Photocatalytic Degradation of Pharmaceuticals through Bulk and Mesoporous g-C₃N₄/TiO₂ Systems

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Abstract: Background: In recent years, pharmaceutical pollutants have emerged as a growing threat to the environment. To mitigate this situation, heterogeneous photocatalysis has been considered a promising advanced oxidation technology, where TiO₂-based systems have exhibited outstanding efficiency in the degradation of organic compounds.

Objective: In this work, we have studied the photocatalytic performance of the coupled g-C₃N₄/TiO₂ system in the degradation of the pharmaceuticals tetracycline, ciprofloxacin, and ibuprofen. Moreover, the effect of the graphitic carbon nitride (g-C₃N₄) was examined through the study of two different samples, a bulk g-C₃N₄ prepared from the direct calcination of melamine and a mesoporous g-C₃N₄ synthesized through a nanocasting process using SBA-15 silica as hard template.

Methods: The hybrid photocatalysts were prepared by forced hydrolysis of titanium isopropoxide using two g-C₃N₄ samples, a bulk material and a mesoporous one. The samples were characterized by X-ray powder diffraction (XRD), Diffuse Reflectance Spectroscopy (DRS), Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and N₂ adsorption-desorption measurements. The photocatalytic activity was examined through the degradation of tetracycline, ciprofloxacin, and ibuprofen under simulated solar irradiation.

Results: The textural properties of g-C₃N₄ play a preponderant role in the photoactivity of the g-C₃N₄/TiO₂ system. In this sense, high dispersion of the TiO₂ nanoparticles could be obtained using a mesoporous g-C₃N₄ sample. All hybrid photocatalysts exhibit higher degradation rates than the pristine materials, including bare TiO₂. In this regard, the samples with 1 wt.% g-C₃N₄ attained the highest photocatalytic performance in the degradation of tetracycline, ciprofloxacin, and ibuprofen.

Conclusion: The coupling of TiO₂ with graphitic carbon nitride leads to the formation of hybrid photocatalysts with outstanding photoactive properties in the degradation of pharmaceutical pollutants. In this way, the g-C₃N₄/TiO₂ samples can be considered as excellent photocatalysts for the degradation of organic pollutants.

Keywords: g-C₃N₄, TiO₂, photocatalysis, ciprofloxacin, tetracycline, ibuprofen.

1. INTRODUCTION

Pharmaceuticals are natural or synthetic chemicals containing active ingredients with the aim of providing a pharmacological effect to be used for the benefit of human, animal or even plant health [1, 2]. The excessive use of these pharmaceutical compounds has led to their release mainly into aquatic systems, significantly affecting the environment. In this sense, heterogeneous photocatalysis is an advanced oxidation process that has emerged as a promising technique for the removal of organic pollutants in aqueous systems as well as in renewable energy processes [3, 4]. Anatase TiO₂ is considered the most widely used photocatalyst due to its high photocatalytic behavior under UV light. Numerous strategies have been reported to increase the photoactivity of anatase, such as the increase in surface area, doping, the formation of defined morphologies, heterojunctions, and so on [5-8]. The formation of TiO₂-based hetero-
junction systems has gained considerable interest in recent years in order to extend light absorption and decrease the recombination of the photogenerated charge carriers [9, 10].

Graphitic carbon nitride (g-C₃N₄) is a metal-free semiconductor that has been reported to have outstanding photocatalytic activity [11]. Its structure consists of stacked graphite-type layers of carbon and nitrogen atoms formed via sp² hybridization. Bulk g-C₃N₄ is commonly prepared through pyrolysis of melamine at temperatures above 500 °C. This bulk material exhibits a low surface area, less than 10 m²·g⁻¹, and is used as reference material in the study of the photocatalytic behavior of g-C₃N₄ [12]. The graphitic carbon nitride is an ideal candidate to be coupled with TiO₂. For instance, Senthil et al. have reported the preparation of the g-C₃N₄/TiO₂ heterojunction system through a wet impregnation method for the degradation of acid orange 7 (AO7) under visible light irradiation [13]. This coupled system has also been used for the degradation of other organic pollutants such as phenol, formaldehyde, methylene blue, ciprofloxacin, and so on [14-17]. The surface modification of g-C₃N₄ favors a better physical junction with the TiO₂ nanoparticles, providing an adequate transport of the photogenerated charge carriers between both semiconductors. The surface properties of the graphitic carbon nitride can be improved by the formation of controlled mesoporosity via nanocasting using hard templates such as SIO₂ nanospheres, SBA-15, and KIT-6 [18-20].

