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Long-term stable Ag/TiO_2 thin films for photocatalytic degradation of fluoroquinolones in water: Kinetics and operational stability

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ABSTRACT

Immobilized photocatalytic systems are promising for the removal of emerging contaminants from water. In this study, Ag/TiO_2 (0.15 wt% Ag) thin films immobilized on glass substrates were evaluated for the degradation of fluoroquinolone antibiotics (ciprofloxacin, norfloxacin, and levofloxacin) under UVA irradiation ($\lambda = 365$ nm) and compared with direct photolysis. The films were characterized by XRD, Raman, AFM, and SEM/EDS, confirming the predominance of the anatase phase and morphological stability after extended use. Photocatalysis promoted faster degradation of the parent compounds and their fluorescent transformation products than photolysis. The degradation followed pseudo-first-order kinetics ($R^2 > 0.98$), with significantly higher apparent rate constants in the presence of the catalyst. Levofloxacin showed the highest enhancement, with an eightfold increase in degradation rate. The system maintained performance after prolonged operation (>645 h) without activity loss. In real tap water, degradation efficiencies reached up to 94% within 3 h, indicating tolerance to matrix constituents. ANOVA confirmed significant differences between photolysis and photocatalysis. These results demonstrate that immobilized Ag/TiO_2 thin films are a stable and effective strategy for the photocatalytic treatment of fluoroquinolone-contaminated water.

1. Introduction

Frequently detected fluoroquinolones such as ciprofloxacin, levofloxacin, and norfloxacin have been found in aquatic environments even at trace concentrations (ng L^{-1} to μg L^{-1}) [1]. A key concern is their persistence, due to their low biodegradability and resistance to conventional water and wastewater treatment processes [2,3]. Several studies have reported their presence in treated effluents, surface water, groundwater, and even potable water sources [1].

Associated with their recalcitrance, these substances pose risks to public health and aquatic ecosystems. Their continuous presence in the environment may contribute to the development of microbial resistance, recognized as a global problem [4,5], and adverse ecotoxicological effects in non-target organisms [6]. Fluoroquinolones (FQs) have also been shown to inhibit the growth of algae [6] and cyanobacteria [7], accumulate in the food chain [8] and affect plant physiology and development [9,10]. Therefore, there is an urgent need to develop effective technologies for the removal of these emerging contaminants from water matrices.

Among promising treatment strategies, advanced oxidation

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processes (AOPs), particularly heterogeneous photocatalysis, have shown considerable potential due to their ability to generate highly reactive oxygen species capable of mineralizing persistent pollutants [2,11]. Titanium dioxide (TiO_2) remains the most extensively studied photocatalyst, due to its stability, low cost, non-toxicity, and high activity under UV irradiation [3,12]. Nevertheless, its efficiency is limited by the rapid recombination of photogenerated electron–hole pairs and its wide band gap, which restricts photoactivation mainly to the UV region [13,14].

To overcome these limitations, studies have investigated structural modifications of the photocatalyst, such as silver doping (Ag). The incorporation of silver improves charge separation efficiency and extends light absorption into the visible region, leading to enhanced photocatalytic activity [15–17]. These modifications have demonstrated high removal efficiencies, in some cases approaching complete degradation, across different classes of pollutants, with sustained activity over successive reuse cycles [15,18].

Despite these advances, most photocatalytic studies are still conducted with catalysts in suspension, which pose operational challenges including catalyst recovery and reuse difficulties [2,19]. Immobilizing catalysts as thin films has emerged as an attractive approach facilitating catalyst separation and repeated use, increasing feasibility for practical applications [14,15,20].

More recently, alternative strategies such as the in situ growth of TiO_2 nanostructures on complex substrates, have been explored to enhance surface area and improve photocatalytic performance in immobilized systems [21].

However, sol–gel-derived thin films remain attractive due to their simplicity, reproducibility, and potential applicability in larger-scale systems.

Films of Ag/TiO_2 have shown stable photocatalytic activity under UVA irradiation with promising kinetics and efficiency, particularly in systems designed for repeated use and long-term operation [20,22].

Therefore, this study aimed to evaluate the degradation efficiency and reusability of Ag/TiO_2 (0.15 wt% Ag) thin films synthesized by the sol–gel method for the photocatalytic degradation of ciprofloxacin, levofloxacin, and norfloxacin under UVA irradiation (365 nm). The investigation focused on removal rates, kinetic parameters, performance in real water matrices, film reusability, and a preliminary assessment of phototransformation products, monitored by HPLC coupled to fluorescence detection.

2. Materials and methods

2.1. Reagents and solutions

Ciprofloxacin (CIP), levofloxacin (LEV), and norfloxacin (NOR), with stated purity ≥ 98%, were purchased from Sigma-Aldrich. Chromatography-grade methanol (LiChrosolv®, Merck) was used. All other analytical-grade reagents, including orthophosphoric acid (H_3PO_4, 85.0%) and monosodium phosphate ($NaH_2PO_4{\cdot}H_2O$, 98.0–102.0%), were obtained from Isofar.

Individual stock solutions of CIP, LEV, and NOR were prepared at concentrations of 100 mg L^{-1}, acidified to pH 3 using H_3PO_4, and stored at 8 °C, protected from light. Working solutions (individual and mixed) at concentrations of 100 μg L^{-1} were freshly prepared by dilution of the stock solutions immediately before each experiment.

The pH of the working solutions (~6.8) corresponded to the natural pH of the water used, and no prior adjustment was performed before the photocatalytic experiments. Acidification was carried out only during chromatographic analysis, by addition of the acidic mobile phase, without affecting the reaction conditions.

2.2. Synthesis of Ag/TiO_2 Photocatalytic Thin Films

The Ag/TiO_2 (0.15 wt% Ag) films used in this study were prepared by the sol–gel method and immobilized on borosilicate glass supports, as previously described by Araújo et al. [22]. The synthesis involved the controlled hydrolysis of titanium (IV) isopropoxide in an alcoholic medium, with the addition of TiO_2 P25 and $AgNO_3$ for silver incorporation. The films were applied in photocatalytic systems in subsequent studies, including the work reported by Lima et al. [21], and their structural integrity, stability, and reusability under UVA irradiation are further evaluated and confirmed in the present study.

The films were immobilized on the outer surfaces of borosilicate glass tubes (approximately 2 cm in diameter and 9 cm in length) and used as photocatalysts in the pharmaceutical degradation experiments. The film thickness was previously estimated by cross-sectional SEM analysis for films prepared under similar synthesis conditions, presenting values of approximately 210 nm [22], consistent with earlier reports [23].

In the photodegradation assays, four glass tubes were employed, providing a total active surface area of approximately 0.0176 m^2 (0.0044 m^2 per tube), in contact with 800 mL of aqueous solution containing 100 μg L^{-1} of the target pharmaceuticals (CIP, LEV, and NOR), tested both individually and in mixtures. Preliminary tests using five tubes (0.0220 m^2 total surface area) did not show significant differences in degradation efficiency, and the four-tube configuration was adopted.

Before each degradation or reuse experiment, the films were rinsed with ultrapure water, dried at room temperature, and immediately inserted into the irradiation system.

2.3. Characterization of the Ag/TiO_2 film

The structural and morphological integrity of the Ag/TiO_2 films after photocatalytic application was evaluated using X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). All analyses were performed directly on the films immobilized on the glass substrate.

The crystalline structure of the films was examined by XRD using a D8 Advance diffractometer (Bruker) equipped with a LynxEye linear detector and a Cu Kα radiation source (λ = 1.5406 Å), operating at 40 kV and 40 mA. Diffractograms were recorded in the 2θ range from 15° to 60°, with a step size of 0.02° and a counting time of 7.5 s per step.

