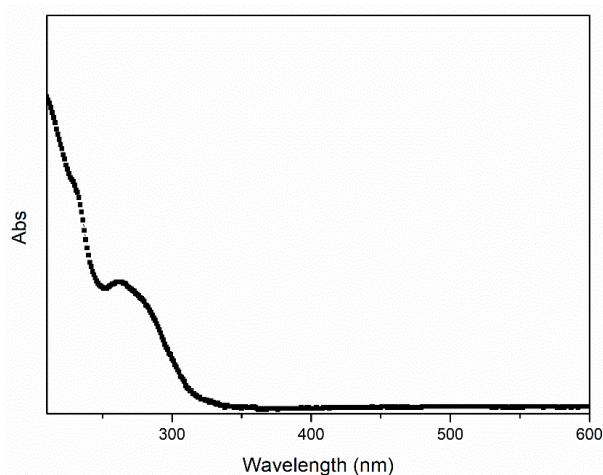


Figure 3. UV-Vis spectrum in a mixture of 1 mg/L of sulfamethoxazole (SMX), carbamazepine (CBZ) and lorazepam (LRZ).

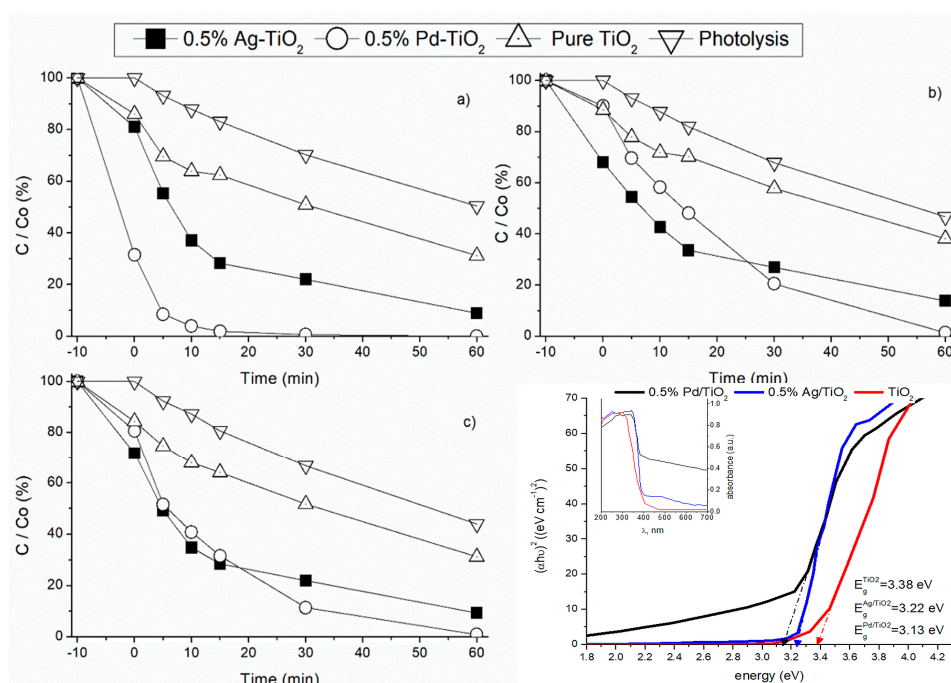


Figure 4. Contaminant ((a) SMX, (b) CBZ and (c) LRZ) degradation over time during photolysis and photocatalytic oxidation using titanium dioxide-based photocatalysts under sunlight radiation. (d) Determination of the catalysts' band gap through the Tauc plot method (inset: catalysts absorbance).

In the photocatalytic experiments, the photocatalysts were put in contact with the pollutants mixture for 10 min in dark conditions to test their adsorption capacity. SMX (Figure 4a) presented high adsorption capacity onto 0.5%Pd-TiO₂ with up to 70% of reduction. The use of sunlight aided by 0.5% Pd-TiO₂ was able to totally remove this contaminant in 15 min. Generally, the catalysts were able to enhance the degradation of all contaminants compared with photolysis. Pure TiO₂ revealed the lowest degradation rate for all compounds compared with the doped photocatalysts, which was attributed to its absorbance ability in comparison to Pd-TiO₂ and Ag-TiO₂. As can be seen in the insert in Figure 4d, TiO₂ was able to absorb wavelengths below 400 nm, while doped photocatalysts shifted the absorbance above 400 nm. Moreover, it was determined that the band gap of modified photocatalysts is lower than that of TiO₂ (3.38eV). The reduction of the band gap to 3.13 eV and 3.22 eV for Pd-TiO₂ and Ag-TiO₂, respectively, confirmed that Pd-TiO₂ has a higher visible light absorption ability (Figure 4d).