This work reports the effect of the g-C₃N₄ surface for the deposition of anatase nanoparticles prepared by the forced hydrolysis of titanium isopropoxide. As it will be discussed, a mesoporous g-C₃N₄ favors the dispersion of the TiO₂ nanoparticles, promoting the formation of a g-C₃N₄/TiO₂ heterojunction with outstanding photocatalytic performance in the degradation of tetracycline, ciprofloxacin and ibuprofen under simulated solar irradiation.

2. MATERIALS AND METHODS

2.1. Preparation of g-C₃N₄ Samples

The graphitic carbon nitride was obtained through two routes, i) the thermal polycondensation of melamine (bulk g-C₃N₄) and ii) by nanocasting using SBA-15 as a hard template (mesoporous g-C₃N₄). For the preparation of bulk g-C₃N₄, 10 g of melamine (Sigma Aldrich, 99%) was calcined at 500 °C for 4 h using a semi-closed crucible. The synthesis of mesoporous g-C₃N₄ was carried out using a procedure reported in our previous work [19]. Briefly, 10 g of urea (ACS reagent) was dissolved in 100 mL of methanol containing 2 g of SBA-15 silica and stirred for 1 h. Then, the alcohol was subsequently slowly evaporated at 70 °C. The obtained powder was calcined at 500 °C for 4 h to yield the formation of mesoporous g-C₃N₄. Finally, the SBA-15 silica was removed using a 20% v/v aqueous solution of hydrofluoric acid.

2.2. Preparation of Pristine TiO₂

The bare TiO₂ was synthesized by means of the forced hydrolysis of titanium alkoxide. First, 5 mL of titanium isopropoxide (Sigma Aldrich, 97%) was dissolved in 100 mL of absolute ethanol at room temperature. Then, 5 mL of distilled water was added to force the hydrolysis of the alkoxide, and subsequently, 1.5 mL of concentrated ammonia was added to adjust the pH–9 of the suspension. The resulting mixture was stirred for 1 h and then centrifugated at 6000 rpm for 30 min. The obtained solid was repeatedly washed with distilled water and dried overnight at 80 °C. The solid precursor was calcined at 400 °C for 4 h to obtain the pristine TiO₂ anatase.

2.3. Preparation of g-C₃N₄/TiO₂ Hybrid Photocatalysts

The g-C₃N₄/TiO₂ hybrid systems were synthesized by a sol-gel method using titanium isopropoxide as Ti precursor. In a typical procedure, 5 mL of titanium isopropoxide was added in 100 mL of ethanol (J.T. Baker, ≥ 99.7%) at room temperature. After 30 min of vigorous stirring, a certain amount of bulk or mesoporous g-C₃N₄ powder was added to the clear solution and then the slurry was placed in an ultrasonic bath at 37 kHz for 15 min. Afterward, 5 mL of distilled water and 1.5 mL of concentrated NH₄OH were added to force the hydrolysis of the titanium isopropoxide as well as to adjust the pH value to ~9.0 of the resulting mixture. The suspension was kept under stirring conditions for 1 h. Then, the slurry was centrifuged and washed repeatedly with distilled water. The obtained solid was dried at 80 °C overnight and subsequently calcined at 400 °C for 6 h. Several samples were prepared using different amounts of g-C₃N₄ and were labeled as x-(b)CN and x-(m)CN, where x represents the percentage (w/w) of the g-C₃N₄ in the TiO₂ and b/m represents the bulk and mesoporous g-C₃N₄, respectively.