Raman spectra were obtained using a triple monochromator Raman spectrometer (model T64000, Horiba/Jobin Yvon) operating in single mode, with slit widths adjusted to achieve a spectral resolution below 2 cm^{-1}. The system was coupled to a liquid-nitrogen-cooled CCD detector. Excitation was provided by a solid-state laser (LAS-532–100-HREV) emitting at 532.0 nm with an output power of 14 mW, focused onto the sample through a 100 × objective lens (Olympus). Spectra were collected at different points on the film surface, with three acquisitions of 10 s each for every spectral grating range (1800 gr mm^{-1}).

Surface morphology and topography were analyzed by AFM using a Multimode 8 instrument (Bruker) operating in PeakForce mode. A silicon probe with a nominal spring constant of 0.8 N m^{-1} was used for all measurements. Topography images were acquired with a resolution of 256 × 256 pixels, a force curve frequency of 1 Hz, and a scan rate of 0.5 Hz, under controlled environmental conditions (25 °C and 51% relative humidity). Data processing and analysis were performed using Gwyddion 2.60 software.

Surface morphology was further examined by SEM using an Evo HD microscope (Zeiss) equipped with a secondary electron detector, operating at magnifications of up to 15,000 × . High-resolution SEM images were obtained using a TESCAN MIRA field-emission scanning electron microscope (FEG-SEM) equipped with a Schottky electron source, enabling enhanced visualization of film morphology. The elemental composition of the Ag/TiO_2 films was determined by EDS using an XFlash 410 M detector (Bruker).

2.4. Photoreactor setup

The heterogeneous photocatalysis experiments were carried out in a closed wooden photoreactor internally lined with reflective aluminum foil to enhance light distribution. The reactor had internal dimensions of 40 × 35 × 55 cm (height × width × length), as schematically illustrated in Fig. 1.

Irradiation was provided by four 28 W blacklight fluorescent lamps (Foxlux, Brazil), symmetrically positioned inside the reactor, with maximum emission at 365 nm (UVA region). The incident irradiance at the surface of the reaction solution was measured using a radiometer and found to be 11.87 W m^{-2}.

Each experiment was conducted in a 1 L glass beaker containing 800 mL of aqueous solution prepared with the target pharmaceuticals (ciprofloxacin, levofloxacin, and norfloxacin), tested individually and in mixtures, using ultrapure water or tap water as matrices.

The solution pH (~6.8) corresponded to the natural pH of the water, and no adjustment was performed prior to irradiation.

During the photocatalytic experiments, the reaction medium was maintained under continuous magnetic stirring at 1440 rpm and constant aeration with atmospheric air supplied by an air pump at a flow rate of approximately 1.5 L min^{-1}, ensuring homogeneous mixing and sufficient dissolved oxygen throughout the assays.

2.5. Adsorption and degradation studies (photolysis and photocatalysis)

Dark adsorption experiments were initially carried out in the photoreactor for 3 h in the presence of Ag/TiO_2 films, in the absence of irradiation, in order to evaluate the adsorption of the pharmaceuticals onto the photocatalyst surface. These experiments were performed to distinguish between adsorption and photocatalytic degradation contributions to overall removal.

Subsequently, degradation assays were performed under two distinct conditions. Direct photolysis experiments were conducted under UVA irradiation (λ = 365 nm) for 24 h, in the absence of photocatalyst, to assess the contribution of direct photodegradation. Photocatalytic experiments were carried out in the presence of Ag/TiO_2 films under UVA irradiation (λ = 365 nm) for 3 h.

During all experiments, aliquots were periodically withdrawn at predetermined time intervals and analyzed by high-performance liquid chromatography coupled with fluorescence detection (HPLC-FL).

2.6. Evaluation of fluoroquinolone degradation: instrumental and kinetic analyses

2.6.1. Quantification and monitoring of fluoroquinolones and phototransformation products by HPLC-FL

The concentrations of the pharmaceuticals and their detectable degradation byproducts were determined using a high-performance liquid chromatograph (HPLC) (model LC-20AT Prominence DGU-20A, Shimadzu) coupled to a fluorescence detector (FL) (RF-10AXL, Shimadzu). The system included two high-pressure pumps and an injector with capacity of 20 µL. Operation was controlled using LC Solution software (version 1.11 SP1, Shimadzu).

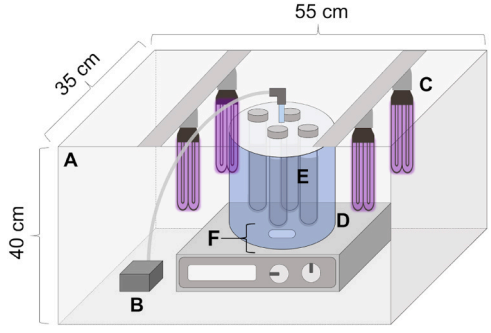

Fig. 1. Schematic diagram of the photoreactor used for photodegradation of the fluoroquinolones, showing the wooden enclosure (A), air pump (B), UV-A lamps (λ = 365 nm) (C), pharmaceutical solution (D), Ag/TiO_2 films (E), and magnetic stirring system (F).

Fluorescence detection (HPLC-FL) was employed due to its higher sensitivity and selectivity at low concentration levels, particularly in the µg L^{-1} range.

Separation was performed on a Luna C18 column (250 × 4.6 mm, 5 µm, Phenomenex). The mobile phase consisted of methanol and phosphate buffer (0.04 M $NaH_2PO_4 \cdot H_2O$, pH adjusted to 3 with 85% H_3PO_4), in a 30:70 (v/v) ratio, with isocratic elution at a flow rate of 1 mL min^{-1}. The excitation and emission wavelengths were set at 280 and 450 nm, respectively [24]. The total chromatographic run time was 1 h.

Calibration curves were constructed in the range from 1.25 to 200 µg L^{-1}, with correlation coefficients (r^2) of 0.9994 for LEV, 0.9992 for CIP, and 0.9998 for NOR. The retention times were 10.0 ± 0.2 min for LEV, 12.2 ± 0.3 min for NOR, and 13.7 ± 0.2 min for CIP. The detection limits (LOD) and quantification limits (LOQ) were, respectively, 0.4 and 1.25 µg L^{-1} for LEV, 0.08 and 1.25 µg L^{-1} for CIP, and 0.063 and 1.25 µg L^{-1} for NOR.

2.6.2. Evaluation of photodegradation kinetics

The remaining concentration of the pharmaceuticals at a given irradiation time was expressed as the ratio between the concentration at time t(C) and the initial concentration (C_0), defined as C_R, according to Eq. (1).

$$C_R = C/C_0 \quad (1)$$

For comparative purposes and graphical representation, the residual concentration was also expressed as a percentage, C_R (%), as shown in Eq. (2).

$$C_R\ (\%) = (C/C_0) \times 100 \quad (2)$$

The degradation percentage was calculated using Eq. (3).

$$Degradation\ (\%) = (1 - C/C_0) \times 100 \quad (3)$$

Photodegradation kinetics were modeled assuming a pseudo-first-order reaction, as described by Eq. (4).

$$\ln (C/C_0) = -kt \quad (4)$$

The apparent rate constants (k) and coefficients of determination (R^2) were obtained by linear regression of the experimental data. The half-life time ($t_{1/2}$), defined as the time required to reduce the initial concentration by 50%, was calculated using Eq. (5).

$$t_{1/2} = ln(2)/k \quad (5)$$

All kinetic calculations and data fitting were performed using OriginPro software, while additional data processing was conducted using Microsoft Excel.

Statistical analysis was carried out using one-way analysis of variance (ANOVA) to assess whether statistically significant differences existed among degradation efficiencies and kinetic parameters obtained under different experimental conditions, considering a confidence level of 95% ($p < 0.05$).

2.7. Collection and preparation of tap water samples

Tap water samples were collected in the municipality of São Luís, Maranhão State, Brazil, following the procedures established by the Brazilian drinking water quality guideline (GM/MS Nº. 888, May 4th, 2021). Samples were collected in 1 L amber glass bottles previously cleaned and sanitized. Prior to sampling, the tap was flushed for 5 min to

minimize potential interference from materials accumulated in the plumbing system.

