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Photocatalytic Degradation of Pharmaceutical Amisulpride Using g-C₃N₄ Catalyst and UV-A Irradiation

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Abstract: In the present study, the photocatalytic degradation of amisulpride using g-C₃N₄ catalyst under UV-A irradiation was investigated. The photocatalytic process was evaluated in terms of its effectiveness to remove amisulpride from ultrapure and real municipal wastewater. High removal percentages were achieved in both aqueous matrices. However, a slower degradation rate was observed using wastewater as matrix that could be attributed to its complex chemical composition. The transformation products (TPs) were identified with liquid chromatography–mass spectrometry (LC–MS) in both ultrapure and real municipal wastewater. Based on the identified TPs, the photocatalytic degradation pathways of amisulpride are proposed which include mainly oxidation, dealkylation, and cleavage of the methoxy group. Moreover, the contribution of reactive species to the degradation mechanism was studied using well-documented scavengers, and the significant role of h⁺ and O₂^{•−} in the reaction mechanism was proved. The evolution of ecotoxicity was also estimated using microalgae *Chlorococcum* sp. and *Dunaliella tertiolecta*. Low toxicity was observed during the overall process without the formation of toxic TPs when ultrapure water was used as matrix. In the case of real municipal wastewater, an increased toxicity was observed at the beginning of the process which is attributed to the composition of the matrix. The application of heterogeneous photocatalysis reduced the toxicity, and almost complete detoxification was achieved at the end of the process. Our results are in accordance with literature data that reported that heterogeneous photocatalysis is effective for the removal of amisulpride from aqueous matrices.

Keywords: photocatalysis; g-C₃N₄; pharmaceuticals; amisulpride; mechanism; reactive species; transformation products; ecotoxicity



Citation: Antonopoulou, M.; Papadaki, M.; Rapti, I.; Konstantinou, I. Photocatalytic Degradation of Pharmaceutical Amisulpride Using g-C₃N₄ Catalyst and UV-A Irradiation. *Catalysts* **2023**, *13*, 226. <https://doi.org/10.3390/catal13020226>

Academic Editors: Kangle Lv and Vasile I. Parvulescu

Received: 14 November 2022

Revised: 18 December 2022

Accepted: 10 January 2023

Published: 18 January 2023



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1. Introduction

Aquatic pollution derived from chemicals that are generated during various anthropogenic activities is an environmental issue of considerable importance. The increasing use of chemicals due to the current model of life and the continued growth of the population is expected to cause greater pressure on natural ecosystems and humans in the near future. Pollution caused by a multitude of pharmaceutical compounds used by humans is an environmental problem that has attracted scientific interest. Pharmaceutical substances are a large and diverse group, usually of organic compounds, which are used in high quantities throughout the world. They are also considered to be a unique class of pollutants because of their characteristics. In many cases, their behavior and fate cannot be simulated with other categories of organic pollutants [1,2].

The main source of pharmaceutical residues in the aquatic environment is wastewater treatment plants (WWTPs), which exhibit frequently limited capacity to remove these pollutants, since most of them cannot be metabolized by microorganisms [3,4]. As a result, pharmaceutical compounds reach aquatic systems at concentration levels from ng L^{−1} to

$\mu\text{g L}^{-1}$, but even at these very low concentrations, they can cause toxicological risks on living organisms [5,6].

Psychiatric drugs are a class of pharmaceuticals often prescribed and used in a wide range of mental health problems, and their use is increasing worldwide. Up to now, many studies have been carried out to investigate the presence of psychiatric compounds in the environment. Amisulpride is a typical antipsychotic drug [7], and its occurrence in the environment has been highlighted in recent monitoring studies. For instance, in hospital WWTP effluent of Ioannina (northwestern Greece), amisulpride has been detected at concentration ranges from 102.0 ng L^{-1} to 929.4 ng L^{-1} [8]. In seawater of the Eastern Mediterranean Sea, amisulpride was detected in the range of $<0.2\text{--}5.5 \text{ ng L}^{-1}$ [9]. Moreover, Gago-Ferrero et al. reported amisulpride detection in the effluent of WWTP of Athens at a concentration of 0.07 ng L^{-1} [10]. During the first wave of COVID-19, amisulpride was quantified at 16.8 ng L^{-1} in wastewater samples of Milano and Monza (Italy) WWTPs [11]. Amisulpride has also been identified as a persistent contaminant that can be introduced into the aquatic environment and able to reach groundwaters. Moreover, the formation of its characteristic non-biodegradable N-oxide product has been verified during its treatment by conventional methods, revealing the need for advanced treatment [12,13]. Incomplete removal of various pollutants including pharmaceuticals from conventional WWTPs clearly shows the need for applying innovative technologies [3,4]. Advanced oxidation processes (AOPs) have been proposed as a tertiary treatment for wastewater [14,15]. Among different AOPs, heterogeneous photocatalysis is a promising method for the removal of organic compounds [13]. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), an organic semiconductor, has drawn widespread attention and become a hotspot for a wide variety of photocatalytic applications (e.g., degradation of organic pollutants, CO_2 and NO_x reduction, hydrogen production, organic selective synthesis, and water splitting). This visible light photocatalyst is an outstanding option due to its properties such as graphene-like structure, chemical and thermal stability, good visible light absorption, and low-cost [16–19]. Previously, $\text{g-C}_3\text{N}_4$ has been used in photocatalytic experiments in various aqueous matrices including real hospital wastewaters [8]. However, the application of $\text{g-C}_3\text{N}_4$ catalysts for the degradation of amisulpride under various matrix parameters, the identification of transformation products (TPs), and the ecotoxicological assessment of the photocatalytic treatment have not been studied so far. For this purpose, the main goal of this study was to investigate the photocatalytic degradation of amisulpride under UV-A irradiation using $\text{g-C}_3\text{N}_4$ catalyst and the identification of the TPs formed in the photocatalytic process. Furthermore, the toxicity by means of microalgae *Chlorococcum* sp. and *Dunaliella tertiolecta* was evaluated. Finally, the contribution of reactive species to the degradation mechanism was estimated.