2.4. Characterization of the Samples

The as-prepared samples were characterized by X-ray diffraction (XRD) on a Siemens D-501 diffractometer with Cu Kα radiation (1.5406 Å). The patterns were recorded in a 20 interval of 10-70° with a step size of 0.05°·s⁻¹ and a time of 1s per step. The crystallite size of TiO₂ was estimated using the strongest intensity of the diffraction peak at 25.2° (20) corresponding to the (101) lattice plane of the anatase, according to the Scherrer equation τ = K·λ·(β·cosθ)⁻¹, where τ is the crystallite size, λ is the X-ray wavelength (0.15406 nm), β is the line width at half-maximum height and K is a dimensionless shape factor, with a value approximately equal to unity [21]. Diffuse reflectance spectra were obtained using a Thermo-Fisher Scientific Evolution 220 UV-Vis spectrophotometer equipped with an integrating sphere for diffuse reflectance measurements. The energy band gap value (Eg) of each sample was calculated by extrapolating a straight line from the absorption curve to the abscissa axis. When α has a value of zero, then E g = hν. ATR-FTIR measurements were recorded by means of a Shimadzu IRAffinity-1S spectrometer. FTIR spectra were measured in the wavenumber range of 4400-400 cm⁻¹. The morphology of the samples was analyzed by field emission scanning electron microscopy (FESEM) using a JEOL JSM 6701F microscope. For the analysis, each powdered photocatalyst was dispersed directly on carbon tape placed in an aluminum sample holder. BET surface area and mean pore size diameter (BJH) were determined by nitrogen adsorption-desorption measurements using a Surface Area & Pore Size analyzer Micromeritics ASAP-2000. The samples were evaluated at −196 °C before pretreatment at 150 °C for 2 h.
2.5. Photocatalytic Tests

The samples were examined by the degradation of three different drugs: tetracycline, ciprofloxacin, and ibuprofen. For each test, 0.2 g of the photocatalyst was added to an aqueous solution of the pharmaceutical pollutant with an initial concentration of 10 mg L\(^{-1}\). The pH value of the aqueous suspensions was less than 5.5. In each case, the resulting suspension was placed in an ultrasonic bath (37 kHz) for 15 min to remove agglomerates from the powdered material. Then, it was left under dark conditions for 1 h to achieve the adsorption-desorption equilibrium between the anti-inflammatory/antibiotic molecules and the particles of the photocatalyst. Afterward, the suspension was irradiated with a 35 W Xe lamp with a radiation intensity of 1,380 \(\mu W \cdot cm^{-2}\). At given times, several aliquots were taken from the system and centrifuged at 4000 rpm for 30 min. The depletion of each pollutant was monitored using a Thermo Scientific Evolution 220 UV-vis spectrophotometer. The concentration was estimated through the evolution of the characteristic absorption band at 357, 270 and 222 nm for tetracycline, ciprofloxacin, and ibuprofen, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the Samples

The g-C\(_3\)N\(_4\)/TiO\(_2\) samples were characterized by X-ray diffraction analysis. (Figs. 1a and 1b) display the diffraction patterns for both heterojunction systems, using bulk- and mesoporous g-C\(_3\)N\(_4\). As seen, the pristine TiO\(_2\) synthesized by forced hydrolysis of titanium isopropoxide shows diffraction peaks related to the anatase phase, according to PDF 12-1272. In addition, no diffraction peaks related to other crystalline structures of TiO\(_2\), such as rutile or brookite, were observed. The graphitic carbon nitride was prepared by two different routes, by a thermal polycondensation (bulk g-C\(_3\)N\(_4\)) and through a partial replication of the SBA-15 hard template (mesoporous g-C\(_3\)N\(_4\)). Both g-C\(_3\)N\(_4\) samples exhibit two diffraction peaks at 13.1° and 27.5° (20). The peak at 13.1° is associated with the diffraction plane (100) corresponding to the periodic arrangement of the tris-s-triazine units of the structural framework, whereas the diffraction peak at 27.5° is attributed to the diffraction plane (002) related to the stacking of the conjugated aromatic system of the g-C\(_3\)N\(_4\) material, respectively [22, 23].