After collection, samples were transported in a thermal cooler at 4 °C, stored under refrigeration (4 ± 2 °C), and used within 24 h. A blank control consisting of deionized water stored under the same conditions was included to monitor potential contamination.

Evaluation of matrix effects was performed by determining selected physicochemical parameters, including chloride, bicarbonate, total iron, calcium, magnesium, and total hardness.

2.8. Ag/TiO_2 film reuse tests

After each 3 h photocatalytic cycle, the Ag/TiO_2 films were removed from the reactor, rinsed with ultrapure water, dried at room temperature for 1 h, and subsequently reused in a new photocatalytic cycle with freshly prepared pharmaceutical solutions. This procedure was repeated for three consecutive cycles for each pharmaceutical compound.

In addition to the reuse cycles evaluated in this study, the films had been previously used in multiple experiments, resulting in a cumulative operation time exceeding 645 h under UVA irradiation, without significant loss of photocatalytic activity.

The photocatalytic film retained degradation activity after extended UVA irradiation, indicating its functional stability under the applied experimental conditions and supporting its potential applicability in water treatment systems.

3. Results and Discussion

3.1. Characterization of the Ag/TiO_2 (0.15 wt% Ag) film

The X-ray diffractogram of the Ag/TiO_2 (0.15 wt% Ag) film (Fig. 2a) revealed a predominance of the anatase phase of TiO_2, identified by characteristic diffraction peaks located at 2θ of around 25.3°, 37.7°, 48.1°, 53.9°, and 55.1°, corresponding to the (101), (004), (200), (105), and (211) crystallographic planes, respectively, according to the ICDD standard No. 21–1272.

The observation of a predominant peak at 2θ = 25.3° (101 plane) indicates that the films maintained the anatase crystalline structure after repeated use, demonstrating the structural stability of the photocatalyst. Similar XRD profiles, characterized by a strong (101) anatase reflection, have also been reported for Ag/TiO_2 materials synthesized by the sol–gel method [25]. The anatase structure is recognized for its superior photocatalytic performance due to more efficient charge separation and improved light absorption [15].

The absence of diffraction peaks associated with Ag can be attributed to the low dopant concentration (0.15 wt% Ag) and the high dispersion of silver species within the TiO_2 matrix, likely in the form of finely distributed nanoparticles or clusters. Under these conditions, Ag detection by XRD becomes limited, which is consistent with reports describing highly dispersed Ag species on TiO_2 surfaces [26]. Additionally, EDS analysis of the material in powder form, obtained from the same synthesis route, confirmed the presence of Ag, supporting its incorporation into the TiO_2 matrix.

Fig. 2b shows the Raman spectra obtained for three different regions of the Ag/TiO_2 film surface. All spectra exhibited bands characteristic of the anatase phase, with signals at 144, 196, 397, 516, and 639 cm^{-1} corresponding to the Eg, B1g, A1g, and Eg vibrational modes, respectively [27,28].

The similarity among the spectra obtained at different positions on the sample was indicative of good homogeneity of the photocatalytic coating on the glass substrate. The minor variations of intensity among the spectra could be attributed to fluctuations in laser focus or slight alterations in the positioning of the objective lens and were not indicative of structural differences.

The absence of Ag-related Raman bands can be attributed to the low dopant concentration (0.15 wt% Ag) and to the inherently weak vibrational modes of metallic silver, which do not significantly affect the TiO_2 lattice polarizability. Similar behavior has been observed in Ag-TiO_2 systems prepared by different synthesis routes [29].

The predominance of the anatase phase (confirmed by XRD) indicates that the films maintained the crystalline structure typically associated with good photocatalytic performance. The same type of Ag/TiO_2 films, prepared by the same sol–gel synthesis and immobilization procedures, were also employed in previous studies for the degradation of other pharmaceuticals [20,22], confirming the reproducibility and stability of this material.

The AFM images of the Ag/TiO_2 film, obtained in two-dimensional (Figs. 3a and 3b) and three-dimensional (Fig. 3c) modes, revealed a surface with homogeneous granular distribution and moderate roughness. The material was coated with well-defined nanostructures that were regularly distributed across the scanned area, indicating good coverage of the glass substrate.

The mean square root roughness (Rq) was estimated at 3.01 nm, over a scanned area of 5 μm^2. The identified nanostructures had an average diameter of 25.2 ± 5.15 nm, while the pores between the agglomerates had an average size of 144.8 ± 10.3 nm. The surface elevations could be explained by the formation of nanoclusters, or variations in the growth of the TiO_2 layer.

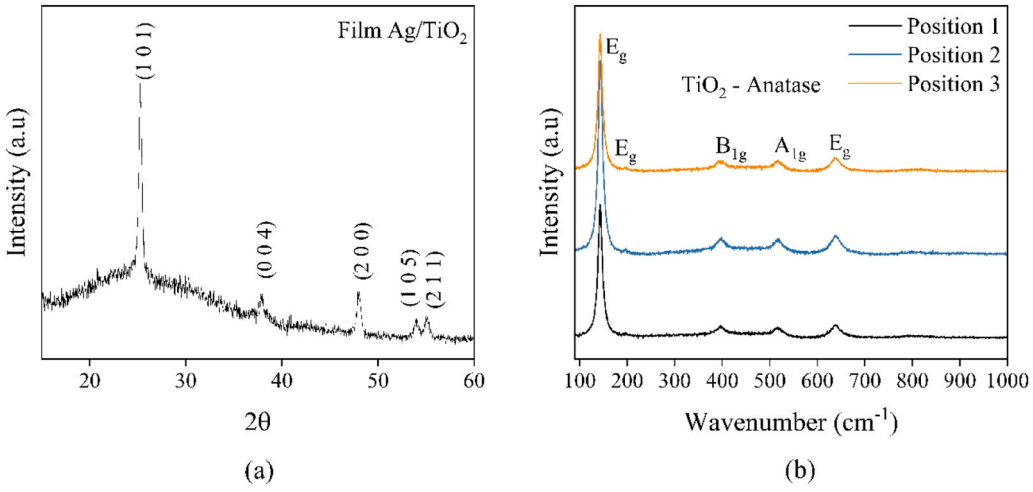

Fig. 2. (a) X-ray diffractogram of the Ag/TiO_2 film (0.15 wt% Ag), showing diffraction peaks characteristic of the anatase phase. (b) Raman spectra collected at three different positions on the same film surface, indicating the presence of anatase TiO_2.

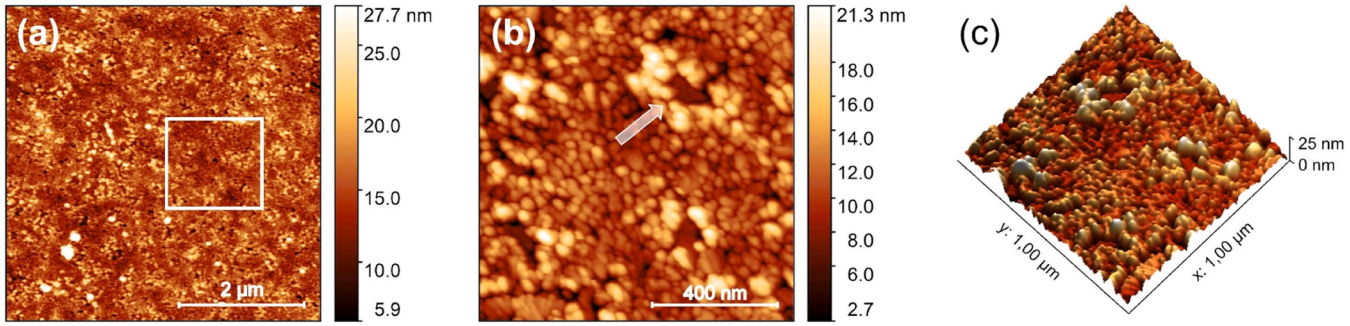

Fig. 3. Atomic force microscopy (AFM) images of the Ag/TiO_2 (0.15 wt% Ag) film. (a) 5 µm × 5 µm surface image, where the dashed square indicates the region analyzed at higher magnification. (b) 1 µm × 1 µm image highlighting surface pores (white arrow). (c) Three-dimensional topography corresponding to image (b).