Ag- and Pd-doped TiO₂ showed a capacity to promote almost total contaminant removal after 1 h of photocatalytic oxidation. Among them, 0.5%Pd-TiO₂ was the most efficient photocatalyst. The presence of noble metals can be helpful to enhance the visible light absorption due to surface plasmon resonance [15,16]. This means that the photogeneration of holes and electrons can occur with low energy sources, in contrast to pure TiO₂. On the other hand, these noble metals can promote better electron-hole pair separation due to the electronegativity which can trap the electron, thus reducing the recombination phenomena [14,25,32]. Moreover, the next sections elucidate the effect of different kinds of wavelengths on the photocatalytic oxidation efficiency.

Photolysis led to a reduction of about 50% of the initial concentration of each contaminant in 60 min (Figure 4). This is a similar result to that obtained by Zanella et al. [33], who verified, using simulated sunlight radiation (Suntest CPS + device 280–800 nm with an irradiance flux of 500 W/m²) for 60 min, that the initial concentration of SMX (30 mg/L) could be reduced by half. Still, the pollutant initial concentration was very different in both works. However, even if in our study the initial load of SMX was 30 times lower, it must be considered that we are dealing with a mixture of three different contaminants. Moreover, the radiation flux used by Zanella et al. [33] was slightly higher. The main reason for such high contaminant degradation with sunlight radiation was determined to be the presence of UVB radiation in the sunlight spectrum (Figure 5).

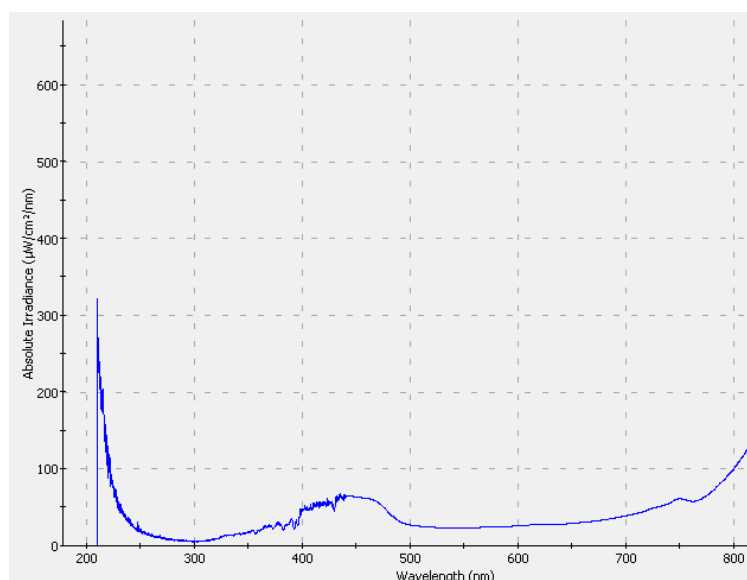


Figure 5. Emission spectrum of sunlight radiation (June 2018; N 40.1865243°, E 8.41797950°).

As mentioned above regarding the spectrum in Figure 3, the mixture light absorption starts near 350 nm and increases for lower wavelengths. Therefore, this portion of UVB can promote the break of homolytic and heterolytic molecules, which may help the formation of radicals and the abatement of the original contaminants.

The average of irradiation fluxes and sunlight spectrum were similar for both photolysis and photocatalytic oxidation (428 ± 12 W/m²). Thus, the differences observed among those experiments is mostly related to the photocatalysts' action. The main reason for the slightly higher efficiency when pure TiO₂ was used as a catalyst when compared with photolysis is related to the production of radical oxidative species, such as hydroxyl and superoxide radicals, which can increase the rate of degradation. However, this difference was not so sharp since the recombination phenomenon occurs quickly on a nanosecond scale and pure TiO₂ does not contain any noble metal capable of electron trapping [34]. So, the recombination phenomenon would not allow a high efficiency enhancement. These results are in accordance with those obtained by Sousa et al. [20]. These authors verified that, using 100 mg/L of TiO₂-P25 with sunlight radiation in a pilot plant, the degradation of 0.2 mg/L of LRZ takes about

50 min considering a solar UV power of 30 W/m^2 . This UV solar power is similar to that of the present study, which reached $30\text{--}40 \text{ W/m}^2$ (Figure 5).

