Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2023, Volume 14, Issue 03, Page 337-347

http://www.jmaterenvironsci.com

Photocatalysis of dioxide for the degradation of ciprofloxacin in an aqueous medium

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Received *29 Jan 2023,*
Revised *12 Mar 2023,*
Accepted *15 Mar 2023*

Citation*: N'Guettia K. R.., Aboua K. N., Soro D. B., Traore K. S. (2023) Photocatalysis of dioxide for the degradation of ciprofloxacin in an aqueous medium, J. Mater. Environ. Sci., 14(3), 337-347.*

Abstract: Ciprofloxacin is a commonly used antibiotic that can be present in wastewater and surface water, potentially leading to environmental contamination and the development of antibiotic resistance in bacteria. The degradation of ciprofloxacin has been studied using two photochemical mechanisms in natural waters. The aim of this study was to monitor the degradation kinetics of this antibiotic in drinking water and pre-treated wastewater. Photodegradation experiments were conducted using UVA irradiation (365 nm) with a concentration of 20 mg/l. The degradation processes involved the photolysis and photocatalysis of titanium dioxide at varying concentrations. Ciprofloxacin was found to be more degraded in tap water-doped solutions by photolysis, which was attributed to the presence of photosensitizing species in this water matrix. Furthermore, the degradation kinetics of ciprofloxacin were further improved by the presence of TiO_2 in natural waters by photocatalysis. The results indicated a complete disappearance of ciprofloxacin in the different water matrices during the evolution of degradation kinetics. However, the total organic carbon content showed mineralization of greater than 50% of the initial carbon concentration.

Keywords: *Titanium dioxide; Antibiotics.; Ciprofloxacin; Aqueous medium; Photodegradation;*

1. Introduction

Ciprofloxacin is a fluoroquinolone antibiotic that is commonly used to treat bacterial infections. However, it has been found to persist in the environment and accumulate in aquatic ecosystems, leading to concerns about its potential impact on human health and the environment, Stahlmann and Lode, 1999). When ciprofloxacin is present in an aqueous medium, it can undergo various chemical and physical processes that affect its behavior and fate. One such process is photodegradation, which involves the degradation of the molecule by exposure to sunlight or other sources of light (Chen *et al.*, 2015). This process can lead to the formation of reactive intermediates that can further react with other molecules in the environment (Kovalakova *et al.*, 2020**).** Despite this, they belong to one of two classes of drugs (the other being nonsteroidal anti-inflammatory drugs) whose phototoxicity is a significant side effect. In general, the mechanisms underlying phototoxic reactions are not

known, and a prerequisite for better understanding is exact knowledge of drug photochemistry (Ashfaq *et al*., 2016**).** Antibiotics have recently been classified as a priority risk group because of their high toxicity to algae and bacteria at low concentrations and their potential to cause resistance among natural bacterial populations (N'guettia et al., 2023.). Therefore, antibiotics in surface waters have the potential to disrupt bacterial cycles/processes essential to aquatic ecology (nitrification/denitrification) or agriculture (soil fertility) and animal production (rudimentary processes) (Akter *et al.*, 2022). Ciprofloxacin is one of the most widely consumed antibiotics corresponding to the classification of fluoroquinolones. FQs have been widely used to treat bacterial infections in humans and animals that then enter aquatic environments through excretion and body excretion after administration (Janecko *et al.*, 2016; Ben Salem *et al.*, 2015). Photocatalysis of dioxide is a process that uses the energy from light to promote chemical reactions on the surface of a catalyst. One application of this technology is in the degradation of organic pollutants in aqueous solutions. One such pollutant is ciprofloxacin, a widely used antibiotic that has been found to persist in the environment and contribute to the development of antibiotic-resistant bacteria (De Bel *et al*., 2009). The degradation of ciprofloxacin can be achieved through photocatalysis using titanium dioxide as the catalyst. When exposed to light, titanium dioxide creates electron-hole pairs that can react with oxygen and water molecules to generate reactive oxygen species. These species can then react with the ciprofloxacin molecule, breaking it down into smaller, less harmful compounds (Daghrir and Drogui, 2013). The efficiency of photocatalytic degradation depends on a number of factors, including the concentration of the catalyst, the intensity and wavelength of the light source, and the initial concentration of the pollutant. Studies have shown that higher concentrations of catalysts lead to faster degradation rates, while longer wavelengths of light are more effective in promoting the generation of reactive oxygen species. The aqueous medium in which the photocatalysis takes place also plays an important role in the degradation process. Factors such as pH, temperature, and the presence of other pollutants can affect the efficiency of the reaction. For example, lower pH values can increase the generation of reactive oxygen species, while high temperatures can increase the rate of degradation (Al-Hamdi *et al.,* 2017). Overall, photocatalysis of dioxide offers a promising solution for the degradation of ciprofloxacin and other organic pollutants in aqueous environments. With further research and development, this technology could be used to mitigate the negative impact of antibiotics on the environment and human health. (Chen *et al*., 2020). This use is more favorable in tropical areas because photocatalysis can be applied throughout the year and climatic constraints are low. The objective of this study is to study the effect of certain parameters on the kinetics of ciprofloxacin in an aqueous medium.