The increased active surface area was associated with the presence of nanostructures and roughness of the material, which enhanced the number of available reaction sites and promoted the absorption of UV radiation, facilitating the efficient generation of electron–hole pairs [15]

The AFM images (Fig. 3) also showed no evidence of surface defects, discontinuities, or delamination, even after several reuse cycles, indicating that the Ag/TiO_2 film retained its physical integrity and surface stability during repeated use.

Scanning electron microscopy (SEM) analysis (Fig. 4) was performed to further evaluate the surface morphology of the Ag/TiO_2 (0.15 wt% Ag) film at different magnifications.

The SEM micrographs (Fig. 4a–c) revealed a continuous and homogeneous coating, without evidence of cracks, delamination, or significant agglomeration. At low magnification (Fig. 4a), the film exhibited uniform surface coverage over the glass substrate, suggesting effective deposition via the sol–gel process. At higher magnifications (Figs. 4b and 4c), a nanostructured morphology composed of well-distributed nanoclusters was observed.

These observations are consistent with the AFM results, confirming the formation of a rough and nanostructured surface, which is favorable for photocatalytic applications due to the increased availability of active sites and improved interaction with UV radiation.

To further investigate the elemental composition of the film, SEM coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) analysis was performed (Fig. 5).

The SEM image used for EDS analysis (Fig. 5a) indicates the selected regions for compositional evaluation. The spectra obtained at two different points (Fig. 5b) indicated the presence of titanium (Ti) and oxygen (O), which are the main constituents of the TiO_2 matrix. The elemental mapping (Fig. 5c–e) demonstrated a homogeneous distribution of Ti and O over the surface, confirming the uniformity and integrity of the deposited film. The presence of silicon (Si) is attributed to the borosilicate glass substrate.

Although silver (Ag) was not clearly detected in the mapping, this result is consistent with its low concentration (0.15 wt%) and high dispersion within the TiO_2 matrix, which may fall below the detection limits of EDS in localized analyses, as reported for similar Ag/TiO_2 systems with low silver loading Wang et al. [26].

Comparable morphological features have been reported in the literature. Gupta et al. [18] described Ag-doped TiO_2 materials composed of uniformly distributed nanograins with well-defined surface microstructures. Additionally, the authors reported that low dopant concentration and high dispersion of silver species contributed to the absence of observable dopant-related diffraction peaks. These findings are consistent with the homogeneous nanostructuring observed in the present study.

Overall, the combined characterization results (XRD, Raman spectroscopy, AFM, and SEM/EDS) confirm the structural integrity, homogeneous coating, and stability of the Ag/TiO_2 films. The predominance of the anatase phase, absence of significant defects, and controlled nanostructured morphology indicate properties suitable for photocatalytic applications. The lack of direct Ag detection by some techniques is consistent with its low concentration and high dispersion within the TiO_2 matrix.

3.2. *Adsorption and direct photolysis assays*

Dark adsorption tests were carried out using the Ag/TiO_2 films in a closed system, under constant stirring and in the absence of light, for a period of 3 h. The results indicated negligible adsorption of LEV, CIP, or NOR on the catalyst surface. The concentrations of the pharmaceuticals remained unchanged at the end of the test, indicating that the removal observed in the subsequent experiments was predominantly due to degradation processes, consistent with previous observations of low

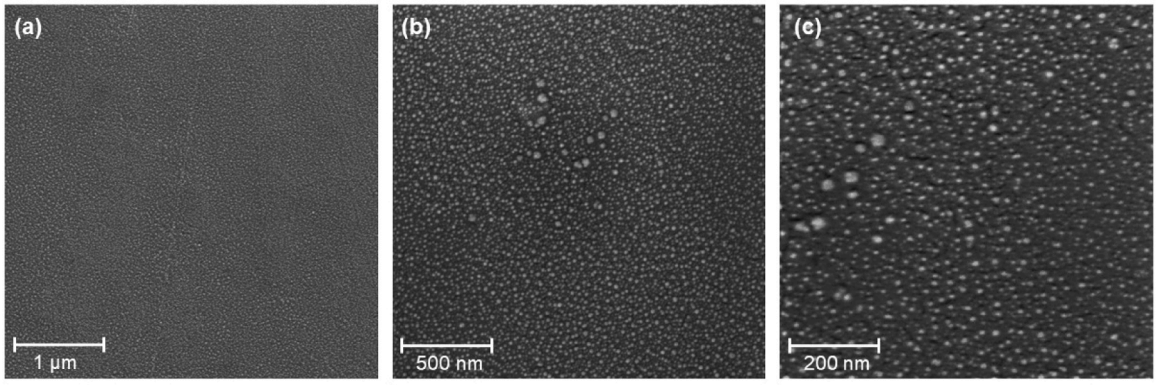

Fig. 4. SEM micrographs of the Ag/TiO_2 (0.15 wt% Ag) film at different magnifications: (a) low magnification showing homogeneous surface coverage, (b) intermediate magnification, and (c) high magnification revealing the nanostructured morphology composed of well-distributed nanoclusters.

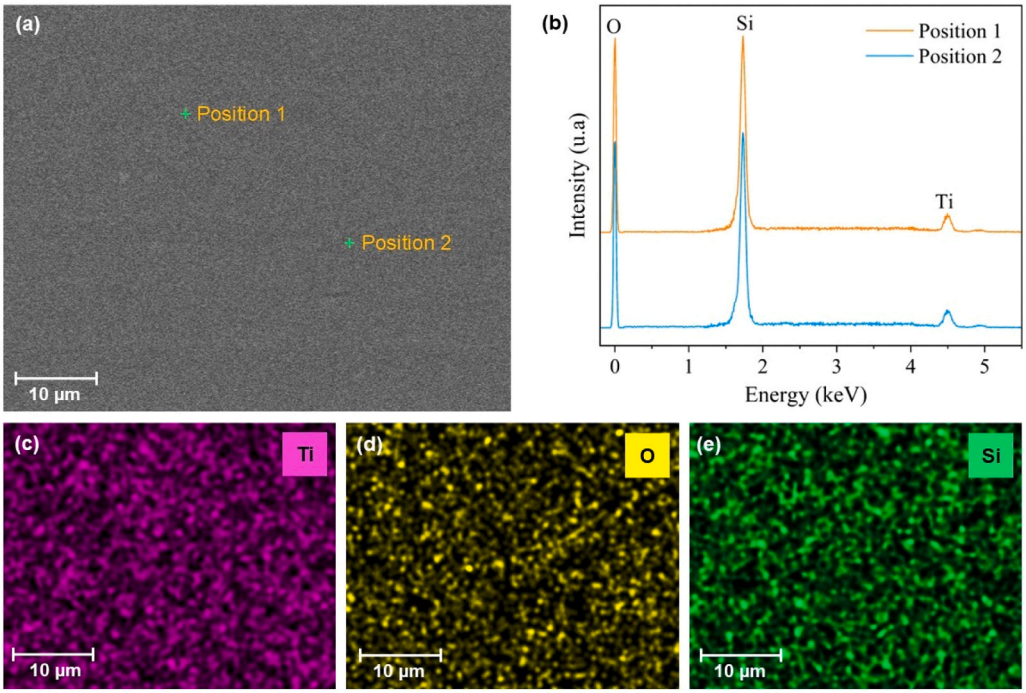

Fig. 5. (a) SEM micrograph of the surface of the Ag/TiO_2 (0.15 wt% Ag) film. (b) EDS spectra acquired at two different positions on the surface. (c–e) Elemental distribution maps of Ti, O, and Si.

dark adsorption of fluoroquinolones on Ag/TiO_2 surfaces [26].