Since the photocatalytic oxidation efficiency is highly enhanced when Ag- and Pd-doped TiO_2 are applied, the performance of these catalysts are explored in the subsequent sections.

3.2. Noble Metal Load Effect under Different Radiation Sources

Different noble metal loads doped on TiO_2 can have a positive or negative impact on the photocatalytic oxidation performance. The noble metal load can enhance the visible light absorption, the number of active sites and the recombination phenomena [15,26]. Therefore, the amount of noble metal load (0.5 and 1 wt.%) should be analyzed to compare the performance of heterogeneous catalysts. This effect was tested under different radiation sources—namely sunlight radiation, UVA and a visible light radiation lamp. Before starting the irradiated experiments, adsorption tests under dark conditions were performed.

3.2.1. Adsorption Effect

The adsorption of contaminants typically increases with the noble metal load [35]. Thus, adsorption experiments were performed using 1%Ag- TiO_2 and 1%Pd- TiO_2 .

As can be seen in Figure 6a, SMX was almost totally adsorbed on the 1%Pd- TiO_2 surface. Depletion occurred initially and a plateau was observed afterwards. On the other hand, 1%Ag- TiO_2 presented high initial adsorption, reaching about 70% of SMX removal. However, desorption occurred later on and a final adsorption efficiency of about 30% was reached. The adsorption at the initial step seemed to be higher for Pd than for Ag, which is related to the high electronegativity of Pd. Kryukova et al. [36] concluded that Pt on TiO_2 can act as an electron sink from the TiO_2 conduction band in order to transfer them to adsorbed oxygen, promoting adsorption under dark conditions. Moreover, Zhang et al. [35] verified that rhodamine B adsorption in dark conditions increased when the Pt load was increased from 1 to 5 wt.%. This indicates that the adsorption increases with the electron trapping capacity, which may explain the higher adsorption observed for Pd- TiO_2 as compared to Ag- TiO_2 . In fact, the electronegativity of Pd (2.28) is similar to that of Pt (2.20) according to the Pauling scale, while that of Ag is much smaller (1.93); therefore, it is expected that the behavior of Pd will be similar to that of Pt.

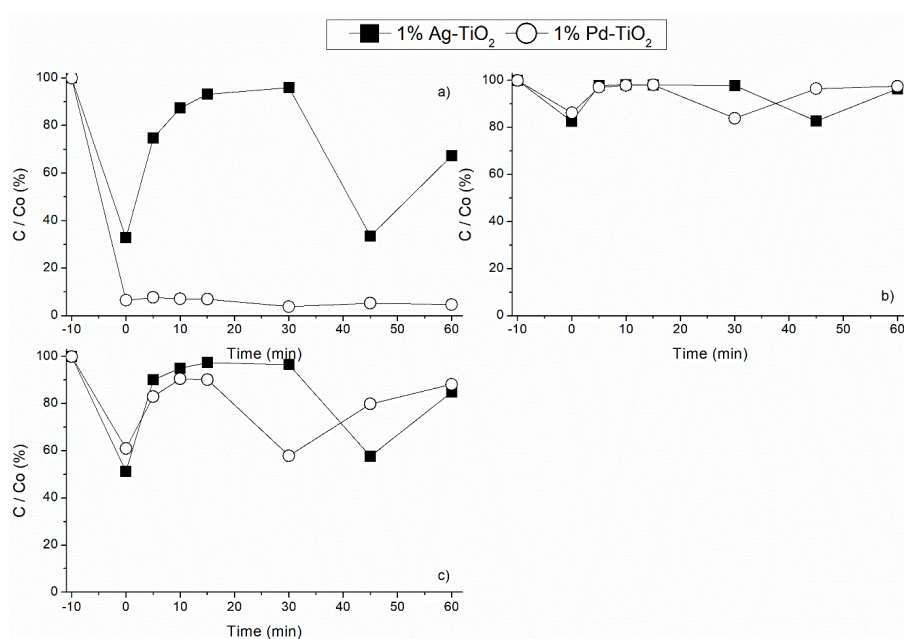


Figure 6. Contaminant ((a) SMX, (b) CBZ and (c) LRZ) adsorption on TiO_2 loaded with 1 wt.% Ag or Pd in dark conditions.

