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Article

Eletrospun Nanofiber Dopped with TiO₂ and Carbon Quantum Dots for the Photocatalytic Degradation of Antibiotics

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Abstract: Novel photocatalysts were synthesized through the association of carbon quantum dots (CQDs) with commercial (P25) titanium dioxide (TiO₂) by sonication. The resulting TiO₂/CQDs composite was then incorporated into the polyamide 66 (PA66) biopolymer nanofibers using the electrospinning technique, considering a composite nanoparticles-to-polymer ratio of 1:2 in the electrospinning precursor solution. The produced nanofibers presented suitable morphology and were tested for the photocatalytic degradation under simulated solar radiation of 10 mg/L of amoxicillin (AMX) and sulfadiazine (SDZ), in phosphate buffer solution (pH 8.06) and river water, using 1.5 g/L of photocatalyst. The presence of the photocatalyst increased the removal of AMX in phosphate buffer solution by 30 times, reducing the AMX degradation half-life time from 62 ± 1 h (without catalyst) to 1.98 ± 0.06 h. Moreover, SDZ degradation half-life time in phosphate buffer solution was reduced from 5.4 ± 0.1 h (without catalyst) to 1.87 ± 0.05 h in the presence of the photocatalyst. Furthermore, the PA66/TiO₂/CQDs were also efficient in river water samples, and maintained their performance in at least three cycles of SDZ photodegradation in river water. The presented results evidence that the produced photocatalyst can be a promising and sustainable solution for antibiotics' efficient removal from water.

Keywords: water treatment; pharmaceuticals; electrospinning; photocatalysis; amoxicillin; sulfadiazine

1. Introduction

Wastewater treatment plants are inefficient for removing antibiotics, so developing more effective methods for eliminating these contaminants from aqueous effluents is essential to reduce their entrance into natural waters. One of the most consumed antibiotics worldwide is amoxicillin (AMX), from the penicillin family, which has been included in the last watch lists published in the context of the European Council Water Framework Directive (3rd watchlist (Decision 2020/1161) and 4th (Decision 2022/1307)). AMX is often detected in the aquatic environment due to the continuous disposal of contaminated effluent, which could increase antimicrobial resistance. Sulfadiazine (SDZ), a sulfonamide, is also a widely used broad-spectrum antibiotic, utilized for treating or preventing bacterial infections in both humans and livestock due to its therapeutic efficacy and affordable cost [1,2]. SDZ and AMX chemical stability and nonbiodegradability promote their persistence in aquatic environments over a long period, impacting human health, being toxic to several organisms, and inhibiting the nitrification process in activated sludge systems [3–6]. The concentrations of SDZ and AMX found in surface and groundwater can range from ng/L to µg/L, while in wastewater increases up to mg L⁻¹ [2,7,8]. Thus, their persistence in the environment may result in antimicrobial resistance and organism distress, causing a serious environmental issue [9].

The application of solar-driven photocatalysis, an advanced oxidation process, using a recoverable and reusable photocatalyst could be a sustainable alternative to efficiently remove antibiotics from water resources. The semiconductor titanium(IV) dioxide (TiO₂) is among the most used photocatalysts due to its advantages, such as strong oxidizing power, commercial availability, economic feasibility, non-toxicity, and biological and chemical inertness [10,11]. However, TiO₂-based photocatalysts are associated with some drawbacks: (i) large band gap energy, restricting the use of TiO₂ primarily with ultraviolet (UV) light; (ii) rapid electron-hole recombination; and (iii) difficult recovery from aqueous systems (where ultrafiltration, for example, is required) making it difficult to reuse, increasing the cost of the treatment process [12].

Carbon quantum dots (CQDs) are zero-dimensional carbon-based semiconductor nanoparticles, possessing several advantages such as biocompatibility, low toxicity, high photostability, strong absorption band, chemical stability, and photoluminescence (PL). These carbon spheres (or quasi-spherical) have predominantly sp² carbon fused by diamond-like sp³ hybridized carbon intersections [13,14]. In recent years, CQDs have emerged as an efficient approach to enhance the catalytic performance of photocatalysts, especially TiO₂, under visible light [15,16]. The association of CQDs with TiO₂ can improve the catalytic performance due to CQDs' suitable band gap, exceptional electron donor/acceptor properties, and exceptional electron transfer features [12,14,17,18].

The immobilization of the photocatalyst has been seen as an alternative to promote easy recovery and reuse from treated water. Polymers such as polyvinylidene fluoride (PVDF), poly(vinyl pyrrolidone) (PVP), polyacrylonitrile (PAN), poly(lactic acid) (PLA), polyether sulfone (PES), and polyamide-6 (PA-6) have been used as polymer matrices to support TiO₂ based-photocatalysts [19,20]. Within the methods used for immobilizing photocatalysts in polymeric matrices, electrospinning has gained substantial attention due to its effectiveness and versatility [19], producing nanofibers with high surface area and porosity [21,22].

The nanofibers-TiO₂ composites have shown great results in the removal of different pollutants, such as organic dyes (methyl orange, rhodamine B, and methylene blue) and antibiotics (sulfamethoxazole and enrofloxacin) [23–25]. Deals et al. [26] incorporated TiO₂ nanoparticles in polyamide 6 (PA6) fibers by electrospinning and observed a good photocatalytic performance, in the degradation of methylene blue (MB). However, in this study, UV light irradiation was used and the photocatalyst reuse was not attempted. In order to use visible light, Almeida et al. [23] prepared TiO₂ and graphene oxide (GO) composites, and incorporated them in poly(vinylidene difluoride-co-trifluoroethylene) (P(VDF-TrFE)) fibers for the photodegradation of MB. Despite the good photocatalytic results, the recovery and reuse of the catalyst were not performed. Recently, Lin et al. [24] incorporated TiO₂/GO composites in PAN membranes for the photodegradation of two antibiotics (5 mg L⁻¹), sulfamethoxazole (SMX) and enrofloxacin (ENR). Under visible light irradiation, TiO₂/GO/PAN enhanced the removal of these antibiotics, achieving a total removal after 180 min, with approximately 50% attributed to adsorption. Furthermore, this TiO₂/GO/PAN composite maintained a good performance after 5 cycles, although requiring a washing step after each use.