For the heterostructured samples, the addition of g-C\(_3\)N\(_4\) during the hydrolysis of the alkoxide modifies the crystallite size of the TiO\(_2\), mainly to the samples with 5% wt. of g-C\(_3\)N\(_4\), as shown in (Table 1). This situation could be related to the exposed surface of the g-C\(_3\)N\(_4\) during the nucleation of the TiO\(_2\), since the higher value in the crystallite size was observed in the system based on the bulk g-C\(_3\)N\(_4\) sample, as shown in (Fig. 1c). It is worth noting that the presence of graphitic carbon nitride does not modify the preparation of the anatase TiO\(_2\), yielding this crystalline material in all samples. Furthermore, no diffraction peaks related to g-C\(_3\)N\(_4\) are noticeable in the hybrid samples, probably due to its low amount in the heterostructured systems. The optical absorption spectra of g-C\(_3\)N\(_4\), TiO\(_2\) and g-C\(_3\)N\(_4\)/TiO\(_2\) samples were performed by UV-vis diffuse reflectance spectroscopy (DRS), as shown in (Fig. 2). The bulk g-C\(_3\)N\(_4\) shows an absorption edge around 457 nm, as it has been reported in previous studies [24, 25]. A slight blue-shift is observed in the mesoporous g-C\(_3\)N\(_4\) sample, which could be related to slight structural differences caused by the synthesis procedure such as a lower degree of condensation and a decrease in the conjugation length [26]. The bandgap values were estimated at 2.71 eV and 2.80 eV for the bulk and mesoporous g-C\(_3\)N\(_4\), respectively. These values demonstrate that graphitic carbon nitride can be excited under visible light irradiation. For pristine TiO\(_2\), the bandgap energy was estimated at 3.07 eV, whereas the g-C\(_3\)N\(_4\)/TiO\(_2\) composites exhibit bandgap values between g-C\(_3\)N\(_4\) and TiO\(_2\) samples, as shown in (Table 1). Furthermore, the values decrease slightly as the content of bulk and mesoporous g-C\(_3\)N\(_4\) increases in the samples. This phenomenon could be related to the formation of intermediate levels by orbital interaction of the pristine g-C\(_3\)N\(_4\) and TiO\(_2\) materials, as it has been discussed by Alcudia-Ramos et al. [27].

The heterojunction systems were also studied through ATR-FTIR analysis. (Fig. 3) shows the g-C\(_3\)N\(_4\)/TiO\(_2\) coupled system developed from g-C\(_3\)N\(_4\) prepared via nanocoating. The mesoporous graphitic carbon nitride shows a broad band centered at 3177 cm\(^{-1}\) which is related to the N=H stretching vibration of the hydrogen atoms linked to the edges of the g-C\(_3\)N\(_4\) [28]. The bands at 1619, 1567, 1412, 1321 and 1245 are commonly attributed to the stretching and rotation vibration modes of the C-N and C=N bonds [29]. The absorption band at 806 cm\(^{-1}\) is related to the
breathing of the tri-s-triazine units from the g-C₃N₄ structure. For pristine TiO₂, the band at 3343 cm⁻¹ is attributed to the symmetrical and asymmetrical stretching vibrations of hydroxyl groups (Ti-OH), whereas the band at 1639 cm⁻¹ is usually associated with water molecules adsorbed on the surface of TiO₂ [30, 31]. The band centered at 408 cm⁻¹ corresponds to the stretching vibration of the Ti-O-Ti bonding. It is worth noting that hybrid samples display a profile similar to pristine TiO₂, probably due to the low g-C₃N₄ content. Similar results were observed for the bulk g-C₃N₄ based system (data not shown).

![Fig. (2).](image1)

**Table 1.** Physicochemical properties of synthesized hybrid photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite Size (nm)</th>
<th>Band Gap (eV)</th>
<th>Surface Area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine TiO₂</td>
<td>8.9</td>
<td>3.07</td>
<td>122.7</td>
</tr>
<tr>
<td>0.5-(b)CN</td>
<td>9.2</td>
<td>3.05</td>
<td>122.5</td>
</tr>
<tr>
<td>1-(b)CN</td>
<td>9.6</td>
<td>3.02</td>
<td>122.3</td>
</tr>
<tr>
<td>2-(b)CN</td>
<td>9.9</td>
<td>3.01</td>
<td>121.1</td>
</tr>
<tr>
<td>5-(b)CN</td>
<td>20.5</td>
<td>2.98</td>
<td>119.9</td>
</tr>
<tr>
<td>0.5-(m)CN</td>
<td>9.0</td>
<td>3.07</td>
<td>124.5</td>
</tr>
<tr>
<td>1-(m)CN</td>
<td>9.8</td>
<td>3.05</td>
<td>126.1</td>
</tr>
<tr>
<td>2-(m)CN</td>
<td>10.6</td>
<td>3.01</td>
<td>130.4</td>
</tr>
<tr>
<td>5-(m)CN</td>
<td>11.5</td>
<td>2.96</td>
<td>133.6</td>
</tr>
<tr>
<td>bulk g-C₃N₄</td>
<td>-----</td>
<td>-----</td>
<td>4.80</td>
</tr>
<tr>
<td>mesoporous g-C₃N₄</td>
<td>-----</td>
<td>2.80</td>
<td>49.8</td>
</tr>
</tbody>
</table>