As for the other contaminants, CBZ (Figure 6b) and LRZ (Figure 6c), initially some adsorption was observed for Pd-TiO₂ but desorption was detected afterwards. CBZ (Figure 6b) revealed the lowest adsorption for both photocatalysts, reaching about 2% after 60 min. Indeed, Ag-TiO₂ also presented some initial adsorption for all contaminants. About 15% of adsorption was reached for LRZ (Figure 6c) for both photocatalysts after 60 min. Therefore, the degradation reached after 60 min during photocatalytic oxidation occurs mainly via oxidation and not merely by adsorption. An exception may be the case of SMX abatement when Pd-TiO₂ is used.

3.2.2. Effect of Visible Light Radiation

Visible light radiation (from 400 to 780 nm) is a relevant fraction of sunlight corresponding to about 45% of the spectrum. Photolysis (data not shown) did not lead to a measurable degradation of the mixture. This was expected since the light spectrum of the sodium lamp used was within the range of 480–700 nm, which is well above the pollutants solution absorption wavelength range (Figure 3). Moreover, the irradiance flux of this lamp (600 W) during the experiments was about 70 W/m² (± 10 W/m²), which is much lower than that observed in the sunlight. Figure 6 shows the results obtained using visible light.

Adsorption was observed for all contaminants during the initial 10 min under dark conditions. However, after 5 min in the presence of visible light, desorption occurred for almost all conditions. The exception was for SMX adsorption at 1%Pd-TiO₂. For 0.5%Pd-TiO₂, the SMX desorption was smaller for the same period as compared with the Ag-TiO₂ catalysts. This reveals the high affinity of Pd for SMX, which increases with this noble metal load. Moreover, it should be highlighted that for the remaining conditions during desorption, the initial concentrations of the pollutants were reached again. Therefore, after this initial 5 min of desorption, oxidation should be the most significant pathway to support decontamination.

These experiments showed that visible light photolysis does not promote significant abatement of SMX, CBZ or LRZ. The presence of photocatalysts enhances the decontamination of the mixture under visible light radiation. Moreover, since some peaks of byproducts were detected in the HPLC chromatograms, it is possible to conclude that oxidation (not only adsorption) occurs under photocatalytic conditions.

As can be seen from Figure 7, the most difficult pollutant to remove was CBZ (Figure 7b), where the result was similar for all photocatalysts with about 20% depletion. For LRZ, the removal rate was about 55% (Figure 7c). The reason for such low degradation can be related to its tricyclic structure ensemble that is hardly broken by the reactive oxidative species. Under these conditions, it was not possible to verify a significant effect of the noble metal load. The exception was for SMX degradation, which may be related to the adsorption effect referred above. Still, the increase in the load of Pd for Pd-TiO₂ seems to slightly enhance LRZ degradation. This indicates that the photogeneration of electron-hole pairs was similar for both loads. Moreover, the visible light could be responsible for producing a low number of electron-hole pairs due to the low energy and therefore a small noble metal load could be enough to trap the photogenerated electrons. The low energy of visible light seems to be the most relevant explanation for this low efficiency of the mixture decontamination as compared to other radiation sources. The effect of the noble metal load under visible light was tested on Rhodamine B [35]. In this case, the authors observed that for Rhodamine B decomposition the increase of the noble metal load of Ag-TiO₂ from 0.5 to 1 wt.% led to significant differences after 6 h of visible light irradiation. During the first hour of reaction, no difference was verified for either noble metal load [35]. The wavelength emission of the visible light seemed to present a relevant impact in terms of decontamination efficiency [35,37–39]. Zielińska et al. [38] found that phenol degradation (initial concentration of 19.7 mg/L) using P25 and 1.5%Ag-TiO₂ (5 g/L) under visible light ($\lambda > 400$ nm) can achieve just 15% of removal for both conditions after 1 h of reaction. Kowalska et al. [37], for the same phenol concentration using P25 and Pt-TiO₂ (1 g/L) under visible light ($\lambda > 450$ nm), attained after 60 min 3% and 10% removal, respectively. Martínez et al. [39] used a medium pressure Hg lamp

placed inside of the reactor with the main emission peaks at 366, 405, 436, 546 and 578 nm (called near UV-Vis radiation) for the photocatalytic oxidation of 8 mg/L of CBZ through 500 mg/L of P25 and 50% of oxygen partial pressure to achieve complete degradation after 30 min of irradiation and a $t_{1/2}$ (half-life time) of about 3.5 min. The explanation for this excellent performance compared to the studies referenced here and the present study is related to the presence of a UVA radiation peak, since the authors did not present the contribution of each wavelength to the CBZ degradation. It should also be related to the fact that the emission of our visible lamp started at 480 nm. Notably, the activity of visible light could be enhanced if the lamp emission started nearer to 400 nm. Moreover, the higher efficiency observed in those works can also be related to the higher amount of catalyst applied. Martínez et al. [39] confirmed that increasing the catalyst concentration from 100 to 500 mg/L led to an exponential improvement on the apparent rate constant.