In this work, a TiO₂/CQDs composite was incorporated in polyamide 66 (PA66) nanofibers by electrospinning and used as a photocatalyst in the removal of antibiotics from different water matrices. Furthermore, the recovery and reusability of the polymeric photocatalyst was evaluated. In previous studies, TiO₂/CQDs composites showed excellent photocatalytic efficiency, under solar light irradiation, for the degradation of antibiotics from water [18,27]. Electrospun PA66 nanofibers were selected for this work due to their insolubility in water, good chemical and thermal resistance, high mechanical strength, and low cost [28,29].

2. Experimental Section

2.1. Synthesis of carbon quantum dots (CQDs)

CQDs with citric acid and urea were prepared by a hydrothermal treatment adapted from Silva et al.[30]. Briefly, citric acid (3.0 g) and urea (1.0 g) were mixed with 10 mL of ultrapure water and

placed into a 70 mL autoclave for 5 h at 180 °C; then, the largest particles were removed by centrifugation at 5000 rpm for 30 min, using a centrifuge (SIGMA 4-10) and the remaining solution was purified by cycles (5 - 7) of precipitation with propan-2-ol and centrifugation at 5000 rpm for 10 min. When the CQDs were aggregated at the bottom, the remaining propan-2-ol was removed and the CQDs were dried at 50 °C.

2.2. Synthesis of TiO₂/CQDs composite

The TiO₂/CQDs composite was synthesized by an easy sonication methodology. Briefly, 1.00 g of TiO₂ powder was dispersed in 30 mL of ethanol in a flask in an ultrasonic bath at 70 °C for 5 min. Then, 0.833 mL of an aqueous solution of 50 g/L of CQDs was added and left to react for 6 h at 70 °C in the ultrasonic bath to obtain the composite with 4% (w/w) of CQDs in TiO₂. Then, the composite was dried at 75 °C.

2.3. Preparation of PA66 nanofibers containing TiO₂/CQDs by electrospinning

The preparation of the polymer solution involved dissolving 0.5 g of PA66 (Polyamide66 or Nylon66) in 5 mL of 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) at room temperature, stirring at 500 rpm until complete dissolution. TiO₂/CQDs (0.25 g) were then reduced to powder in a mortar, sieved through a granulometric sieve with a pore size of 40 µm, and added to the polymer solution. After ultrasonication for 10 minutes to reduce nanoparticle aggregates, the mixture was stirred vigorously to ensure uniform dispersion. For electrospinning (**Figure 1A**), the polymer suspension with TiO₂/CQDs was introduced into a syringe fitted with an 18G needle at a constant flow rate of 2 mL/h applied to the pump. An electric field of 20 kV was applied between the needle and the collector, placed precisely 10 cm apart, to facilitate the formation of uniform polymer fibers on the surface of the collector.

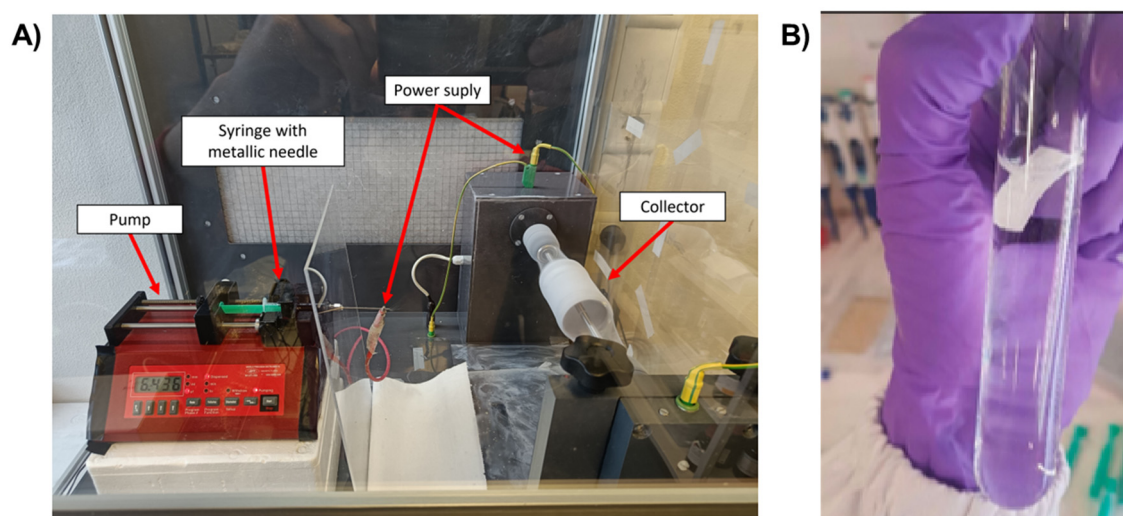


Figure 1. (A) System used for the production of nanofibers (E-fiber EF 100). (B) Photocatalytic experiment of AMX solution in PBS containing the PA66/TiO₂/CQDs nanofibers.

By carefully controlling these electrospinning parameters, a uniform and controlled deposition of polymeric fibers containing the composite (PA66/TiO₂/CQDs) on the collector surface was achieved. The nanofibers were prepared using the ratio of 1:2 TiO₂/CQDs:PA66 (w/w).

As a control, PA66 nanofibers without the TiO₂/CQDs composite were also prepared using the same electrospinning parameters.