2. Methodology

2.1. Reagents.

All reagents used are of greater than 95 % purity. Ciprofloxacin and acetonitrile were acquired from Sigma Aldrich with a purity of 99 %. The photocatalyst used was the titanium dioxide (TiO_2) brand AEROXIDE® DEGUSSA (Evonik). It is composed of 80 % anatase and 20 % rutile with a specific surface area of 50 m^2/g and a particle size of approximately 30 nm. All other products were obtained from Carlo Erba Reagents. All aqueous solutions were prepared with Milli-Q water. The ultrapure water (resistivity greater than 18 $M\Omega.cm^{-1}$ at 25 °C) was produced in the laboratory using a Millipore device.

2.2. Photochemical experiments

The photochemical experiments were conducted in a discontinuous, 2 liters cylindrical borosilicate glass reactor, surrounded by a black plastic film. The UV-A lamp (Sylvania, 8 W, 365 nm) was housed in a quartz tube and vertically inserted in the center of the reactor. A magnetic stirring bar was placed at the bottom of the reactor to maintain a uniform solution mixture. The temperature was maintained at 25 °C using a thermostatic bath **(Figure 1)**.

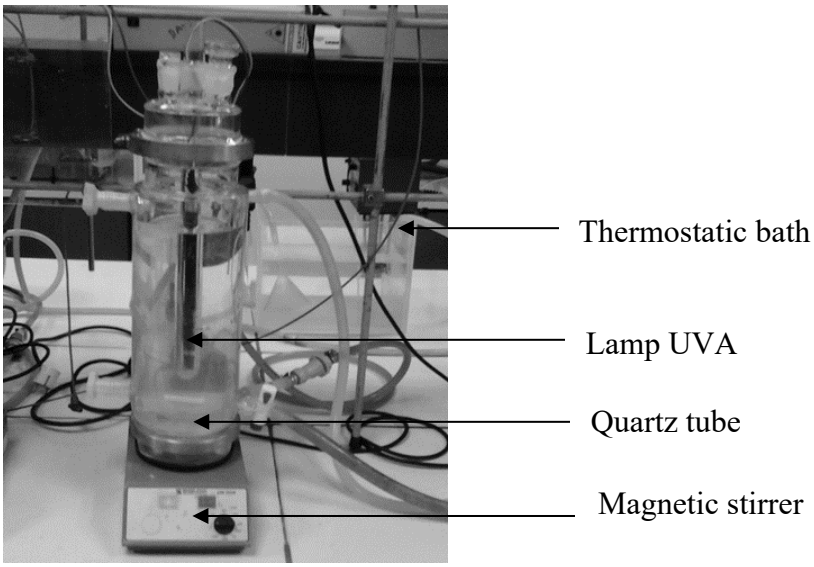

Figure 1: Experimental setup

2.2.1. Direct photolysis degradation protocol

For photolysis, the experiments were performed in a 2 liters reactor with a UVA lamp. Matrices of ultrapure water and tap water doped with 20 mg/l were irradiated for 480 minutes.

2.2.2. Degradation protocol by suspended photocatalysis

For photocatalysis experiments, the UVA lamp was coupled with TiO_2. The titanium dioxide used was of the Degussa P25 type with an average specific surface area (BET) of 50 ± 15 m^2/g. This crystal contains 80 % anatase and 20 % rutile and was chosen for its environmental friendliness and ease of application. Three types of photocatalytic experiments were conducted for the application of this process. The first was the individual degradation of each pharmaceutical molecule in doped matrices at concentrations of 20 mg/l, with TiO_2 doses of 0.1 g/l, 0.5 g/l, and 1 g/l. This experiment aimed to study the individual degradation kinetics of different molecules in both synthetic and real matrices.

2.2.3. Irradiated water matrices

All the experiments were carried out using ultra-pure water and tap water. The objective was to evaluate the effect of the matrix on the degradation kinetics of pharmaceutical molecules in different waters, as well as the effect of certain parameters. The ultra-pure water used was of Milli-Q quality, with a resistivity of < 18 $M\Omega.cm^{-1}$ and a COD of < 0.1 mg C/l. The tap water used was sourced from the city of Poitiers in France, specifically the Vienne-Poitou Charente region. To remove residual chlorine (which is an oxidant) and bicarbonates from the tap water, it was filtered through an activated carbon cartridge with 5 µm pores to eliminate any residual chlorine (Cl_2 or Cl^-).