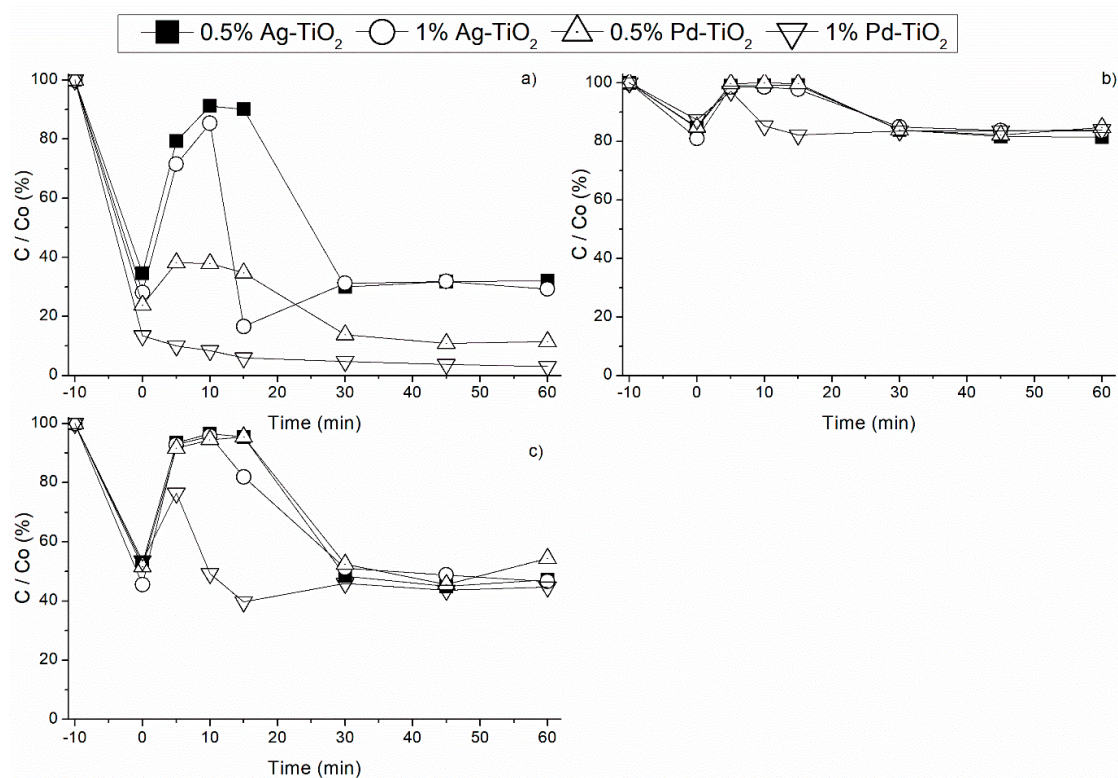


Figure 7. Contaminant ((a) SMX, (b) CBZ and (c) LRZ) degradation during photocatalytic oxidation using visible light.

3.2.3. Effect of UVA Radiation

For comparative purposes, UVA radiation was tested for the degradation of contaminants. UVA is a small fraction of the solar spectrum corresponding to about 4–5% of sunlight. However, this kind of radiation can be helpful for photocatalytic oxidation when titanium dioxide is applied. Photolysis under UVA radiation, in contrast to visible light, promoted some degradation. After 60 min of irradiation, the removal of each contaminant was 11% for SMX, 7% for CBZ and 12% for LRZ (data not shown).