2.4. Nanofibers characterization

The morphology, size, and composition of the produced fibers were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), using a scanning

electron microscope (Hitachi SU70) operating at an accelerating voltage of 2 kV. Before SEM analysis, a conductive carbon thin film was deposited onto the fibers using a carbon rod coater (Emitech K950X). The diameter range of fibers was measured by SEM images using ImageJ 1.53k analysis software (NIH, <https://imagej.nih.gov/ij/>). The average diameter and diameter distribution were determined by measuring 120–140 random fibers from the SEM images.

The crystallinity of the nanofibers was analyzed by X-ray diffraction (XRD) using a Malvern Panalytical Empyrean diffractometer with a Cu anode (K- α 1.54060 Å wavelength) handled at 45 kV and 40 mA in a 2 θ range of 3–70°, at 25 °C.

Fourier transform infrared with attenuated total reflectance (FTIR-ATR) spectroscopy (Avatar 360 Thermo Nicolet spectrometer) was used to evaluate the chemical composition of PA66 and PA66/TiO₂/CQDs nanofibers. For this, each sample was placed on the ATR window and scanned in the 500 – 4000 cm⁻¹ range, with a resolution of 2 cm⁻¹ in transmittance mode, and presented as an average of 64 readings.

2.5. Water matrices characterization

For the photocatalysis experiments, two water matrices were used in this study, namely: phosphate buffer solution (PBS, pH 8.06) and river water. River water was collected between May and June of 2024 in Douro River at Marina Santiago Melres (Gondomar, Portugal, pH 7.08) (41°04'21.8"N, 8°24'53.9"W), filtered through 0.45 µm nitrocellulose membrane filters (Millipore), stored in the dark at 4 °C, and used for no longer than 15 days after collection. Both water matrices were characterized by measuring pH, salinity (PSU), conductivity (µS/cm), total dissolved solids (TDS), and dissolved oxygen (DO, %), using a Multi 3320 m from WTW.

Dissolved organic carbon was also measured using a Total Organic Carbon analyzer, TOC-VCPH, from Shimadzu. For that purpose, a stock solution of 1000 mg/L potassium hydrogen phthalate (KHC₈H₄O₄) was prepared in ultrapure water. The calibration curve was performed using standard solutions of KHC₈H₄O₄ in ultrapure water (0.0-5.0 mg/L), by dilution of proper amounts of the stock solution. The coefficient of determination (R²) and limit of detection (LOD) for the calibration curve obtained were 0.9991 and 0.34 mg/L, respectively. Samples were filtered using a syringe filter of PVDF 0.22 µm (Whatman), and acidified with 2% (v/v) of HCl 2 mol/L and covered with Parafilm M®, previously to the analysis. The water matrices characterization values can be found in **Table 1**.

Table 1. Characterization values of the water matrices used.

Matrix	pH	Conductivity (µS cm ⁻¹)	Salinity (PSU)	TDS (mg L ⁻¹)	DO (%)	TOC (mg L ⁻¹)
PBS	8.06 ± 0.01	105	0.05	53	88	1.81 ± 0.02
River Water	7.08 ± 0.01	171	0.1	101	120.5	4.8 ± 0.1

2.6. Photocatalytic experiments

As described elsewhere [18,30], irradiation experiments were carried out in a solar radiation simulator Solarbox 1500 (Co.fo.me.gra, Italy) equipped with a xenon arc lamp (1500 W) and UV filters that limit the transmission of light below 290 nm. All experiments were performed with a constant irradiation of 55 W m⁻² (290–400 nm), which corresponds to 550 W m⁻² in the spectral range, according to the manufacturer. The level of irradiance and temperature was monitored by a multimeter (Co.fo.me.gra, Italy) equipped with a UV 290–400 nm band sensor and a black standard temperature sensor. A parabolic reflection system was used to ensure irradiation uniformity in the chamber, which was kept refrigerated by an air-cooling system.

Antibiotics aqueous solutions (20 mL, 10 mg L⁻¹) were irradiated throughout time, in triplicate, in quartz tubes (internal diameter × height = 1.8 × 20 cm) to obtain the respective kinetic photodegradation curves in the absence of photocatalyst. As for the photocatalytic experiments, the

irradiation was carried out under the same conditions, but in the presence of the photocatalyst (PA66/TiO₂/CQDs, 1.5 g L⁻¹, **Figure 1B**). Each set of experiments was accompanied by dark controls under identical conditions except for irradiation (quartz tubes covered by aluminum foil), maintained inside the solar simulator during the same time as the irradiated solutions. Aliquots (1.0 mL) of replicates and dark controls were withdrawn at pre-set irradiation times (t, h), stored in the dark at 4 °C and analysed within 24 h for the antibiotic concentration (details are given in section 2.7. Chromatographic analyses). The same experiments were carried out in the presence of the PA66 fibers (1.5 g/L), to evaluate the contribution of the fibers in the removal of the antibiotics under study.

The remaining concentration of antibiotic in irradiated solutions (C) was compared with that in the respective dark control (C₀) for determining the percentage of degradation at each irradiation time (t, h). GraphPad Prism 8 was used to determine the fittings of experimental data to the pseudo first-order kinetic equation $C/C_0 = e^{-kt}$, where k is the pseudo first-order degradation rate constant (h⁻¹). Also, antibiotics' half-life times (t_{1/2}) were calculated as $\frac{\ln(2)}{k}$.