2. Results and Discussion

2.1. Photocatalytic Degradation Kinetics

Before the study of amisulpride photocatalytic degradation, preliminary control experiments (adsorption and UV-A photolysis) were conducted in ultrapure water (UW), and the results are depicted in Figure 1. Adsorption experiments showed that the equilibrium succeeded at 30 min, and about 13% removal of amisulpride was observed. Photolysis under UV-A light resulted in a negligible decrease ($\sim 6.0\%$) of amisulpride and can be explained by the UV-Vis spectra of the pharmaceutical (Figure S1). Direct photolysis under UV-A light and the employed conditions was not expected since amisulpride does not absorb at 365 nm (maximum emission wavelength of the employed irradiation source), justifying the observed trend. Negligible photodegradation of the studied pharmaceutical under UV-A irradiation [13] and simulated solar irradiation [8] was also reported in previous studies.

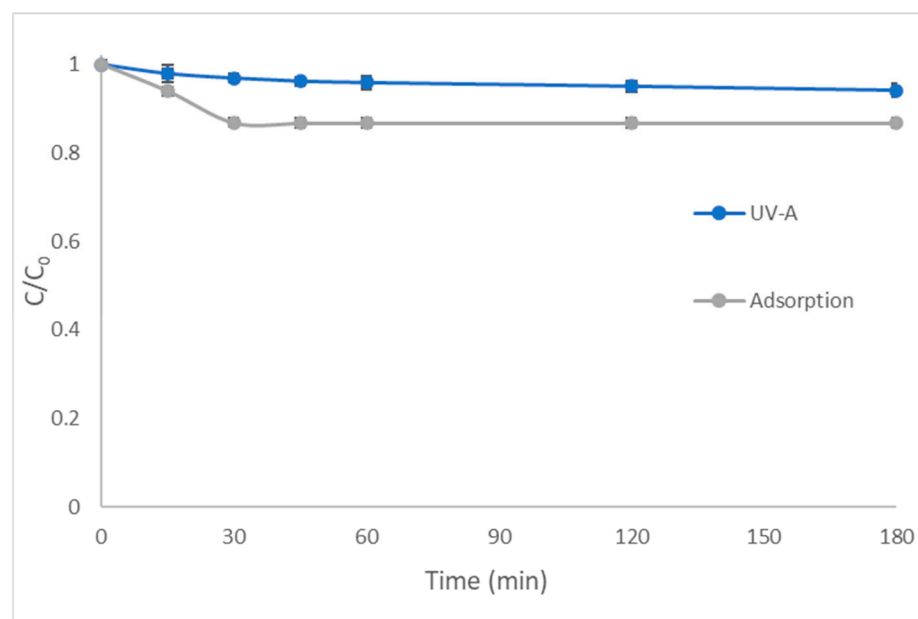


Figure 1. Adsorption and UV-A photolysis of amisulpride in UW ($[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$).

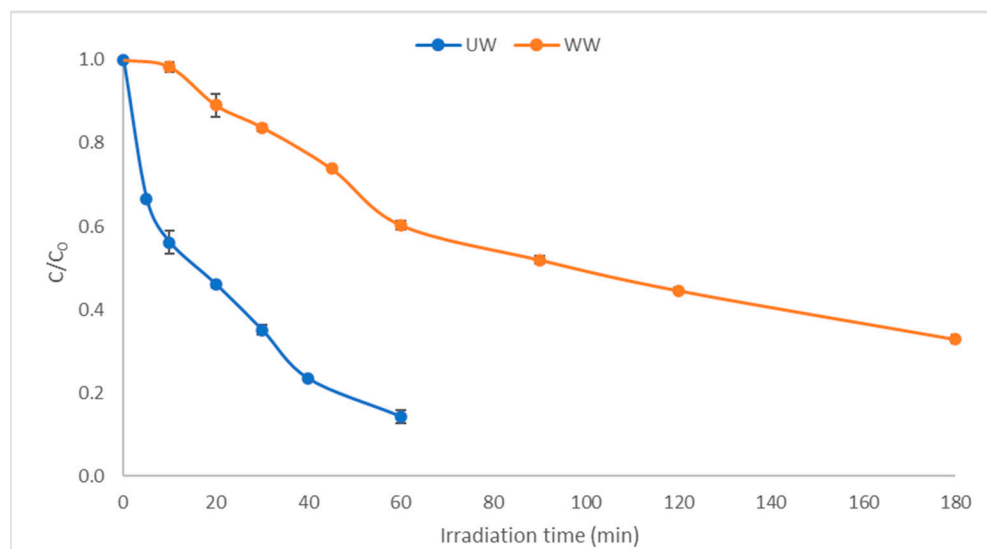
The photocatalytic performance of $\text{g-C}_3\text{N}_4$ was evaluated under UV-A light in both UW and treated municipal wastewater (WW), and the results are presented in Figure 2. The photocatalytic study reveals that $\text{g-C}_3\text{N}_4$ can be activated with the adsorption of photon energy larger than its bandgap ($\sim 2.82 \text{ eV}$) and subsequently generates a photo-induced electron-hole pair ($e^- - h^+$) as well as other reactive species responsible for amisulpride degradation. The reaction kinetics of amisulpride degradation were studied in both matrices, the experimental data were fitted in pseudo-first order reaction kinetics, and the corresponding kinetics parameters (degradation rate constants, half-lives, and correlation coefficients) are reported in Table 1. High removals were achieved in both matrices (Figure 2). The degradation percentages were about 86.0% within 60 min in UW and about 67.0% within 180 min in WW. Our results are in agreement with previous photocatalytic studies in which high removal percentages (up to 98%) of amisulpride were achieved in aqueous matrices using various photocatalysts, i.e., TiO_2 , C-doped TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{SrTiO}_3/\text{g-C}_3\text{N}_4$ [8,13].