The presence of catalysts clearly enhanced the degradation of the contaminants under UVA radiation (Figure 8). Low wavelength radiation ($\lambda < 400$ nm) can promote a suitable photogeneration of holes and electrons, which improves the production of reactive oxidative species (such as hydroxyl radicals) that can be helpful for the mixture degradation. Moreover, the UVA lamps were located inside of the reactor covered by a quartz tube, which enhanced the radiation propagation through all the solutions. SMX (Figure 8a) was totally removed by Pd-TiO₂ for both loads. Meanwhile, for Ag-TiO₂, it was possible to observe that photodegradation increased with Ag load. This could be due to the higher production of hydroxyl radicals since the load increase reduced the recombination

phenomenon. Xekoukoulotakis et al. [40], using UVA radiation and TiO_2 (0.25 g/L), achieved the total removal of SMX (10 mg/L) in 45 min of irradiation. Considering hydroxyl radicals as the main factor responsible for the degradation of these contaminants, CBZ (Figure 8b) was revealed to be the most difficult to treat. For the best condition, 1%Pd- TiO_2 , the removal was about 80% after 60 min of reaction—indicating that it was difficult for the hydroxyl radicals to break the tricyclic structure.

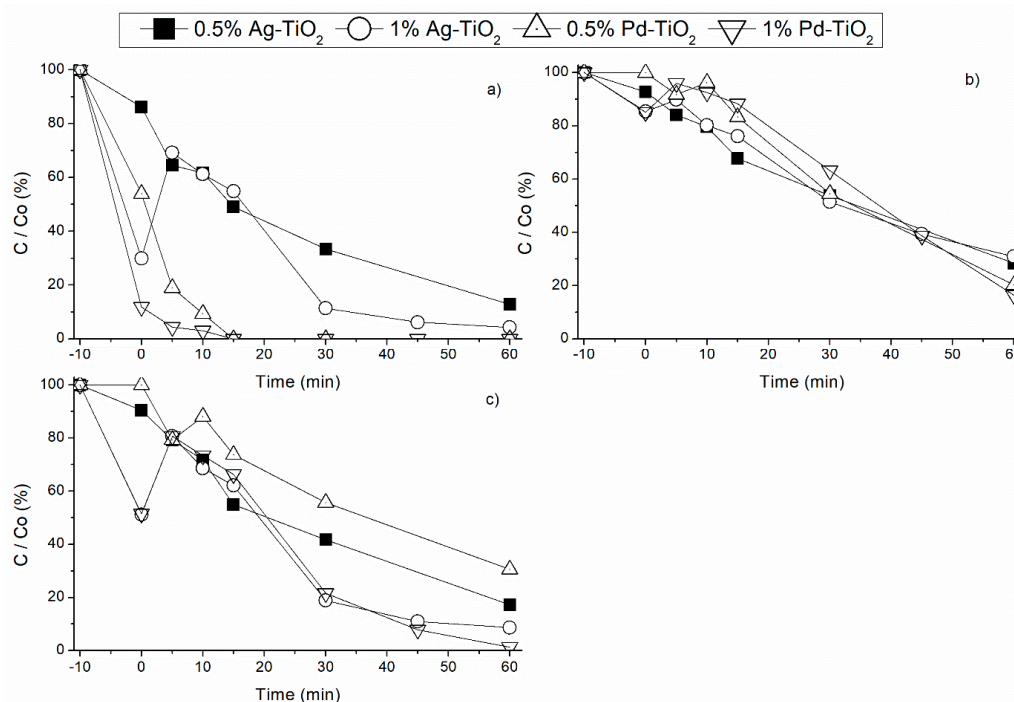


Figure 8. Contaminants' ((a) SMX, (b) CBZ and (c) LRZ) normalized concentrations during photocatalytic oxidation under UVA radiation.

Another important feature is the fact that when 1%Pd- TiO_2 was applied, after total SMX removal (after 15 min of photocatalytic oxidation), the degradation rates of the other contaminants exhibited a significant increase. This could be related to the higher number of active sites available for the photogeneration of reactive oxidative species that were probably occupied by SMX before.

Compared to the visible light radiation results (Figure 7), the use of lower wavelengths in the case of UVA radiation improved the degradation of this mixture of contaminants. This could be related to the higher capacity of the higher energy radiation to promote the photogeneration of holes and electrons, aiding in the production of more reactive oxidative species, which in turn increase the rate of degradation.

3.2.4. Sunlight Radiation

Sunlight radiation seemed to present to the best results (Figure 9) in terms of the compounds degradation as compared to other sources of radiation (visible and UVA light). This was expected since the sunlight spectrum covers both radiations and has a small range of UVB, which enhances the degradation of these contaminants. The presence of different wavelengths in the UV radiation spectrum is an important factor to increase the decontamination rate [41]. Bayarri et al. [41] concluded that the presence of UV-ABC radiation is more efficient for decontamination than UVA radiation.