2.7. Chromatographic analysis

Quantitative analysis of the antibiotics in the aqueous phase was performed using high-performance liquid chromatography (HPLC). The device consisted of a Waters Alliance 2695 Separations Module equipped with a Waters 2487 Dual Absorbance detector. Separation was carried out using a 150 mm × 4.6 mm i.d. ACE® C18 column-PFP (5 µm particle size) connected to a 4.6 mm i.d. ACE® 5 C18 guard column at 25 °C. The mobile phase consisted of methanol: 0.1% formic acid, 20:80 (v/v) for both AMX and SDZ, at a flow rate of 0.8 mL min⁻¹. Before use, the mobile phase was filtered through a 0.2 µm polyamide membrane filter (Whatman). Samples and standards were filtered by a syringe filter of PTFE 0.22 µm (Labfil®, Alwsci). The volume of injection was 60 µL for AMX and 20 µL for SDZ, while the detection of AMX was performed at 230 nm and of SDZ was obtained at 270 nm. In order to obtain the calibration curve for each matrix, the corresponding standard solutions, with concentrations between 0.1 and 10 mg/L, were prepared from the stock solutions in PBS (10 mg/L) and analysed in triplicate. The linear regression equations for each antibiotic were obtained and the respective limits of detection (LOD), in mg/L, were determined by $[LOD] = \frac{(3 \times S_b)}{m}$, where S_b is the standard deviation of the y-interception and m is the slope.

3. Results and Discussion

3.1. Preparation of PA66 nanofibers containing TiO₂/CQDs by electrospinning

During the electrospinning process, the flow of the polymer solution at the tip of the needle was steady, and there were no current fluctuations. The resulting fibers were white in appearance and exhibited a high degree of flexibility. For the PA66 fibers, SEM images (**Figure 2A and B**) presented homogeneous fibers with an average diameter of 253 ± 55 nm, and no beads or crystallites were observed on the surface of the fabricated fibers. However, SEM images of PA66/TiO₂/CQDs (**Figure 2C and D**) revealed that the fibers exhibited increased roughness and greater heterogeneity, with diameters ranging around 300 ± 82 nm, indicating the incorporation of TiO₂/CQDs into the fibers.

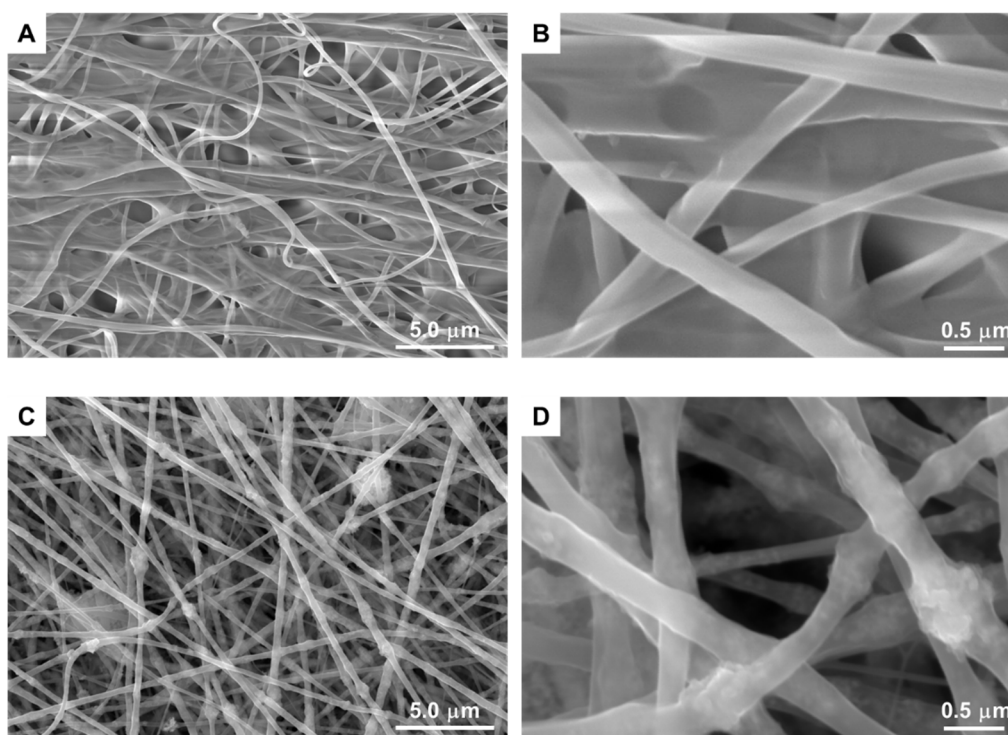


Figure 2. SEM images of PA66 (A and B) and PA66/TiO₂/CQDs (C and D) nanofibers.

EDS analysis (**Figure 3**) confirmed the presence of Ti in the PA66/TiO₂/CQDs fibers, distributed uniformly throughout the polymer, corroborating the uniform distribution of TiO₂/CQDs in the fibers.