Fig. (3). FTIR spectra of the g-C₃N₄/TiO₂ samples based on mesoporous g-C₃N₄. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

The morphological features were examined by scanning electron microscopy (SEM). Fig. (4) shows the SEM images of some representative samples of the studied systems, where it can be seen that the morphology of the bulk g-C₃N₄ consists of micrometric particles with irregular shapes (Fig. 4a). It is logical to consider that the synthesis of the graphitic carbon nitride by simple heat treatment and without any morphology directing agent yields a material with undefined shape and uncontrolled size. In fact, this morphology is consistent with that observed in previous works [32]. Fig. (4b) shows the morphology of the mesoporous g-C₃N₄, where the mesoporous structure of the SBA-15 silica was partially replicated. It is worth noting that the loss of mass and densification of the precursor considerably affect the control of a defined morphology. Likewise, the nanotexturing of g-C₃N₄...
Fig. (4). SEM images of (a) bulk g-C₃N₄; (b) mesoporous g-C₃N₄; (c) pristine TiO₂; (d) 1-(m)CN sample.

Fig. (5). (a) N₂ adsorption-desorption isotherm and (b) pore size distribution for pristine TiO₂, bulk and mesoporous g-C₃N₄ samples.
is usually restricted due to the weak interaction of the silica with the nitrogen-rich precursors of the graphitic carbon nitride [33]. On the other hand, pristine TiO$_2$ exhibits a well-defined morphology based on spherical particles with an average diameter of 30 nm. These nanoparticles tend to form agglomerates of hundreds of particles reaching micrometric sizes, as shown in (Fig. 4c). For the g-C$_3$N$_4$/TiO$_2$ systems, the 1-(m)CN sample was chosen as a representative sample of hybrid photocatalysts, as shown in (Fig. 4d). However, the presence of the mesoporous g-C$_3$N$_4$ was not clearly observed, probably due to its low content and/or it was covered by the TiO$_2$ nanoparticles during the preparation of the composites. The surface area values were estimated using the BET method from nitrogen physisorption measurements, as shown in (Fig. 5). The specific surface area of pristine TiO$_2$ was calculated at 122.7 m$^2$·g$^{-1}$, the expected value for the preparation of titanium dioxide by forced hydrolysis of an alkoxide precursor. For bulk g-C$_3$N$_4$, a surface area of 4.8 m$^2$·g$^{-1}$ was estimated, which coincides with the value reported for the direct calcination of melamine [16]. This bulk material is usually used as a reference for the study of the degradation of organic pollutants as well as for its coupling with other photocatalysts [34]. Otherwise, the surface area of the mesoporous g-C$_3$N$_4$ was estimated at 49.8 m$^2$·g$^{-1}$, about an order of magnitude higher compared to bulk g-C$_3$N$_4$. As reported in our previous work, this mesoporous graphitic carbon nitride exhibits a narrow pore size distribution at 3.8 nm, confirming its mesoporous nature [23]. The surface properties of g-C$_3$N$_4$ should strongly condition the deposition of the TiO$_2$ nanoparticles prepared during the hydrolysis of the alkoxide. (Fig. 6) displays the surface area values of the g-C$_3$N$_4$/TiO$_2$ samples prepared using bulk and mesoporous g-C$_3$N$_4$ samples. Two different trends can be observed for the studied systems. First, the system based on bulk g-C$_3$N$_4$ shows a slight decrease in the surface area as the g-C$_3$N$_4$ content increases. This situation could be attributed to a saturation of the TiO$_2$ seeds on the surface of the g-C$_3$N$_4$ during the hydrolysis-condensation process, which would lead to the formation of larger TiO$_2$ particles. Moreover, a higher ratio of bulk g-C$_3$N$_4$ should lead to a decrease in the surface area of the g-C$_3$N$_4$/TiO$_2$ composite. A different situation occurs in the preparation of the coupled system based on the mesoporous g-C$_3$N$_4$. Since it has a surface area around 10 times larger than bulk g-C$_3$N$_4$, the TiO$_2$ seeds can be dispersed over a larger surface favoring their dispersion. In this regard, a gradual increase in the surface area of the hybrid photocatalysts is observed as the amount of the mesoporous g-C$_3$N$_4$ increases. Such dispersion of the TiO$_2$ nanoparticles on the g-C$_3$N$_4$ surface could favor the physical junction