Direct photolysis of the pharmaceuticals was evaluated using the photoreactor (Fig. 1), under UVA irradiation (λ = 365 nm), with constant stirring and aeration. These experiments were performed in the absence of the catalyst, allowing evaluation of photoinduced degradation under identical conditions.

The chromatograms obtained after a 3 h exposure period (Fig. 6a-c) revealed different levels of photosensitivity of the drugs. CIP and NOR presented faster degradation, with significant reductions in the chromatographic peak intensities, while LEV showed greater persistence under the same conditions.

The higher photosensitivity of CIP and NOR could be attributed to the structural fragility of these molecules, particularly in relation to piperazine ring cleavage, defluorination, and decarboxylation, which are commonly reported pathways in the direct photolysis of fluoroquinolones [30,31]. The structural similarity of CIP and NOR supports their comparable photochemical behavior under UVA irradiation.

As shown in Fig. 6a (CIP) and 6b (NOR), the direct photolysis of these drugs resulted in the formation of multiple degradation products, evidenced by secondary peaks in the chromatograms. Some of these peaks had very close or even identical retention times (such as the C_1/N_2 and C_2/N_3 pairs), suggesting the formation of structurally analogous degradation intermediates. This observation reinforces the hypothesis that CIP and NOR, as structural congeners, exhibit similar photochemical behavior under UVA irradiation.

To further evaluate the stability of the photolysis products, long-term chromatographic analyses (Fig. 7) revealed that certain degradation products revealed that certain degradation products persisted longer than the parent compounds. For CIP, peaks C_3 and C_5 remained detectable for up to 15 h, while the NOR peak N_5 persisted for up to 24 h of irradiation. The formation of persistent transformation products during the photolysis of fluoroquinolones has frequently been widely reported, reflecting the complexity of the reaction pathways and the potential environmental persistence of the resulting degradation products [30,31].

Overall, CIP and NOR tended to form structurally similar degradation products, mainly associated with modifications of the quinolone core and cleavage of the piperazine ring, which in many cases retained

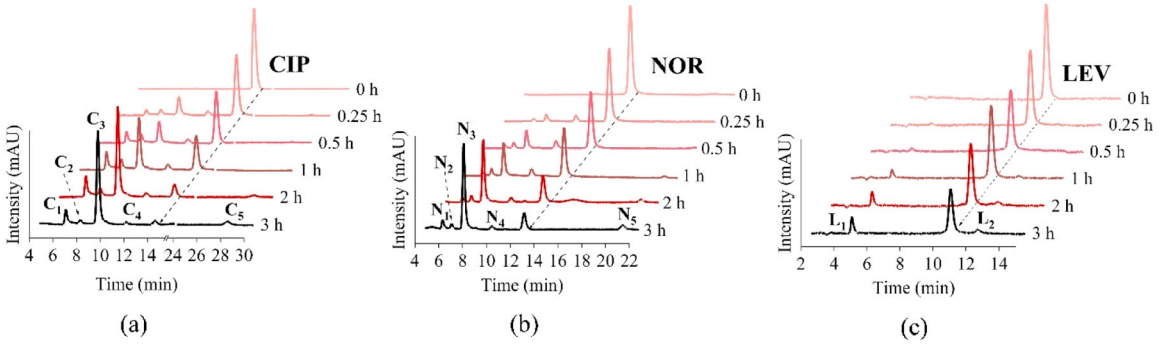

Fig. 6. Evaluation of direct photolysis of the pharmaceuticals under UVA irradiation (λ = 365 nm). (a–c) HPLC-FL chromatograms of (a) ciprofloxacin (CIP), (b) norfloxacin (NOR), and (c) levofloxacin (LEV) at different irradiation times (up to 3 h), showing the decrease of the parent compounds and the appearance of phototransformation products.

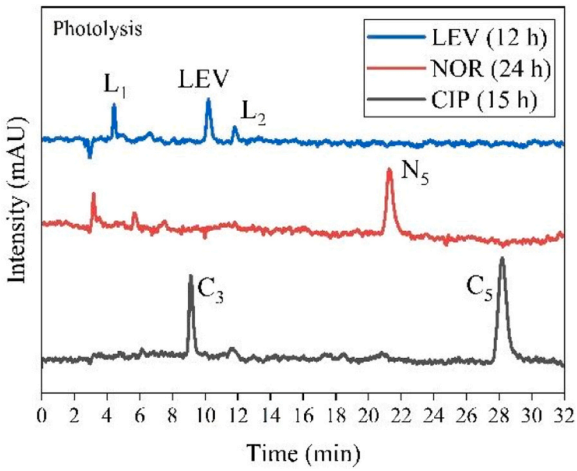

Fig. 7. HPLC-FL chromatograms illustrating the persistence of the pharmaceuticals and their degradation products after long-term direct photolysis (UVA, λ = 365 nm): (a) ciprofloxacin (CIP) after 15 h, highlighting peaks C_3 and C_5; (b) norfloxacin (NOR) after 24 h, highlighting peak N_5; (c) levofloxacin (LEV) after 12 h, highlighting LEV, L_1, and L_2.

fluorescent properties and were therefore detectable by spectrofluorimetric analysis. Such behavior has been consistently reported for fluoroquinolones under direct photolysis, reflecting common photoreaction mechanisms involving defluorination, decarboxylation, and piperazine ring transformation [31,32].

In contrast, LEV exhibited a distinct photochemical behavior, showing higher resistance to direct photolysis under the applied conditions. Although an initial decrease in concentration was observed, LEV remained detectable for up to 12 h of UVA exposure, together with two main degradation products (L_1 and L_2), as shown in Fig. 7. The persistence of LEV and its photoproducts over extended irradiation times has been widely reported and is commonly attributed to specific structural features of the molecule, including its chiral configuration and substitution pattern at position 8, which influence electronic distribution and reduce photochemical reactivity [19,32].

The high sensitivity and selectivity of the HPLC-FL technique were crucial for monitoring both the pharmaceuticals and their fluorescent degradation products. These results highlighted the complexity of fluoroquinolone photodegradation processes and demonstrated the limitations of direct photolysis in achieving complete elimination of these compounds [11].

Although direct photolysis effectively reduced the concentrations of the fluoroquinolones, it was unable to ensure complete degradation. The persistent presence of fluorescent degradation products, particularly for CIP and NOR, suggests that transformation products with potential residual bioactivity may remain in the aqueous matrix [11,32]. The similarity of the retention times observed for several degradation products indicates the formation of structurally related intermediates, following convergent phototransformation pathways, which may represent an additional environmental concern due to their potential accumulation and residual toxicity or bioactivity [33].

Therefore, these findings reinforce the limitation of direct photolysis as a standalone treatment approach and emphasize the need for more effective technologies, such as heterogeneous photocatalysis, capable of promoting comprehensive degradation of both the parent compounds and their persistent degradation intermediates [11,33].

3.3. Performance of the Ag/TiO$_2$ film for the degradation of the pharmaceuticals and fluorescent byproducts

3.3.1. Photocatalytic performance compared to direct photolysis

The presence of the Ag/TiO₂ film resulted in enhanced degradation performance compared to direct photolysis, not only by reducing the irradiation time required for pharmaceutical removal but promoting a more effective reduction in fluorescent transformation products. This behavior is evidenced by the remaining concentration curves (C/C₀) shown in Fig. 8 and by the HPLC-FL chromatographic profiles presented in Fig. 9.

In contrast to photolysis, where persistent transformation products were observed, the photocatalytic process led to a more efficient reduction of both the parent compounds and their associated byproducts, indicating a more effective overall degradation process.