A higher degradation rate was observed in UW than WW. In particular, a rate constant of $k = 3.04 \times 10^{-2} \text{ min}^{-1}$ and a half-life of $t_{1/2} = 22.80 \text{ min}$ were calculated for amisulpride in UW. The amisulpride degradation was significantly lower in WW ($k = 0.7 \times 10^{-2} \text{ min}^{-1}$ and $t_{1/2} = 99.02 \text{ min}$).

This trend indicates the significant effect of the constitution of the water matrices on the photocatalytic performance. It is well-documented in the literature that the organic as well as inorganic content (e.g., Cl^- , HCO_3^- , NO_3^- , SO_4^{2-}) that co-exist in WW can affect the photocatalytic performance, acting mainly as scavenger of the reactive species [20,21]. Moreover, the constituents of WW can be adsorbed onto a catalyst's surface leading to the change of the surface charges as well as to the reduction of the available active sites [8]. Metal ions, also present in WW, can significantly affect the photocatalytic performance. The effects of Cu^{2+} , Zn^{2+} , Fe^{3+} , and Al^{3+} were studied, and an inhibition influence on the photocatalytic performance was observed in all cases under the studied experimental conditions (Figure S2). The addition of metal ions can affect the photocatalytic degradation through (i) the decrease of O_2 reduction by photogenerated conduction electrons and subsequent suppression of reactive oxygen species formation and (ii) alteration of the pollutant's adsorption [22].

Table 1. Kinetic parameters (rate constants, correlation coefficients (R^2), half-lives ($t_{1/2}$)) of amisulpride photocatalytic degradation in UW and WW.

Matrix	$k \times 10^{-2} \text{ (min}^{-1}\text{)}$	$t_{1/2} \text{ (min)}$	R^2
UW	3.04	22.80	0.9420
WW	0.7	99.02	0.9809

**Figure 2.** Photocatalytic degradation of amisulpride under UVA irradiation in UW and WW ($[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$).

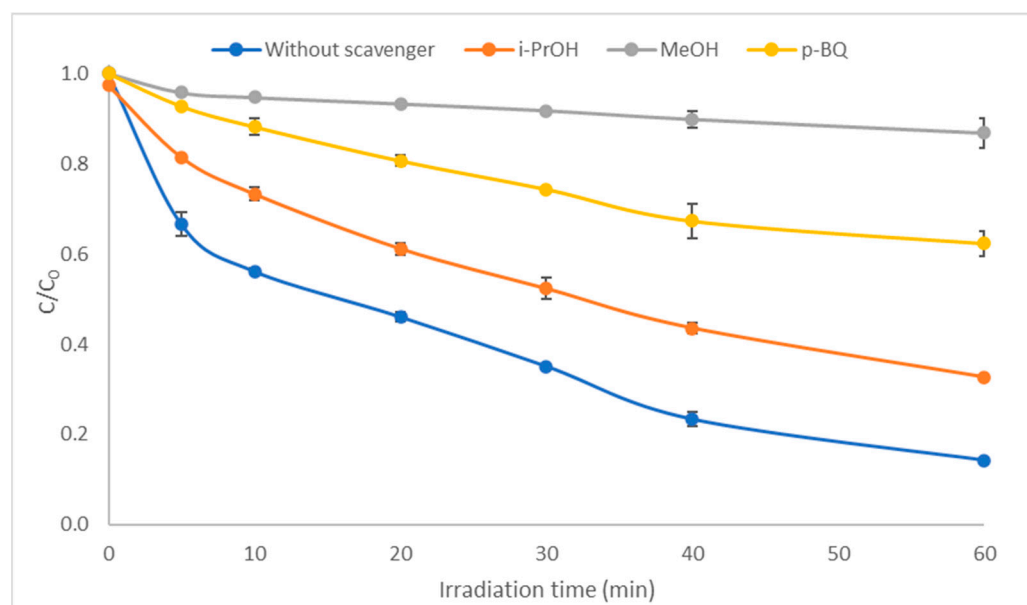
The effect of initial pH was also evaluated for the degradation of amisulpride under similar conditions in WW as matrix (Figure S3). The highest removal of amisulpride was observed at natural pH (about 7.6). The pH_{PZC} of the used catalyst was determined to be ~ 4.9 . Below or above this value, the charge of the catalyst surface is positive and negative, respectively. Similarly, amisulpride (pK_a 9.37) molecules are mainly protonated at $\text{pH} \sim 7.6$. Subsequently, under the experimental conditions, electrostatic attractions occur between amisulpride and negatively charged catalyst's surface also leading to the highest removal. On the other hand, under pH 4, electrostatic repulsions of positive charged catalyst, and amisulpride molecules significantly decrease the degradation. Under pH 10, some electrostatic repulsion of negative charged catalysts and partially negatively charged amisulpride molecules could also be considered that verified the slight decrease of the observed degradation.