between both semiconductors leading to an adequate separation of the photogenerated charge carriers, thus enhancing the photocatalytic performance of the hybrid samples. The performance of the photocatalysts was studied through the degradation of the tetracycline, ciprofloxacin, and ibuprofen pharmaceuticals under simulated sunlight irradiation. It is worth noting that the aqueous solutions of the pharmaceuticals exhibited a negligible decrease in the initial concentration after 4 h of irradiation, denoting their stability in the photolysis process. The degradation of the molecules can be modeled following pseudo-first order kinetics according to the Langmuir-Hinshelwood model. (Fig. 7) displays the reaction rates for the degradation of the tetracycline antibiotic using the bulk and mesoporous g-C$_3$N$_4$-based systems. The reaction rates using graphitic carbon nitride were 0.23x10$^{-6}$ s$^{-1}$ (dash line) and 1.34x10$^{-6}$ s$^{-1}$ (dot line) for the bulk and mesoporous g-C$_3$N$_4$, respectively. For pristine TiO$_2$, the reaction rate was calculated at 1.53x10$^{-6}$ s$^{-1}$. The hybrid photocatalysts exhibit a photoactivity superior to pristine TiO$_2$, where the samples with 1% wt. of g-C$_3$N$_4$ show the highest reaction rates, 8.85x10$^{-6}$ and 15.52x10$^{-6}$ s$^{-1}$ for the samples 1-(b)CN and 1-(m)CN, respectively. Amounts higher than 1% wt. of g-C$_3$N$_4$ provided a gradual decrease in the photoactivity of the composites. According to Palominos et al., the photocatalytic degradation of the tetracycline antibiotic using TiO$_2$ occurs through the direct participation of the hydroxyl radicals and the photogenerated holes in the photoexcited semiconductor [35]. Due to the spectrophotometric determination of the pharmaceutical compounds in this study, it was not possible to elucidate the intermediates formed during the photocatalytic process. However, the mechanism of degradation of the tetracycline is usually explained by open-ring reactions to form low-molecular-weight compounds such as alcohols and organic acids [36].
The g-C3N4/TiO2 systems were also examined for the degradation of ciprofloxacin, as shown in (Fig. 8). Ciprofloxacin is a second-generation fluoroquinolone antibiotic that is frequently used to treat bacterial infections in humans and animals. In a similar way to the degradation of the tetracycline, the samples 1-(b)CN and 1-(m)CN exhibit the higher photocatalytic behavior of both systems with reaction rates of 4.12x10^{-6} s^{-1} and 5.32x10^{-6} s^{-1}, respectively. These values are higher than the reaction rate exhibited by pristine TiO2 (3.2x10^{-6} s^{-1}), demonstrating the effectiveness of the coupled systems. This situation could be attributed to the adequate dispersion of the TiO2 nanoparticles on the surface of the g-C3N4 materials, mainly in the mesoporous graphitic carbon nitride. Previous studies have reported that the photocatalytic degradation of the ciprofloxacin occurs through the loss of the piperazine ring to form the intermediate 7-[(2-aminoethyl)amino]-6-fluoroquinoline, which is subsequently fragmented until its mineralization [37]. The reaction rates calculated for bare g-C3N4 samples were 0.91x10^{-6} s^{-1} and 2.49x10^{-6} s^{-1} for bulk and mesoporous materials, respectively. The outstanding performance of the g-C3N4/TiO2 systems was also verified by the photodegradation of the ibuprofen. It is a nonsteroidal anti-inflammatory drug (NSAID) used widely to relieve any pain in general and is considered one of the most consumed pharmaceuticals in the world [38]. (Fig. 9) displays the estimated pseudo-first-order constant rates for the degradation of ibuprofen using the studied systems. As seen, all samples exhibit higher photoactivity than pristine materials, including bare TiO2. Among them, the 1-(m)CN sample shows the highest photocatalytic performance with a reaction rate of 5.17x10^{-6} s^{-1}, a value around three times higher than that estimated using pristine TiO2 (1.67x10^{-6} s^{-1}). Through ultra-high-performance liquid chromatography coupled to quadrupole-time of flight mass spectrometry, Jiménez-Salcedo and coworkers have detected more than twenty by-products from the photocatalytic degradation of ibuprofen using TiO2 as photocatalyst under UV light irradiation [39]. Méndez-Ar-