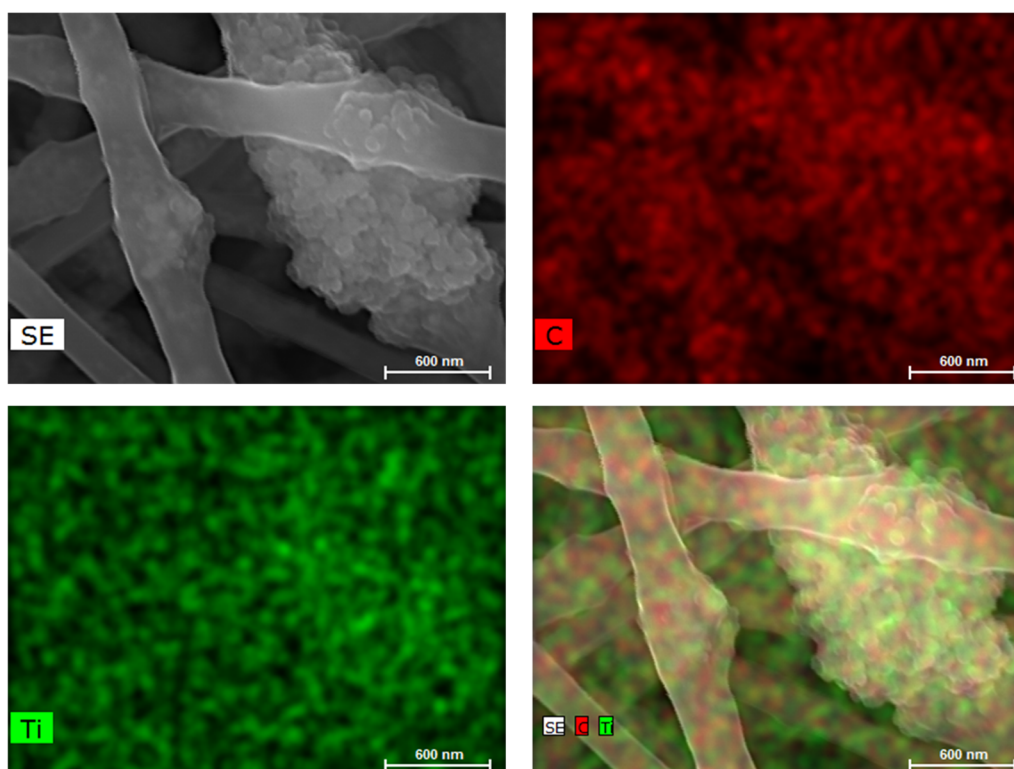


Figure 3. EDS mapping of PA66/TiO₂/CQDs nanofibers, confirming the presence of C and Ti.

X-ray diffractogram of PA66/TiO₂/CQDs nanofibers showed a high similarity with the TiO₂/CQDs XRD pattern (**Figure 4**), indicating the successful incorporation of the TiO₂/CQDs composite. Both XRD patterns showed the presence of TiO₂ anatase and rutile crystalline phases. The

XRD peaks at $2\theta = 25.5^\circ$, 38.0° , 48.3° , 55.3° , 62.9° , and 70.4° , correspond to the anatase (101), (004), (200), (211), (204), and (220) crystal planes, respectively. The rutile pattern can be observed in the reflections at $2\theta = 27.6^\circ$, 36.3° , 41.4° , and 54.1° , respectively corresponding to (110), (101), (111), and (211) crystal planes. These results are in accordance with the previous works and with the standard pattern (Joint Committee on Powder Diffraction Standards (JCPDS)) for anatase TiO_2 (card No. 00-021-1272) and rutile TiO_2 (card No. 00-021-1276) [31,32]. Moreover, the broad peaks at 2θ angles of 20.9° and 23.5° of the PA66/ TiO_2 /CQDs nanofibers could be attributed to the presence of the PA66 polymer [33,34].

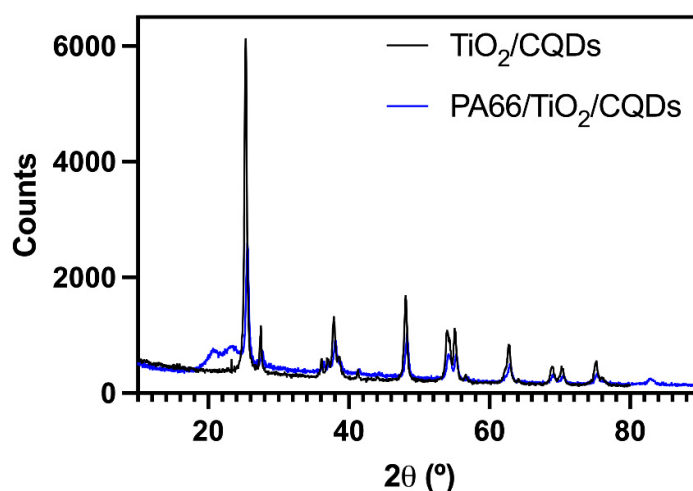


Figure 4. X-ray diffraction pattern of TiO_2 /CQDs and PA66/ TiO_2 /CQDs composites.

FTIR-ATR spectra of PA66 and PA66/ TiO_2 /CQDs (Figure 5) showed the presence of the same peaks at 3296 and 3084 cm^{-1} corresponding to the amino group stretching vibrations, 2932 and 2860 cm^{-1} from stretching vibrations of CH_2 , 1634 cm^{-1} attributed to the stretching vibration of the amide carbonyl group, 1538 cm^{-1} from bending and stretching vibrations of $-\text{NH}$, and 1464 cm^{-1} corresponding stretching vibrations of CH_2 [35,36]. Furthermore, the PA66/ TiO_2 /CQDs presented a broad peak at 666 cm^{-1} that can be attributed to the stretching of $\text{Ti}-\text{O}$ bonds [30]. These results indicated that the composite was incorporated into the fibers without affecting the polymer formation.

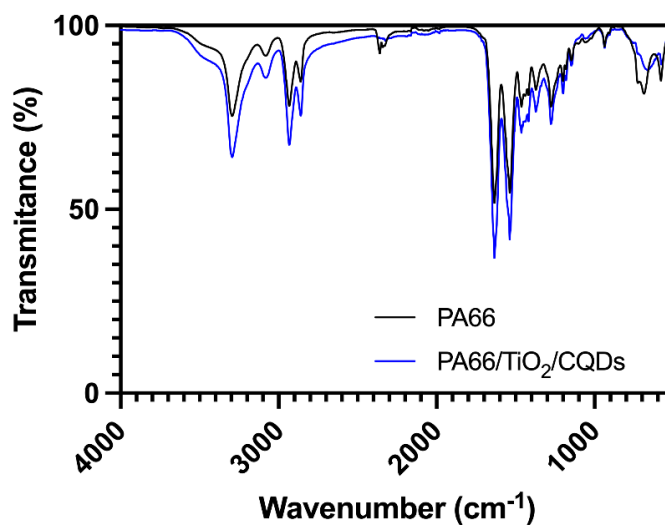


Figure 5. FTIR-ATR of PA66 and PA66/ TiO_2 /CQDs nanofibers.