2.2. Role of Reactive Species to the Degradation Mechanism

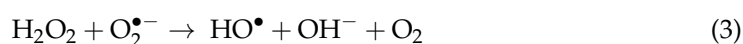
The contribution of $\text{HO}^\bullet$, h^+ , and $\text{O}_2^{\bullet-}$ was evaluated using isopropanol (i-PrOH), methanol (MeOH), and p-benzoquinone (p-BQ), respectively. The scavengers were selected due to their high-rate constant reaction with the corresponding species. More specifically, i-PrOH is a well-documented $\text{HO}^\bullet$ scavenger presenting a high-rate constant reaction with the radical equal to $1.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [23,24]. MeOH can quench both $\text{HO}^\bullet$ and h^+ and react with $\text{HO}^\bullet$ with a rate constant of $1 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [20,25]. Para-benzoquinone (p-BQ) can quench $\text{O}_2^{\bullet-}$ with a rate constant of $1.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [20]. The pseudo-first order rate constants as well as the degradation profile in the presence of scavengers are presented in Table 2 and Figure 3, respectively.

Table 2. Kinetic parameters (rate constants, correlation coefficients (R^2)), and percentages of inhibition (% Δk) of amisulpride photocatalytic degradation in the presence of scavengers.

Scavenger	$k \times 10^{-2} \text{ (min}^{-1}\text{)}$	R^2	$\Delta k \text{ (%)}$
Without Scavenger	3.04	0.9420	-
i-PrOH	1.76	0.9800	42.1
MeOH	0.21	0.9292	93.1
p-BQ	0.80	0.9720	73.7

**Figure 3.** Photocatalytic degradation of amisulpride in the presence of scavengers ($[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$; $[\text{i-PrOH}] = 0.1 \text{ M}$; $[\text{MeOH}] = 0.1 \text{ M}$; $[\text{p-BQ}] = 0.2 \text{ mM}$, matrix: UW).

Among the employed scavengers, MeOH caused the highest inhibition (93.1%), as it can quench both $\text{HO}^\bullet$ and h^+ . In contrast, the addition of i-PrOH provoked only 42.1% inhibition, highlighting the significant role of h^+ and the low contribution of $\text{HO}^\bullet$. This is in agreement with the literature data, as during the activation of $\text{g-C}_3\text{N}_4$ photocatalysts, the formation of $\text{HO}^\bullet$ through direct water or OH^- oxidation by holes is not promoted, since VB edges of $\text{g-C}_3\text{N}_4$ catalysts are still less positive than the redox potential of $\text{OH}^-/\text{HO}^\bullet$ (1.99 eV vs. NHE) [26,27]. The significant role of h^+ was further verified with experiments using acetonitrile as reaction media (data not shown). The addition of p-BQ led to an inhibition of 73.7%. Superoxide anions can directly degrade organic pollutants through oxidative mechanisms. In addition, $\text{O}_2^{\bullet-}$ can lead to the formation of $\text{HO}^\bullet$ through the following reactions [27]:



Our results are consistent with a previous study [28] that reported that h^+ and $\text{O}_2^{\bullet-}$ are the main species in the photocatalytic degradation of refractory contaminants using $\text{g-C}_3\text{N}_4$ -based catalysts. According to the above analysis, the proposed photocatalytic mechanism involves the formation of electron-hole pairs in the conduction band (CB) and valence band (VB) of $\text{g-C}_3\text{N}_4$. The holes (h^+) in the VB of $\text{g-C}_3\text{N}_4$ participate directly in the degradation process, whereas the e^- on the CB can reduce O_2 to $\text{O}_2^{\bullet-}$.

2.3. Photocatalytic Degradation Mechanism

The TPs that are produced at the first stages of the photocatalytic processes were identified in both UW and WW using mass spectrometry techniques and interpretation of their mass spectra obtained in positive ionization mode. In total, three TPs were detected in both matrices, and their structural identification was based on their molecular and fragment ions (Table 3) as well as on previous literature data [13].

Table 3. Mass measurements ($[M + H]^+$) and molecular formula of the identified TPs.

TPs	$[M + H]^+$	Molecular Formula
AMI	370.30	$C_{17}H_{27}N_3O_4S$
AMI1	340.37	$C_{16}H_{25}N_3O_3S$
	342.39	
AMI2	242.05	$C_{15}H_{23}N_3O_4S$
	196.01	
AMI3	386.26	$C_{17}H_{27}N_3O_5S$
	196.01	

Three pathways are proposed and depicted in Figure 4. The first pathway includes the scission of the methoxy group of the amisulpride molecule and the formation of AMI1. This TP was also identified by Skibiński et al., 2011 [29] during the photodegradation of the studied pharmaceutical. Similarly, it was identified during the photocatalytic treatment of pharmaceuticals mixture also containing amisulpride [13]. The other pathway proceeds through dealkylation and more specifically through the cleavage of the ethyl group linked to the N-atom (AMI 2). The last route leads to the formation of a characteristic N-oxide TP via an oxygen transfer mechanism [24]. N-oxide amisulpride is a characteristic TP that has been identified during the treatment of amisulpride by photolysis [29] and heterogeneous photocatalysis [13]. The absence of hydroxylated TPs verifies the low contribution of $HO^\bullet$ to the degradation mechanism, reported in the previous section. The proposed degradation routes are consistent with previous work focused on the photocatalytic degradation of pharmaceuticals mixture also containing amisulpride [13].