![Fig. (8)](image)

**Fig. (8).** Apparent first-order constants for the degradation of ciprofloxacin using the g-C3N4/TiO2 samples. *(A higher resolution / colour version of this figure is available in the electronic copy of the article).*

![Fig. (9)](image)

**Fig. (9).** Apparent first-order constants for the degradation of ibuprofen using the g-C3N4/TiO2 samples. *(A higher resolution / colour version of this figure is available in the electronic copy of the article).*

![Fig. (10)](image)

**Fig. (10).** Schematic diagram of the Z-scheme heterojunction in the g-C3N4/TiO2 system. *(A higher resolution / colour version of this figure is available in the electronic copy of the article).*

As is well-known, the g-C3N4/TiO2 system exhibits a direct Z-scheme charge transfer pathway, as shown in (Fig. 10) [41]. The valence and conduction band potentials of bulk g-C3N4 have previously been calculated at +1.69 and -1.10 eV, respectively [19]. For the anatase TiO2, the reported values are around +2.70 and -0.50 eV for the valence and conduction bands [42]. According to this well-matched band edges potentials, the photoexcited electrons in the conduc-

riaga et al. have proposed that the degradation of ibuprofen using TiO2 as photocatalyst is caused mainly by the hydroxyl radicals generated by the reaction between the water molecules and the positive holes (h+) from the photoexcited semiconductor [40].
tion band of the TiO$_2$ can combine with the photogenerated holes in the valence band of the g-C$_3$N$_4$. This charge transfer helps to extend the lifetime of the holes in the photoexcited TiO$_2$, where chemical oxidation reactions can take place, such as the degradation of organic compounds. In this sense, an adequate interfacial junction favors the special distribution of the photogenerated charge carriers between both semiconductors. This situation has been corroborated in the present work, where a mesoporous g-C$_3$N$_4$ provides a higher dispersion of the TiO$_2$ nanoparticles, improving the photocatalytic performance of the hybrid system. In this way, the g-C$_3$N$_4$/TiO$_2$ system is ideal for the removal of organic pollutants such as pharmaceutical compounds.

CONCLUSION

In summary, the g-C$_3$N$_4$/TiO$_2$ system was prepared by the forced hydrolysis of titanium isopropoxide using bulk and mesoporous g-C$_3$N$_4$ samples. The higher surface area of mesoporous g-C$_3$N$_4$ favors an adequate dispersion of the TiO$_2$ nanoparticles, yielding g-C$_3$N$_4$/TiO$_2$ materials with enhanced photocatalytic performance under simulated sunlight irradiation. The highest photoactivity was reached with the 1-(m)CN sample, with reaction rates of 15.52x10$^{-6}$, 5.32x10$^{-6}$ and 5.17x10$^{-6}$ s$^{-1}$ for the degradation of the pharmaceuticals tetracycline, ciprofloxacin and ibuprofen, respectively. These results confirm the g-C$_3$N$_4$/TiO$_2$ hybrid photocatalysts as excellent candidates for the photocatalytic degradation of organic pollutants.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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