3.2. Photocatalytic experiments

In previous works, TiO₂/CQDs composites (500 mg L⁻¹) evidenced good performance as photocatalysts in the solar-driven removal of antibiotics from water resources [18,30]. As mentioned before, these composites have two main setbacks: recovery from treated water and reuse. Therefore, to address these disadvantages, the TiO₂/CQDs composite here produced was incorporated in nanofibers of PA66 with a ratio of 1:2 TiO₂/CQDs:PA66 (*w/w*). To maintain the photocatalyst dosage used in previous works (0.5 g L⁻¹ of TiO₂/CQDs) [18,30], 1.5 g L⁻¹ of PA66/TiO₂/CQDs was used for the photocatalytic experiments.

For each antibiotic, photodegradation kinetics studies (**Figure 6**) were carried out in (i) the absence of the photocatalyst (photolysis), (ii) with bare PA66 fibers, and (iii) with PA66/TiO₂/CQDs photocatalyst. The kinetics parameters [rate constants (*k*, h⁻¹), determination coefficient (*R*²), and half-life times (*t*_{1/2}, h)] for photolysis and photocatalytic experiments carried out in PBS and river water, for both antibiotics, were obtained by applying pseudo-first-order equation fittings (**Table 2**).

For AMX, initially, the comparison between photolysis, bare fiber PA66, and PA66/TiO₂/CQDs photocatalyst was performed in PBS. The results showed that the bare fiber PA66 and the photolysis had similar behavior (**Figure 6A**), showing almost no AMX removal after 6 h of irradiation, demonstrating that the removal of AMX was not impacted by the polymer. The rate of removal of AMX has greatly increased with the incorporation of TiO₂/CQDs in the PA66 fibers (**Table 2** and **Figure 6A**). The application of PA66/TiO₂/CQDs was able to remove AMX from water much faster than only photolysis, increasing the kinetic rate by around 30 and 17 times in PBS and river water, respectively.

In fact, the *t*_{1/2} decreased from 60 ± 1 h (in the absence of photocatalyst) to 1.98 ± 0.06 h when the PA66/TiO₂/CQDs photocatalyst was applied in PBS (pH 8.06). Furthermore, the results showed a good AMX removal even in river water, reducing the *t*_{1/2} for the AMX removal to 3.52 ± 0.09 h. In this case, the photodegradation of AMX in river water was lower when compared to PBS, which can be attributed to the matrix complexity or the pH. River water presented a higher content of organic matter than PBS (**Table 1** shows higher values of TOC than PBS), thus, the photocatalyst could be used to degrade organic matter present in this matrix at the same time as AMX, having a competitive behavior in the photodegradation. Moreover, the literature reports that the photodegradation of AMX is influenced by the matrix pH, being faster at higher pH values [6].

A control was performed during the photocatalysis experiments, where the same experimental conditions were applied, but the tubes were maintained in complete darkness. These controls confirmed that all the antibiotic removal can be attributed only to photodegradation, excluding other processes like adsorption and thermal decomposition.