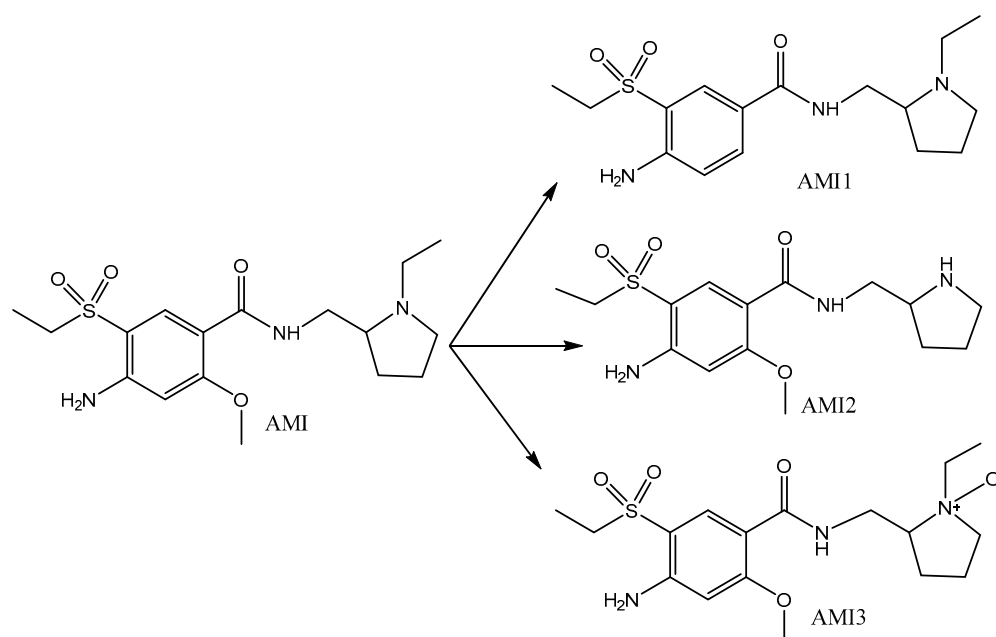
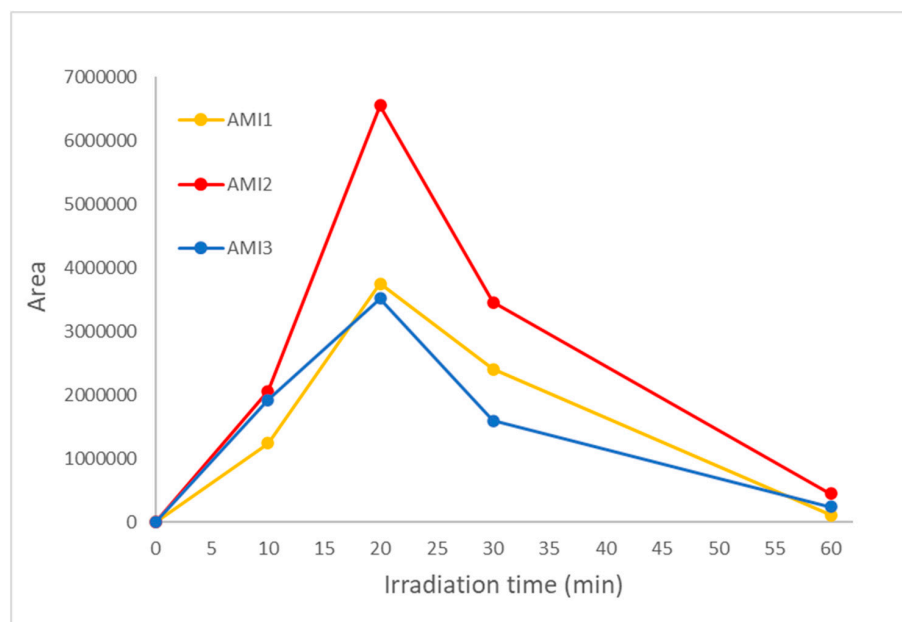


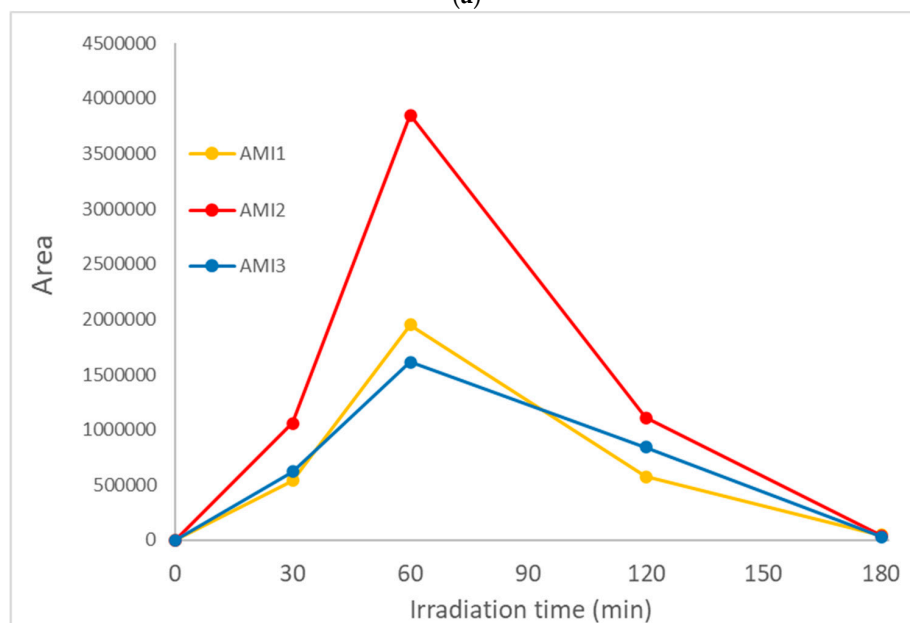
Figure 4. Photocatalytic degradation pathways of amisulpride.

The formation of TPs was also followed during the photocatalytic treatment. As presented in Figure 5, the TPs in UW and WW attained their maximum area in 20 min and

60 min, respectively. Thereafter, the area of the three TPs in both matrices were readily reduced. Subsequently, the cleavage of the rings can take place, and low molecular weight TPs can be produced before complete mineralization. After prolonged application of heterogeneous photocatalysis, two low-molecular-weight carboxylic acids, i.e., formic and acetic acid, were identified.



(a)



(b)

Figure 5. Evolution profiles of TPs identified during the photocatalytic degradation of amisulpride in: (a) UW; and (b) WW ($[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$).