SMX (Figure 9a) removal for all catalysts was found to be closely related to the initial adsorption on their surface. For instance, with 1%Ag- TiO_2 in the period of 10 and 15 min, a desorption phenomenon and the subsequent SMX concentration abatement were verified, indicating that the degradation occurred via oxidation instead of adsorption. In fact, Pd achieved a high initial SMX removal after 10 min of contact under dark conditions due to adsorption, which increased with the increasing noble

metal load. The worst result for the contaminant degradation was achieved for 0.5%Ag–TiO₂, where the removal rate reached about 90%, while for the other photocatalysts total contaminant abatement was obtained.

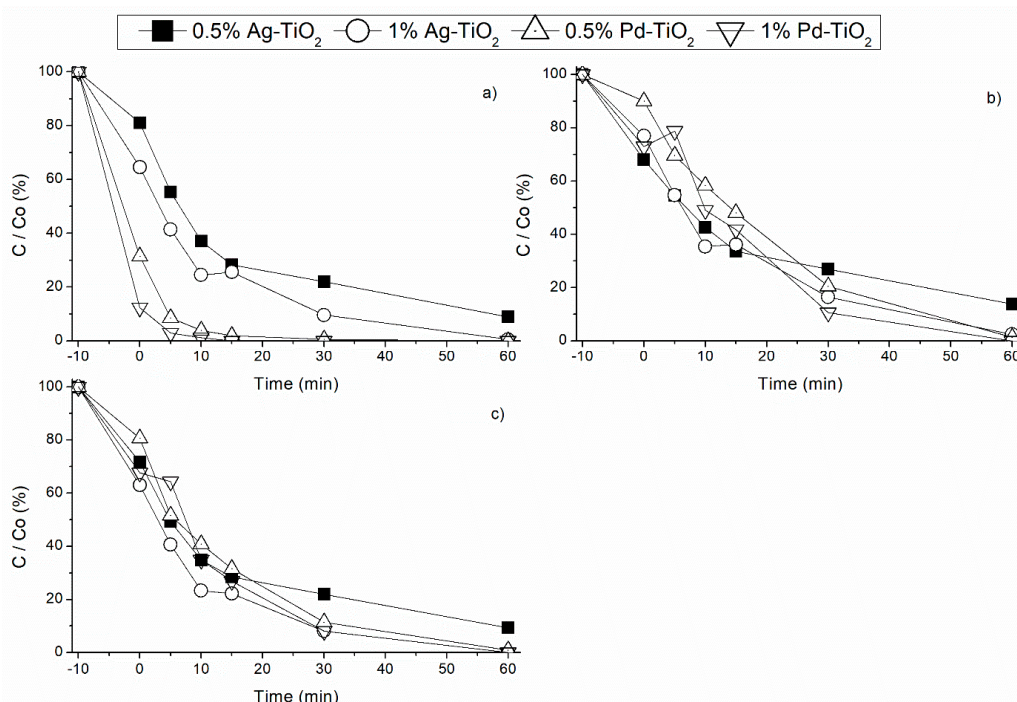


Figure 9. Contaminants' (a) SMX, (b) CBZ and (c)—LRZ) normalized concentrations during photocatalytic oxidation under sunlight radiation.

Comparing these results with those obtained with UVA (Figure 8), it is clear that the main difference is the fact that when UVA was applied, CBZ did not reach total degradation. The explanation for the increase of the decontamination efficiency when sunlight was used could be related to two main factors: the reactor design and the presence of UVB and visible light in the sunlight spectrum. The reactor design can have a real impact on contaminant degradation. Figure 2 shows both reactor configurations. The reactor used in the sunlight experiments was horizontal and equipped with a compound parabolic collector (CPC) to concentrate the light, allowing it to work with 0.5 L of solution (Figure 2a). The area exposed to radiation was higher than that in the UVA radiation reactor (Figure 2b) since the lamps were smaller than the length of the sunlight reactor and only 10 cm of each lamp was submerged into the solution volume.

3.3. Decontamination Kinetic Studies

Sunlight and UVA radiation allowed the determination of kinetic rates to easily compare the performance of each photocatalyst and both radiation sources. The photocatalytic degradation of SMX, CBZ and LRZ can be described by the pseudo-first-order kinetic Equation (4) [30]. After the dark conditions, a portion of each contaminant was adsorbed on the photocatalyst surface, after which desorption occurred; therefore, data regarding adsorption were not considered for the kinetic rate determination.