Previous studies have reported efficient photocatalytic degradation of ciprofloxacin under different experimental conditions, including higher concentrations, shorter irradiation wavelengths, and suspension systems [33]. In this context, the performance observed in the present study, achieved under UVA irradiation using an immobilized Ag/TiO₂ film, demonstrates the effectiveness of the proposed system under milder and more practical conditions.

3.3.2. Kinetic aspects of photocatalytic degradation

Investigation of the degradation kinetics of ciprofloxacin (CIP), norfloxacin (NOR), and levofloxacin (LEV) employed the pseudo-first-order kinetic model, described by the linearized equation $\ln(C/C_0) = -kt$, where C_0 and C are the initial concentration and the concentration at a given time, respectively [3,34]. This model is commonly used in heterogeneous photocatalysis studies involving organic contaminants at low concentrations, where the degradation rate is proportional to the pollutant concentration.

Table 1 summarizes the values of the apparent rate constant (k), determination coefficient (R^2), and half-life time ($t_{1/2}$) obtained for each compound under direct photolysis and photocatalytic conditions. The model provided a good fit to the experimental data, with determination coefficients (R^2) greater than 0.98 in most cases (Table 1). The corresponding linear regression plots are presented in Figs. 10a and 10b.

The presence of the Ag/TiO₂ film led to marked increases in the rate constants (k), indicating faster degradation kinetics compared to direct photolysis.

The most pronounced effect was observed for levofloxacin (LEV), which exhibited the lowest degradation rate under photolysis ($k = 0.1710\ h^{-1}$) and the highest enhancement under photocatalytic conditions ($k = 1.4121\ h^{-1}$), corresponding to an approximately eight-fold increase. This behavior was also reflected in the reduction of the half-life time from 4.05 h to 0.49 h.

The reactivity in the presence of the catalyst followed the order LEV > CIP > NOR, which differed from the trend observed under direct photolysis (CIP > NOR > LEV). This shift indicates that photocatalysis not only accelerates the degradation rates but also modifies the relative reactivity profiles of the investigated compounds. The enhanced degradation of LEV may be attributed to more favorable interactions with reactive species generated during photocatalysis, such as hydroxyl radicals, as well as differences in adsorption behavior and surface interactions with the Ag/TiO₂ film. The photocatalytic process also promoted a more efficient removal of transformation products, as discussed in Section 3.2.

Although a detailed mechanistic interpretation would require additional experiments, such as adsorption studies or selective radical scavenging tests, the results obtained here are consistent with previous reports describing preferential degradation behavior of fluoroquinolones in photocatalytic systems [3,11].

The statistical significance of the observed effects was evaluated by application of one-way analysis of variance (ANOVA) to the k values obtained under photolysis and photocatalytic conditions. The differences were statistically significant ($p < 0.0001$), confirming a clear improvement in the degradation kinetics in the presence of the Ag/TiO$_2$ film. This statistical analysis supports the robustness of the observed kinetic trends, without implying further mechanistic conclusions.

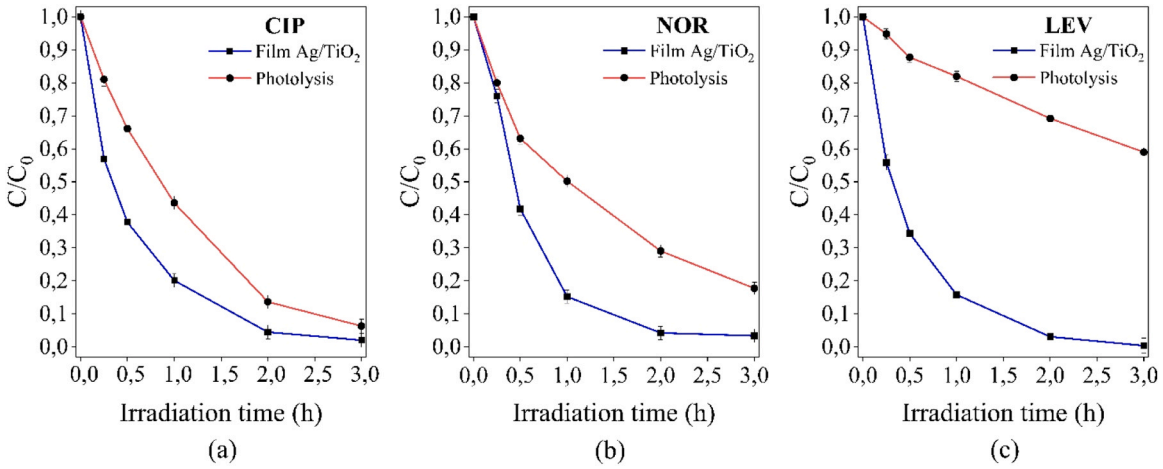

Fig. 8. Degradation curves showing the remaining concentration (C/C_0) as a function of irradiation time. Comparison between direct photolysis (red line) and photocatalysis using the Ag/TiO_2 (0.15 wt% Ag) film (blue line) under UVA irradiation ($\lambda = 365$ nm) for (a) ciprofloxacin (CIP), (b) norfloxacin (NOR), and (c) levofloxacin (LEV) in tap water (n = 3).

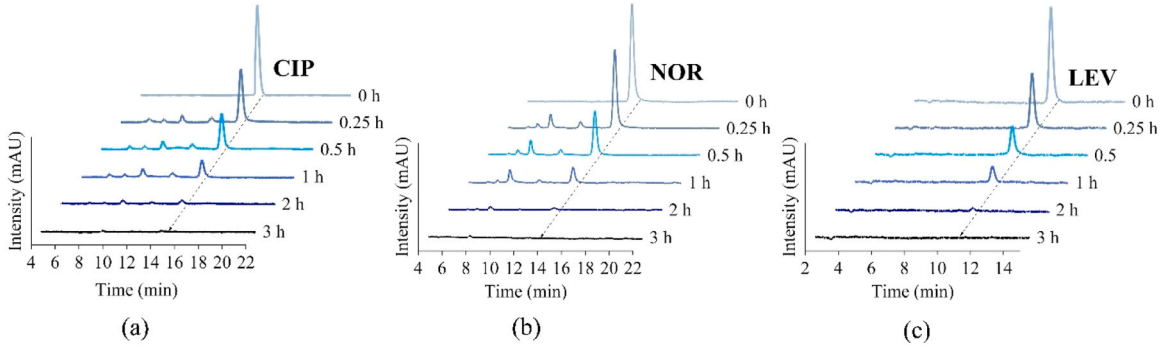

Fig. 9. HPLC-FL chromatograms illustrating the degradation of the pharmaceuticals under photocatalysis using the Ag/TiO_2 (0.15 wt% Ag) film, at different times of UVA irradiation ($\lambda = 365$ nm), for (a) ciprofloxacin (CIP), (b) norfloxacin (NOR), and (c) levofloxacin (LEV).

Table 1
Apparent pseudo-first order rate constants (k), half-life times ($t_{1/2}$), and determination coefficients (R^2) for degradation of the pharmaceuticals by photolysis and photocatalysis (n = 3).

Compound	Process	k (h^{-1})	R^2	$t_{1/2}$ (h)	Augmentation factor
CIP	Photolysis	0.9496	0.9953	0.7299	–
	Ag/TiO_2 film	1.3024	0.9831	0.5322	1.37
NOR	Photolysis	0.5595	0.9906	1.2389	–
	Ag/TiO_2 film	1.2103	0.9247	0.5727	2.16
LEV	Photolysis	0.1710	0.9938	4.0535	–
	Ag/TiO_2 film	1.4121	0.9847	0.4909	8.26

3.3.3. Application using real samples and matrix effects in photocatalytic degradation

Evaluation of the efficiency of photocatalytic processes using real matrices is a step in validating systems in validating systems with potential for environmental applications. Complex matrices such as tap water or wastewater contain organic and inorganic constituents that can affect the generation or activity of reactive oxygen species (ROS) through competitive scavenging of radicals, light screening effects, or inhibition of adsorption at the catalyst surface [2,11].