2.4. Ecotoxicity Evolution

The evolution of toxicity against freshwater and marine microalgae was evaluated in both matrices (Figures 6 and 7). According to the results, low toxicity was observed at 0 min of the process in UW (Figures 6a and 7a). In contrast, the untreated solution of amisulpride in WW (0 min) led to over 25% inhibition of growth rate for both microalgae at contact time of 72 h (Figures 6b and 7b). The high growth inhibition rates observed in

WW can be correlated with the composition of this matrix that can contain compounds that exert toxic effects to the exposed microalgae. This was verified by the initial toxicity of the wastewater sample which showed an inhibition of 18.1%. Similar trends were also observed by Gomes et al., 2019 [30] and Antonopoulou et al., 2016 [20]. Only a slight increase in toxicity was observed at the first stages of the photocatalytic treatment in both matrices. This increase can be correlated with the formation of the identified TPs. It is worth mentioning that the highest % growth inhibition rates were observed at 20 min and 60 min in UW and WW, respectively, where the TPs showed their maximum formation. Similar to our results, enhanced toxicity at the first stages was also noticed during the photocatalytic degradation of various contaminants in aqueous matrices by different AOPs [20,31]. However, the contribution of the TPs in the overall toxicity can be characterized as low. With the application of photocatalytic treatment, the % inhibition was significantly reduced in all cases. This clearly indicates that heterogeneous photocatalysis using g-C₃N₄ can proceed without the formation of toxic TPs. It is also able to significantly reduce the toxicity derived from municipal wastewater.

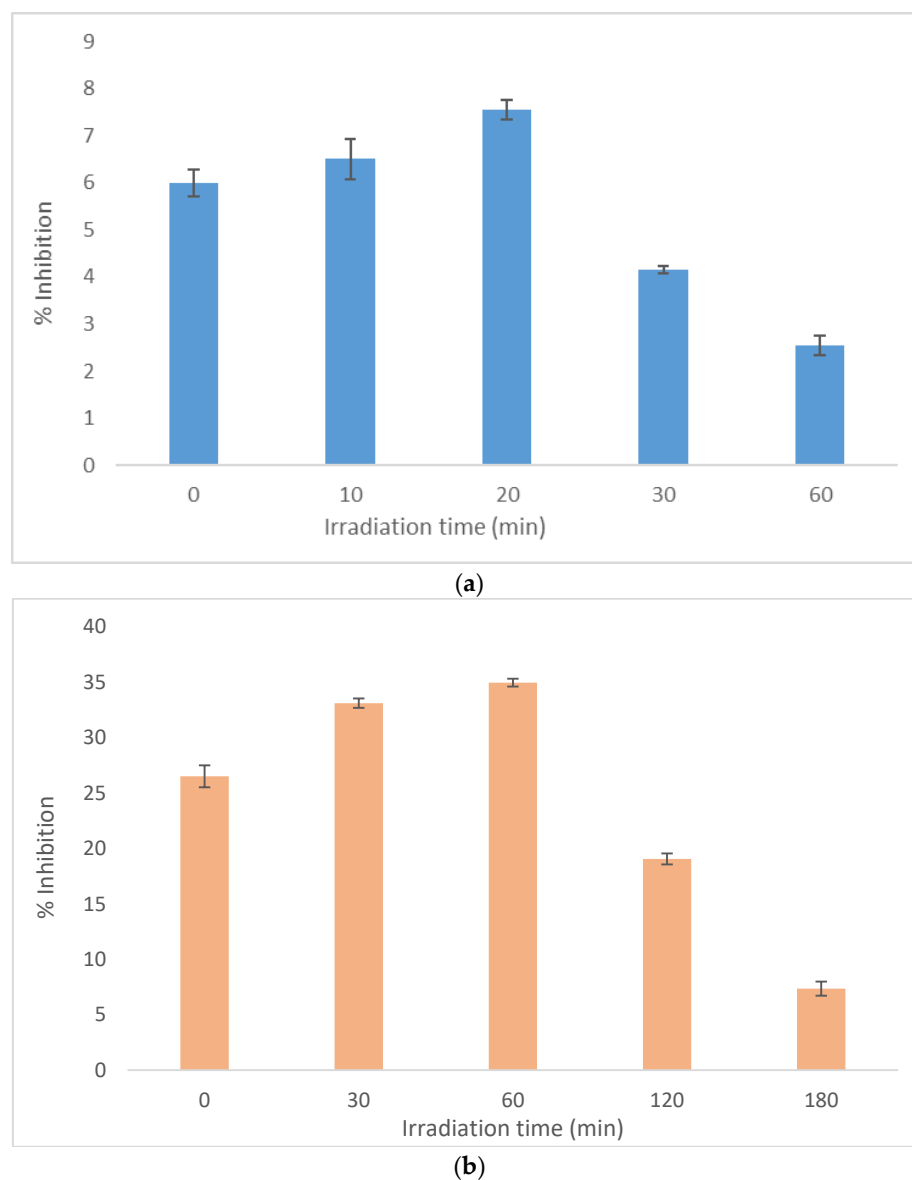


Figure 6. Evolution of toxicity during the photocatalytic process in: (a) UW; and (b) WW using *Chlorococcum* sp. ([amisulpride]₀ = 1 mg L^{−1}; [g-C₃N₄] = 300 mg L^{−1}).