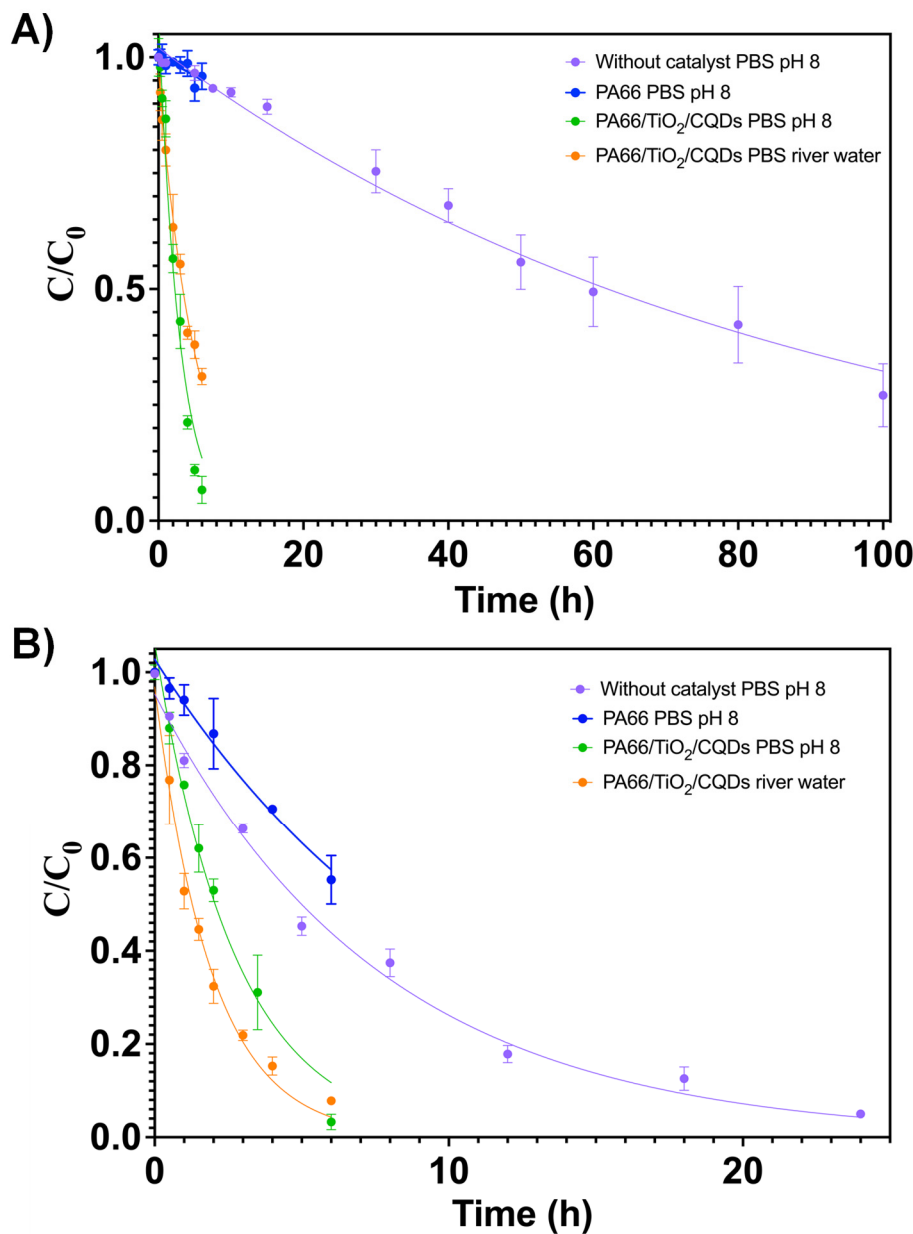


Figure 6. Photodegradation kinetic experimental data together with pseudo-first order fittings for the photodegradation of (A) AMX and (B) SDZ (10 mg L⁻¹), in the absence of the photocatalyst (photolysis), in the presence of PA66 fibers (1.5 g L⁻¹), and with the photocatalyst (PA66/TiO₂/CQDs, 1.5 g L⁻¹), in PBS pH 8.06 or river water. The error bar represents the standard deviation (n=3).

Table 2. Fitting of the experimental data to the pseudo-first order kinetic model, including pseudo-first order rate constants (k (h⁻¹)), determination coefficient (R²) and half-life times (t_{1/2} (h)) obtained for the photodegradation of 10 mg L⁻¹ of antibiotic in PBS (pH 8.06) and river water in absence and presence of the photocatalyst. Note: SD is the standard deviation (n = 3).

Antibiotic	Matrix	Catalyst	k ± SD (h ⁻¹)	R ²	t _{1/2} (h)
AMX	PBS	n.a.	0.012± 0.002	0.9572	60 ± 1
	PBS	PA66/TiO ₂ /CQDs	0.35± 0.01	0.9625	1.98 ± 0.06
	River water	PA66/TiO ₂ /CQDs	0.197± 0.005	0.9702	3.52 ± 0.09
SDZ	PBS	n.a.	0.129± 0.003	0.9887	5.4 ± 0.1

PBS	PA66/TiO ₂ /CQDs	0.37± 0.01	0.9649	1.87 ± 0.05
River water	PA66/TiO ₂ /CQDs	0.52± 0.02	0.9641	1.33 ± 0.05

n.a.: non-aplicable; n.a.: Not determined

As for AMX, the SDZ removal was studied for all the different conditions in PBS, and then, the photocatalyst performance was tested in river water (**Figure 6B** and **Table 2**). The bare fiber PA66 showed a slower kinetic rate of photodegradation of SDZ than photolysis, indicating that the PA66 fiber exerts a filter effect that inhibits the photodegradation of SDZ. However, the application of the PA66/TiO₂/CQDs photocatalyst was not affected by this phenomenon, as verified by a significant increase in the removal of SDZ. In fact, the $t_{1/2}$ of SDZ decreased from 5.4 ± 0.1 h to 1.87 ± 0.05 h with the application of the photocatalyst in PBS. SDZ removal was faster in river water than in PBS, with a $t_{1/2}$ decrease from 1.87 ± 0.05 h to 1.33 ± 0.05 h. This evidenced that the matrix slightly affects SDZ photodegradation, which is in accordance with literature where the same behavior was observed [37]. As for the results of the dark controls of SDZ, it was confirmed that all the observed removal can be attributed to photodegradation, as was found for AMX.

Table 3 presents some studies reported in the literature regarding the photocatalytic degradation of AMX and SDZ using TiO₂-based catalysts and simulated solar light irradiation. It is important to observe that a direct comparison between these photocatalysts is complex since different parameters were used, such as antibiotic concentration and matrix pH. For example, Gao et al. [38] obtained one efficient photocatalyst for the degradation of AMX (5 mg L⁻¹) in ultrapure water, with a constant rate of 0.0614 min⁻¹, preparing a composite based on TiO₂, graphite carbon nitride (g-C₃N₄), and silver nanoparticles. Meanwhile, Thi et al. [39] coupled TiO₂ to ZnO nanoparticles to remove AMX (50 mg L⁻¹) by photocatalysis in the presence of O₃, obtaining a k ranging from 0.0032 to 0.0198 min⁻¹ when the pH varies from 3 to 11. Regarding SDZ removal, Louros et al. [27] prepared TiO₂/CQDs composites (by an in situ method), obtaining a rate constant of 0.71 ± 0.02 h⁻¹ for the photocatalytic removal of this antibiotic (10 mg L⁻¹) in PBS (pH 8.3), under solar irradiation. Also, Silva et al. [18] prepared similar composites using TiO₂ P25, achieving better photocatalytic performance with a k of 4.81 ± 0.06 h⁻¹, in PBS pH 8.6.

Table 3. Literature studies regarding the photocatalytic degradation of AMX and SDZ.