Simultaneous pharmaceutical degradation assays were performed using previously characterized tap water samples containing relevant concentrations of inorganic ions, including Cl^- (17.64 mg L^{-1}), HCO_3^- (25.13 mg L^{-1}), Ca^{2+} (25.90 mg L^{-1}), and Mg^{2+} (5.70 mg L^{-1}), as well as trace amounts of iron (0.05 mg L^{-1}). These parameters represent a realistic environmental matrix with moderate total hardness (26.9 mg L^{-1}), which is known to influence photocatalytic processes. The results were compared with those obtained using ultrapure water under identical experimental conditions (UVA irradiation ($\lambda = 365$ nm), mixed fluoroquinolone solution, and the configuration employing four Ag/TiO_2 films).

Fig. 11 shows the degradation percentages of ciprofloxacin (CIP), norfloxacin (NOR), and levofloxacin (LEV) in ultrapure and tap water matrices during the first 3 h of UVA irradiation ($\lambda = 365$ nm).

For ciprofloxacin (CIP) in ultrapure water, degradation rates of 80%, 95%, and 98% were obtained after 1, 2, and 3 h, respectively, while the values obtained using the real tap water sample were 94%, 88%, and 94%. Application of one-way ANOVA showed that the difference was not statistically significant ($p > 0.05$), indicating robust performance of the photocatalytic system in the presence of matrix-related interferents.

Similar results were obtained for norfloxacin (NOR), with degradation rates of 85%, 96%, and 97% in ultrapure water and 87%, 90%, and 94% in tap water. The slight differences ($\leq 6\%$) were also statistically insignificant ($p > 0.05$), confirming the limited influence of the water matrix on NOR degradation under the investigated conditions.

The absence of statistically significant matrix effects for CIP and NOR suggests that the influence of inorganic ions was compound-dependent rather than a general inhibition of the photocatalytic system. In contrast, the degradation of levofloxacin (LEV) was more strongly

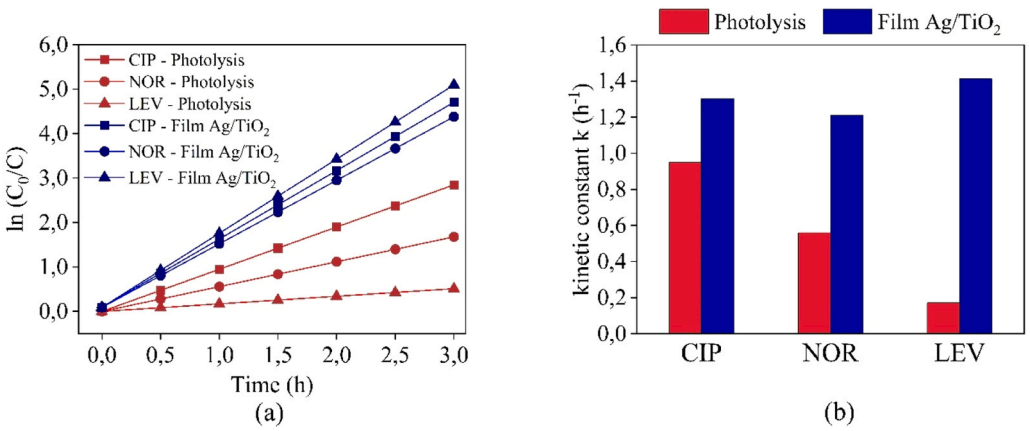

Fig. 10. (a) Linear regression fits of the pseudo-first order kinetic equation ($\ln(C_0/C) = kt$) for ciprofloxacin (CIP), norfloxacin (NOR), and levofloxacin (LEV), comparing direct photolysis and photocatalysis with Ag/TiO_2 (0.15 wt% Ag) films under UVA irradiation ($\lambda = 365$ nm). (b) Comparison of the apparent rate constants (k, h^{-1}) obtained for each pharmaceutical using the two processes, highlighting the significantly increased degradation rates achieved with the immobilized catalyst.

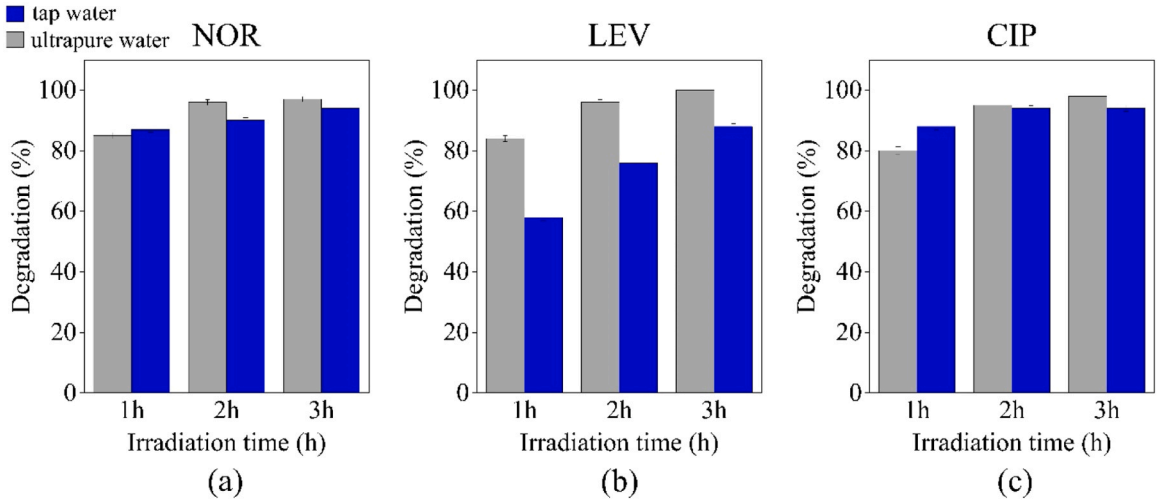

Fig. 11. Comparison of simultaneous degradation of (a) ciprofloxacin (CIP), (b) norfloxacin (NOR), and (c) levofloxacin (LEV) in ultrapure water and tap water samples during the first 3 h of UVA irradiation ($\lambda = 365$ nm) in the presence of the Ag/TiO_2 (0.15 wt% Ag) film (n = 3).

affected by matrix interference. Although the compound was completely degraded (100%) within 3 h in ultrapure water, only 58% degradation was achieved after 1 h in tap water, increasing to 76% after 2 h and 88% after 3 h, with 97% degradation reached only after 5 h of irradiation. The difference between the results obtained in the two matrices was statistically significant ($p < 0.0001$), particularly during the initial irradiation period.

This behavior indicates a higher susceptibility of LEV to matrix effects, which may be related to differences in molecular structure, reactivity toward reactive species, and/or interactions with the catalyst surface, its molecular structure exhibiting higher stability toward photocatalytic activation, and/or weaker interactions with the catalyst surface [11,35].

Structurally, LEV is the optically active S(−)-enantiomer of ofloxacin and is reported to exhibit a more rigid molecular conformation, with steric hindrance around the piperazinyl substituent and strong intramolecular stabilization [36–39]. Such features may reduce the accessibility of reactive oxygen species to key functional groups, particularly under competitive conditions imposed by inorganic ions present in tap water, thereby contributing to the delayed degradation observed in real matrices.

These findings suggest that ions such as carbonate and bicarbonate, which are known scavengers of hydroxyl radicals, may have acted as competitors for reactive species and/or as absorbers of UVA radiation, partially inhibiting the photocatalytic degradation of LEV. Additionally, competitive adsorption of inorganic ions on the catalyst surface cannot be excluded, which may further limit heterogeneous degradation pathways [40,41].