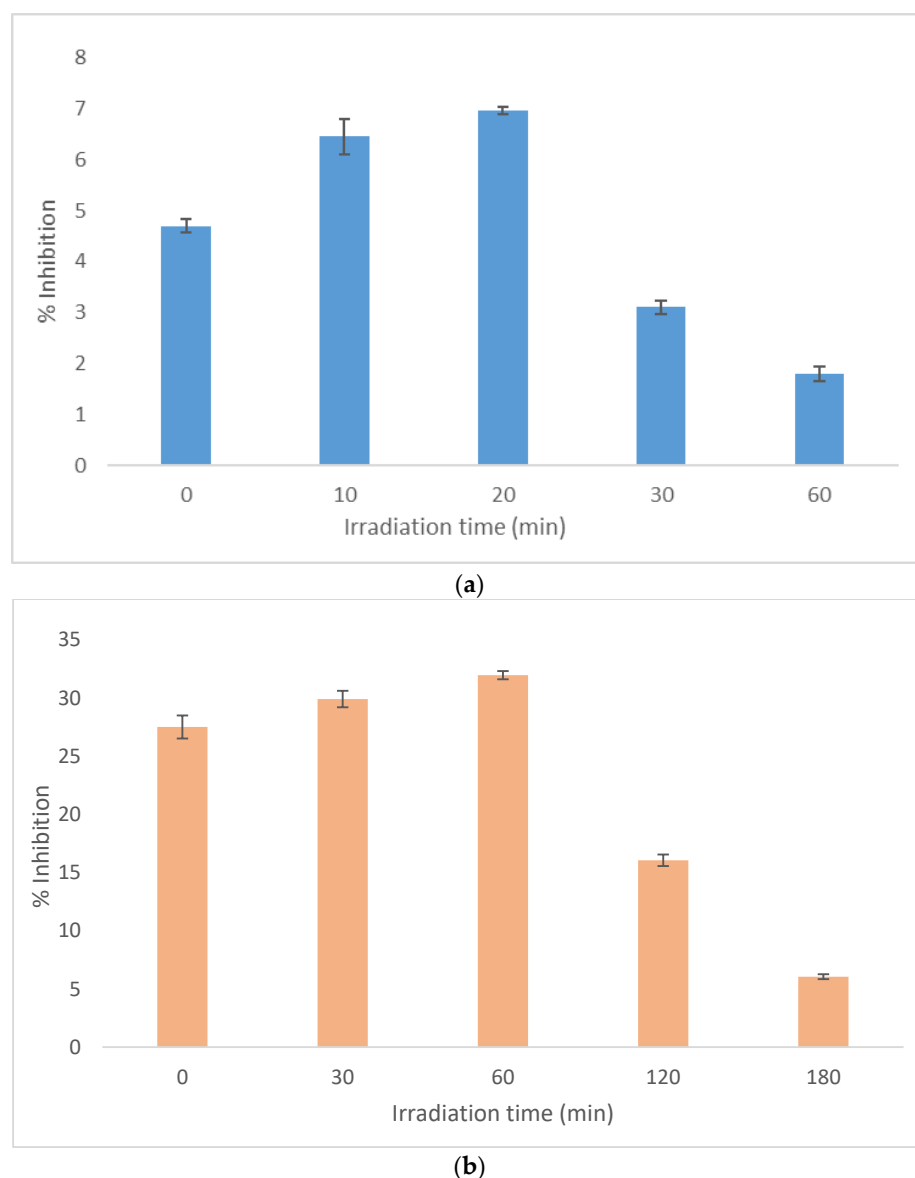


Figure 7. Evolution of toxicity during the photocatalytic process in: (a) UW; and (b) WW using *Dunaliella tertiolecta* ($[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$).

3. Materials and Methods

3.1. Chemicals and Reagents

Amisulpride (98%) was obtained from Tokyo chemical industry Co., Ltd. (Tokyo, Japan). Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) (BET SSA $35 \text{ m}^2 \text{g}^{-1}$, particle size of 25 nm, $E_g = \sim 2.82 \text{ eV}$) was used as the photocatalyst [8,32]. Acetonitrile, isopropanol, methanol, and water of HPLC-grade solvents were supplied by Fisher Chemical (Waltham, MA, USA). *p*-benzoquinone ($\geq 98\%$), formic acid, BG-11 medium (Cyanobacteria BG-11 Freshwater Solution), and F/2 medium (Guillard's (F/2) Marine Water Enrichment Solution) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water and treated wastewater ($\text{pH} = 7.45 \pm 0.02$; conductivity = $312.81 \pm 20.3 \mu\text{S cm}^{-1}$; total suspended solids = $1.97 \pm 0.022 \text{ mg L}^{-1}$; chemical oxygen demand = $17.6 \pm 1.92 \text{ mg L}^{-1}$; $\text{PO}_4^{3-} = 3.85 \pm 0.024 \text{ mg L}^{-1}$; $\text{SO}_4^{2-} = 32.1 \pm 1.56 \text{ mg L}^{-1}$; $\text{NO}_3^- = 24.2 \pm 0.78 \text{ mg L}^{-1}$) were used as matrices. The microalgae species *Chlorococcum* sp. (strain SAG 22.83) and *Dunaliella tertiolecta* (strain CCAP 19/6B) were purchased from the bank SAG collection of the Göttingen University (Germany) and Scottish Marine Institute, Oban, Argyll, Scotland, respectively.

3.2. Photocatalytic Experiments

Photocatalytic experiments were carried out on a system equipped with 4 black light tubes from Sylvania (maximum emission at 365 nm) and electric fans to avoid overheating. A cylindrical pyrex glass cell with a maximum capacity of 200 mL was used as a photoreactor. In a typical experiment, the following experimental conditions $[\text{amisulpride}]_0 = 1 \text{ mg L}^{-1}$; $[\text{g-C}_3\text{N}_4] = 300 \text{ mg L}^{-1}$ were adopted. The suspensions were kept in the dark for 30 min under continuous stirring to achieve adsorption equilibrium before starting the radiation. The photon flux (I_0) entering the solution was calculated to be $1.1 \pm 0.02 \mu\text{Einstein s}^{-1}$ under the applied conditions, periodically using potassium ferrioxalate as actinometer [33,34]. PVDF 0.22 μm by Millex-GV was used to remove the catalyst particles.