The compound degradation using different catalysts fitted well with a pseudo-first-order kinetic model with coefficients of determination (R^2) ranging from 0.920 to 0.998. The pseudo-first-order kinetic constants of the conditions tested are summarized in Table 1. The values of these constants were between 0.019 min^{-1} for 0.5%Ag–TiO₂ on the CBZ degradation using UVA radiation and 0.279 min^{-1} for 1%Pd–TiO₂ on the SMX degradation using sunlight radiation. For all the photocatalysts and contaminants tested, the highest rate of decontamination was obtained for sunlight radiation, in

accordance with the discussion of the previous sections. For all photocatalysts, the rate for CBZ degradation was the lowest compared to the other contaminants in the mixture. Perhaps this result is due to the tricyclic structure ensemble. In a general way, the degradation rate of SMX was higher compared to LRZ, except for the sample with 1%Ag-TiO₂. Moreover, the increase of load from 0.5 to 1% improved the kinetic rate for both radiation conditions, which seems to be related to the better separation of photogenerated electron holes and the reduction of the recombination phenomena.

Table 1. Pseudo-first-order kinetic rate constants (k') for SMX, CBZ and LRZ degradation during photocatalytic oxidation for different catalysts and radiation sources. The respective determination coefficients (R^2) are between brackets.

Catalyst	UVA Radiation			Sunlight Radiation		
	k'_{SMX} (min ⁻¹) (R^2)	k'_{CBZ} (min ⁻¹) (R^2)	k'_{LRZ} (min ⁻¹) (R^2)	k'_{SMX} (min ⁻¹) (R^2)	k'_{CBZ} (min ⁻¹) (R^2)	k'_{LRZ} (min ⁻¹) (R^2)
0.5%Pd-TiO ₂	0.203 (0.993)	0.023 (0.921)	0.020 (0.991)	0.239 (0.994)	0.047 (0.991)	0.066 (0.989)
1%Pd-TiO ₂	0.179 (0.980)	0.024 (0.940)	0.048 (0.940)	0.274 (0.998)	0.052 (0.920)	0.064 (0.954)
0.5%Ag-TiO ₂	0.032 (0.978)	0.019 (0.993)	0.028 (0.987)	0.059 (0.930)	0.033 (0.940)	0.050 (0.920)
1%Ag-TiO ₂	0.054 (0.934)	0.020 (0.992)	0.047 (0.960)	0.074 (0.967)	0.057 (0.971)	0.080 (0.980)

Abellán et al. [42] verified a pseudo-first-order kinetic constant of 0.149 min⁻¹ for UV radiation with a TiO₂ load of 0.5 g/L and an SMX concentration of 25 mg/L. In our study, a lower concentration of contaminants was used to be more comparable with the concentration observed in real wastewater. However, the values obtained are in accordance with the findings of Abellán et al. [42]. On the other hand, Rizzo et al. [43], using UV-AB radiation (peak emission maximum at 350 nm) for CBZ (5 mg/L) decontamination, determined that the kinetic constant rate for 0.2 g/L of TiO₂ was about 0.0317 min⁻¹. This value is comparable to our kinetic rates for CBZ (Table 1).

4. Conclusions

The present study revealed that low-cost radiation can be a suitable solution for the decontamination of these compounds. Therefore, a good reactor design and/or a proper photocatalyst that can be activated with this type of radiation is needed. The presence of noble metals at low loadings (0.5 and 1 wt.%) on the TiO₂ structure was capable of enhancing the photocatalytic oxidation independent of the radiation source. The photocatalytic oxidation using visible light was able to remove just about 20% of the initial CBZ concentration (1 mg/L) independent of the photocatalyst tested. However, for SMX, Pd presented the best results compared to Ag—this could be related to the high SMX adsorption verified for Pd catalysts. UVA and sunlight radiation presented similar results. The main difference was related to the CBZ degradation (the most recalcitrant compound) since UVA radiation was only able to remove 80% of this compound whereas, using sunlight radiation, it was possible to achieve total removal. This could be related to the presence of UVB radiation in the solar spectrum. Moreover, higher pseudo-first-order kinetic constants rates were obtained for sunlight, revealing that this photocatalytic process is suitable for wastewater decontamination.

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