Despite this evidence of matrix interference, it is noteworthy that the catalytic system remained effective in tap water, even in the presence of inorganic interferents. The effective degradation of LEV after 5 h of irradiation, together with the consistent performance observed for CIP and NOR, supports the potential applicability of the Ag/TiO_2 film for water treatment under realistic conditions

3.3.4. *Reusability and stability of the Ag/TiO_2 (0.15 wt% Ag) film*

Evaluation of the reusability and stability of the Ag/TiO_2 film was based on the maintenance of photocatalytic efficiency throughout all the experiments conducted in this study. Tests conducted over cumulative operation times exceeding 645 h of UVA irradiation, including repeated use of the same films across multiple experiments, showed no detectable loss of degradation performance for the target pharmaceuticals. In addition, no visible evidence of film defects, delamination, or mechanical degradation was observed, indicating sustained structural and

functional stability of the material under the applied experimental conditions.

The preservation of catalytic activity was confirmed by the consistent degradation of the pharmaceuticals and the effective elimination of the main detectable fluorescent degradation products, demonstrating that the photocatalytic behavior remained stable after successive reuse cycles. This observation was further supported by morphological analyses using SEM and AFM, which revealed no significant surface alterations, accumulation of residues, or features indicative of catalyst deactivation or saturation.

Immobilization of the catalyst on a glass substrate provided clear operational advantages, including direct reuse without recovery steps, minimized catalyst loss, and suitability for repeated or continuous operation. The same Ag/TiO_2 films physically reused in the present work had also been employed in previous studies by Lima et al. [22], demonstrating consistent photocatalytic performance over extended experimental periods. In addition, other studies from the same research group reported the successful application of Ag/TiO_2 films synthesized using the same sol–gel methodology and composition, although prepared as independent samples, for the degradation of different classes of organic contaminants, including steroid hormones [20,23].

Together, these results indicate both the long-term reusability of the same immobilized films and the reproducibility of the Ag/TiO_2 material when independently prepared, supporting the robustness of the photocatalytic system. The results obtained in the present study therefore confirm the suitability of the Ag/TiO_2 film for extended use in photocatalytic water treatment applications, including those involving real water matrices.

3.3.5. *Fluoroquinolone degradation mechanisms*

Elucidation of the possible main transformation pathways of the fluoroquinolones was based on the experimental findings and reports available in the literature. The chromatographic profiles obtained during the photolysis and photocatalysis assays provided relevant information concerning the behaviors of the compounds under UVA irradiation.

During direct photolysis of CIP and NOR, the appearance of secondary peaks with similar or identical retention times (such as C_1/N_2 and C_2/N_3) suggested the generation of structurally related degradation products, as expected for fluoroquinolones with similar chemical scaffolds [42–44]. The persistence of these intermediates for up to 24 h of exposure reflected their stability under the experimental conditions and indicated the challenges associated with their removal using photolysis alone.

In contrast, the absence or rapid elimination of these degradation products under photocatalysis with Ag/TiO_2 indicates that the system promotes more extensive degradation pathways, likely involving the action of reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide anions ($O_2^{\bullet-}$) generated at the film surface under UVA irradiation [16].

The enhanced photocatalytic performance of the Ag/TiO_2 system can be attributed to the role of silver in promoting charge separation and interfacial electron transfer. Under UVA irradiation, TiO_2 generates electron–hole pairs (e^-/h^+), and metallic Ag deposited on the semiconductor surface acts as an electron sink, facilitating the transfer of photogenerated electrons from the conduction band of TiO_2 to Ag particles. This process is associated with the formation of a Schottky barrier at the Ag/TiO_2 interface, which suppresses electron–hole recombination and increases the lifetime of charge carriers. As a result, there is an enhanced generation of reactive oxygen species such as hydroxyl radicals (•OH), superoxide radicals ($O_2^{\bullet-}$), and hydrogen peroxide, which are recognized as the main oxidative agents responsible for the degradation of organic contaminants [45,46].

In the case of fluoroquinolones, these reactive species promote transformation pathways involving piperazine ring opening, hydroxylation, defluorination, and decarboxylation, as consistently reported in studies based on chromatographic and mass spectrometric identification of degradation products [47–49]

Although the transformation products were not structurally identified in this study, it is important to highlight that the elucidation of degradation pathways of fluoroquinolones typically requires advanced analytical techniques such as high-performance liquid chromatography coupled with mass spectrometry (HPLC–MS/MS or HRMS). However, for monitoring the degradation of target compounds at environmentally relevant concentrations, HPLC with fluorescence detection represents a highly sensitive and selective analytical approach, widely applied for the determination of fluoroquinolones in aqueous matrices.

Previous studies have demonstrated that chromatographic methods are suitable for accurately tracking the decay of parent compounds, whereas the identification of intermediate species and detailed transformation pathways relies on mass spectrometric techniques [47,48].

Therefore, the use of HPLC-FL in the present study provides reliable and robust information on the degradation behavior of the target antibiotics.

Despite the absence of structural identification of the final products, the results provide relevant insights into the effectiveness of the catalytic system in promoting the transformation of fluoroquinolones. Future studies involving mass spectrometry and toxicity assays are recommended to enable detailed identification of the intermediates formed and assessment of their potential environmental impacts.

4. Conclusions

The Ag/TiO_2 (0.15 wt% Ag) thin films employed under UVA irradiation ($\lambda = 365$ nm) demonstrated effective photocatalytic performance for the degradation of ciprofloxacin, norfloxacin, and levofloxacin. The immobilized photocatalytic system consistently outperformed direct photolysis, promoting faster degradation of the parent compounds and enhanced removal of fluorescent transformation products, indicating more complete oxidative pathways.

Kinetic evaluation indicated that the degradation profiles were well described by a pseudo-first-order model, with higher apparent rate constants obtained in the presence of the Ag/TiO_2 film. Statistical analysis (ANOVA) confirmed the significance of these differences and supported the robustness of the photocatalytic system. The performance was maintained in real water matrices, with compound-dependent matrix effects observed, particularly for levofloxacin, demonstrating applicability under environmentally relevant conditions.

In addition, the Ag/TiO_2 films preserved their structural and functional integrity after more than 645 cumulative hours of operation, without the need for regeneration, confirming their long-term operational stability.

Taken together, these results support the suitability of immobilized Ag/TiO_2 (0.15 wt% Ag) films for photocatalytic water treatment applications targeting fluoroquinolone antibiotics, from a process-oriented perspective that emphasizes durability, reproducibility, and applicability under realistic conditions.

Although this study demonstrated the effectiveness and operational stability of the Ag/TiO_2 (0.15 wt% Ag) film for the degradation of fluoroquinolones under UVA irradiation, some limitations remain that should be addressed to further advance the system toward broader application.

The characterization of degradation byproducts was based on chromatographic profiles and fluorescence detection, which provided relevant information regarding degradation behavior. However, complementary analyses using techniques such as liquid chromatography coupled with mass spectrometry (LC–MS/MS) would enable direct structural identification of transformation products, allowing a more detailed evaluation of degradation pathways and potential toxicological relevance.

In addition, the experiments were conducted in a batch reactor under controlled laboratory conditions. The evaluation of the Ag/TiO_2 film in

continuous-flow systems and at pilot scale represents an important step toward assessing its performance under conditions closer to practical implementation. Future studies may also investigate the application of this immobilized photocatalytic system to other classes of emerging contaminants, contributing to a broader assessment of its versatility and limitations.

Overall, the results obtained in this study provide a consistent basis for further development of immobilized photocatalytic systems, indicating that Ag/TiO_2 thin films are suitable for the treatment of fluoroquinolone-contaminated water under environmentally relevant conditions.

CRediT authorship contribution statement

Auro A. Tanaka: Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition, Conceptualization. **De Menezes Alan S.:** Writing – review & editing, Formal analysis. **Karla C.M. de Araujo:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alencar Luciana M. R.:** Writing – review & editing, Formal analysis, Data curation. **Clenilton C. dos Santos:** Writing – review & editing, Funding acquisition, Formal analysis. **Mayara C. Sá:** Writing – review & editing, Visualization, Formal analysis, Data curation. **Adriana B. Araújo:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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