3.3. Scavenging Experiments

The contribution of hydroxyl radicals ($\text{HO}^\bullet$), superoxide anion radicals ($\text{O}_2^{\bullet-}$), and positive holes (h^+) in the degradation mechanism was evaluated using well-known scavengers, i.e., isopropanol (0.1M), p-benzoquinone (0.2mM), and methanol (0.1M), respectively [13].

3.4. Analytical Methods

The concentration of amisulpride was quantified by a Dionex (Thermo Scientific) Ultimate 3000 UHPLC using an AcclaimTM RSLC 120 C18 (2.2 μm , $2.1 \times 100 \text{ mm}$) column (Thermo Scientific) and an Acquity UPLC BEH C18 VanGuardTM pre-column (1.7 μm , $2.1 \times 5 \text{ mm}$) from Waters. The mobile phase was a mixture of ultrapure water with 0.1% formic acid (80%) and acetonitrile (20%) with a flow rate of 0.15 mL min^{-1} . The detection was performed at pollutant's λ_{max} .

3.5. UHPLC/MS Analysis

TPs were identified by a UHPLC/MS system (Ultimate 3000 RSLC System (Thermo Scientific)/amaZon SL ion trap mass spectrometer from Bruker with an ESI source). A full description of the analysis is reported in our previous work [13]. For the determination of small-molecules TPs (carboxylic acids) that can be generated after the decay of the first-stage TPs in heterogeneous photocatalysis, a Dionex P680 HPLC equipped with a Dionex PDA-100 Photodiode Array Detector and a Thermo Scientific AQUASIL C18 (250 mm length $\times$ 4.6 mm ID $\times$ 5 μm particle size) analytical column with a flow rate of 1 mL min^{-1} was used. The mobile phase consisted of 1% acetonitrile and 99% 0.05 M KH_2PO_4 , pH 2.8. The detection was performed at 210 nm.

3.6. Algal Biotest

Algal bioassays were conducted using *Chlorococcum* sp. (strain SAG 22.83) and *Dunaliella tertiolecta* (CCAP19/6B) according to OECD 201 protocol [35], under sterile conditions and continuous illumination (4300 lux). BG-11 and F/2 were used as culture mediums for fresh and saltwater algal strains, respectively. The experiments were initiated by appropriate transfers of stock algal cultures to conical flasks containing the appropriate medium to maintain a supply of cells ($1 \times 10^4 \text{ cells mL}^{-1}$) in the logarithmic growth phase (final volume 100 mL). The samples collected at different stages were tested in duplicate cultures for 72 h with continuous stirring under the abovementioned conditions. The cell numbers were determined by using a Neubauer hemocytometer. Thereafter, the growth rate (μ) and the % inhibition of growth rate were calculated. The results are expressed as the mean $\pm$ SD.

4. Conclusions

The photocatalytic degradation of the pharmaceutical amisulpride was studied in UW and treated WW using UV-A irradiation and g-C₃N₄ as the photocatalyst. High removal percentages were observed in both matrices. However, a slower degradation rate was ob-

served in WW that could be attributed to its complex composition containing both inorganic and organic substances. A scavenging study proved the significant contribution of h^+ and $O_2^{\bullet-}$ in the reaction mechanism. Oxidation, dealkylation, and cleavage of methoxy group were found to take place during the photocatalytic degradation of the studied pharmaceutical. Low inhibition in the growth rates and consequently low toxicity were observed at the beginning and during the photocatalytic process when UW was used as matrix, using microalgae *Chlorococcum* sp. and *Dunaliella tertiolecta*. In contrast, higher adverse effects were observed when WW was used as matrix. However, an overall abatement of the effects was noticed at 180 min. Based on the results, heterogeneous photocatalysis using g-C₃N₄ showed good performance for the removal of amisulpride without the formation of harmful TPs. Considering that g-C₃N₄ has a response to visible light and consequently solar light can be used for its activation, heterogeneous photocatalysis using g-C₃N₄ is considered to be a promising method for removal of pharmaceuticals after the efficient separation of the photocatalyst or its immobilization on appropriate supports.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020226/s1>, Figure S1: UV-Vis spectrum of amisulpride ([amisulpride]₀ = 1 mg L⁻¹); Figure S2: Effect of metal ions on the photocatalytic degradation of amisulpride in UW ([amisulpride]₀ = 1 mg L⁻¹, [metal ion]₀ = 10 mg L⁻¹, [g-C₃N₄] = 300 mg L⁻¹); Figure S3: Effect of pH on the photocatalytic degradation of amisulpride in WW ([amisulpride]₀ = 1 mg L⁻¹, [g-C₃N₄] = 300 mg L⁻¹).

Author Contributions: Conceptualization, M.A.; methodology M.A., I.K. and I.R.; validation M.A.; formal analysis M.A.; investigation M.A., M.P., I.K. and I.R.; resources M.A.; data curation, M.A.; writing—original draft M.A. and I.R.; writing—review and editing M.A. and I.K.; visualization M.A.; supervision M.A.; project administration M.A.; funding acquisition M.A. All authors have read and agreed to the published version of the manuscript.

Funding: This paper has been financed by the funding program “MEDICUS”, of the University of Patras (Number: 81654).

Data Availability Statement: Data are contained within the article.

Acknowledgments: This paper has been financed by the funding program “MEDICUS”, of the University of Patras. The authors would like to thank the Laboratory of Instrumental Analysis of the University of Patras for UHPLC-MS analysis.

Conflicts of Interest: The authors declare no conflict of interest.

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