Antibiotic	[Antibiotic] (mg L ⁻¹)	Matrix	Photocatalyst	[Catalyst] (g L ⁻¹)	k (h ⁻¹)	Ref.
AMX	5	Ultra-pure Water	Ag/TiO ₂ (P25)/C ₃ N ₄	1.0	3.68	[38]
	50	Distilated water pH 9.0	TiO ₂ /ZnO	0.1	0.47	[39]
	100	Distilated water pH 6.7	Chitosan/TiO ₂ (P25)	*	0.56 ± 0.01	[40]
	10	PBS pH 8.06	TiO ₂ /CQDs/PA66	1.5	0.35± 0.01	This work
	10	River water	TiO ₂ /CQDs/PA66	1.5	0.197± 0.005	This work
SDZ	10	PBS pH 8.3	TiO ₂ /CQDs	0.5	0.71 ± 0.02	[27]
	10	PBS pH 8.6	TiO ₂ (P25)/CQDs	0.5	4.81 ± 0.06	[18]
	10	*	Magnetic biochar/TiO ₂	0.1	0.124 ± 0.008	[41]

10	PBS pH 8.06	TiO ₂ /CQDs/PA66	1.5	0.37± 0.01	This work
10	River water	TiO ₂ /CQDs/PA66	1.5	0.52± 0.02	This work

* no information available

As a proof of concept, some recovery and reuse studies were performed, using PA66/TiO₂/CQDs in subsequent cycles for the removal of SDZ from river water (**Figure 7**). The results showed that until the 3rd cycle of reuse, the same removal of SDZ was obtained. In fact, even after 3 cycles, it was possible to remove 88% of SDZ in river water in 4 h, a slightly higher value than in the 1st cycle. Thus, the results here presented evidence the efficiency and stability of the PA66/TiO₂/CQDs photocatalyst and the potential to be applied to remove antibiotics from water environments. Comparatively to the literature (**Table 3**), for AMX, both Gao et al. [38] and Thi et al. [39] performed reuse cycles for antibiotic removal. On one hand, Gao et al. tested until the 4th cycle with a gradual small loss of efficiency at each cycle, concluding that the photocatalyst maintained high catalytic activity after four cycles and, therefore, has excellent stability in visible light photodegradation reactions. On the other hand, Thi et al. also tested the photocatalyst for 4 cycles of reutilization, the wash and thermic treatment of the photocatalyst after each cycle, and verified a small drop (5%) in AMX mineralization efficiency. Thus, the authors conclude that the photocatalyst used maintained its stability and catalytic activity for the removal of AMX from wastewater. For SDZ, only Louros et al. [41] performed the recovery and reuse of the materials up until the 5th cycle. In this case, the authors found no significant differences between $t_{1/2}$ obtained for the successive cycles so the results showed after-use recovery photocatalysts, excellent photostability, and reusability of this photocatalyst.

The PA66/TiO₂/CQDs photocatalyst developed in this study presented an average performance when compared with others found in the literature. However, these nanofibers have the potential to be easily reused, allowing their use as sustainable photocatalysts for water treatment and contributing to water circularity.

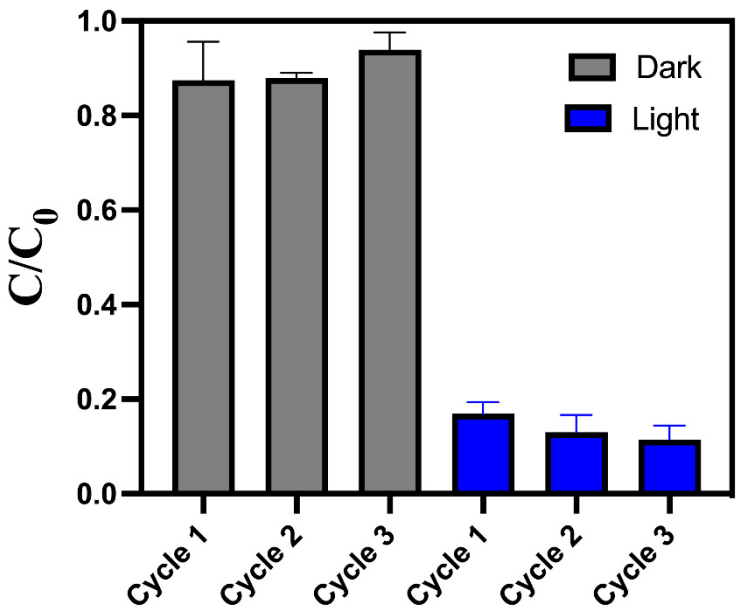


Figure 7. Reuse cycles of PA66/TiO₂/CQDs (1.5 g L⁻¹) in the photodegradation of SDZ (10 mg L⁻¹), in the absence of light (Dark, grey bars) and with irradiation for 4 h (Light, blue bars), in river water. The error bar represents the standard deviation (n=3).

4. Conclusions

TiO₂/CQDs composite was successfully incorporated into polyamide 66 (PA66) fibers by electrospinning, using a nanoparticles-to-polymer ratio of 1:2. The characterization of the resulting composite (PA66/TiO₂/CQDs) confirmed the presence of TiO₂/CQDs in its composition. Meanwhile, the degradation studies demonstrated that PA66/TiO₂/CQDs improved the removal of AMX and SDZ under solar irradiation, in PBS pH 8.06 and river water. Under the presence of the composite, the $t_{1/2}$ of AMX was reduced 30 and 17 times, in PBS and river water, respectively, when compared with the degradation in the absence of the photocatalyst. For SDZ, the $t_{1/2}$ was 3 and 4 times shorter, for PBS and river water, respectively, compared with the photolysis studies. Furthermore, the PA66/TiO₂/CQDs could be reused at least in three consecutive cycles of the photodegradation of SDZ in river water, consistently achieving a degradation of up to 88% after 4 h. Therefore, PA66/TiO₂/CQDs nanofibers were demonstrated to be efficient photocatalysts under solar irradiation and easy to reuse, having high potential to be used in the removal of antibiotics from aquatic environments.

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