2.3. Analytical technics

2.3.1. Chromatographic analysis

Residual concentrations were measured using high-performance liquid chromatography (HPLC) equipment from the WATERS brand. The separation was performed on a KROMASIL C18 column, with dimensions of 4.6 mm x 150 mm. Elution was carried out using a gradient of acetonitrile and water in the ratio of 90:10, which were acidified with 0.1 % formic acid. The elution was performed at a flow rate of 1 ml/min over a period of 20 minutes. The peak corresponding to the ciprofloxacin molecule was detected at 275 nm with a retention time of 8.5 minutes.

2.3.2. UV-visible spectroscopy

The principle is based on Beer Lambert's law. It is expressed as equation 1.

$$Abs = \varepsilon_{(\lambda)} l \times C \qquad \text{(Equation 1)}$$

Abs: Absorbance at one wavelength λ (nm), C: Concentration of the compound (mol/l), l: Optical path of the solution crossed by the light (cm), $\varepsilon_{(\lambda)}$ Molar absorption coefficient at one wavelengthλ. It is expressed in l/mol/cm or M/cm. In this study, we used the second unit.

2.3.2. Determination of total organic carbon

For the determination of total organic carbon, the method used is based on the oxidation of carbonaceous molecules contained in the water by thermal catalysis, which mineralizes them into carbon dioxide (CO_2). The amount of CO_2 produced is then measured using an infrared analyzer. To eliminate carbonates, the water sample is degassed in an acidic medium before analysis, allowing for direct determination of the organic carbon content. The TOC meter used is a Shimazu TOC-CV model.

3. Results and Discussion

3.1. Photolysis of ciprofloxacin

The degradation of ciprofloxacin was achieved by UVA photolysis in ultrapure water and tap water matrices doped to 20 mg/l **(Figure 2)**. The results showed that ciprofloxacin degraded more in tap water than in ultrapure water.

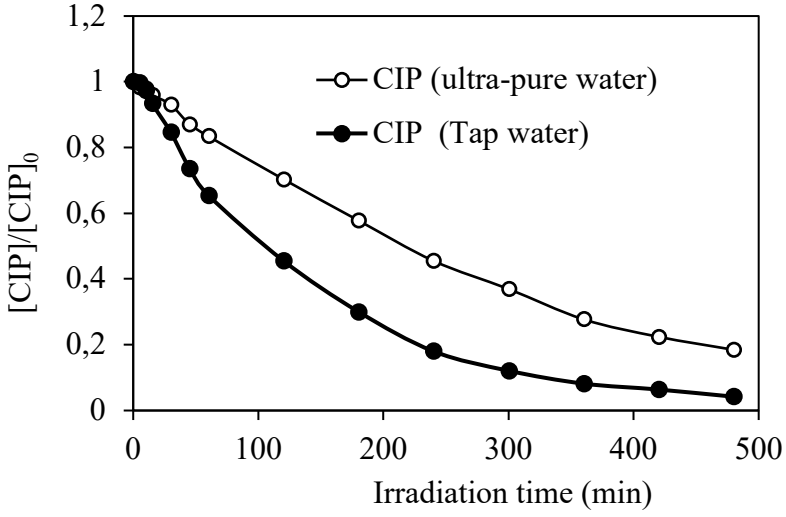

Figure 2: Photolysis of ciprofloxacin, UVA, pH=6, [CIP] = 20 mg/l in ultrapure water and tap water

3.1.1. Expression of the rate equation of photolysis

Figure 3 and Table 1 show the removal kinetics for ciprofloxacin in ultrapure water and tap water. The results indicated that the rate in tap water is double that of ultrapure water, with half-life times 97 minutes. It is evident that the matrix significantly influenced the photodegradation of this antibiotic, highlighting the chemical quality of water matrices. Tap water is hard water with a full alkalimetric title (TAC) equal to 30 °F, representing water with a very high load of calcium and magnesium chloride ions, as represented by the TAC. The results indicate that the carbonate radical may play an important role in the degradation of organic compounds such as ciprofloxacin in the UVA system in the presence of carbonate or bicarbonate commonly found in the natural environment (Moor *et al.*, 2019, Leresche *et al.*, 2020). In tap water matrices, the photochemical process induced by UVA form induces sensitized photolytic activity due to the presence of carbonate (CO_3^{2-}) or hydrogen carbonate (HCO_3) ions (Warren *et al.*, 2023). On the other hand, the degradation of CIP in ultrapure water could be attributed to direct photolysis.

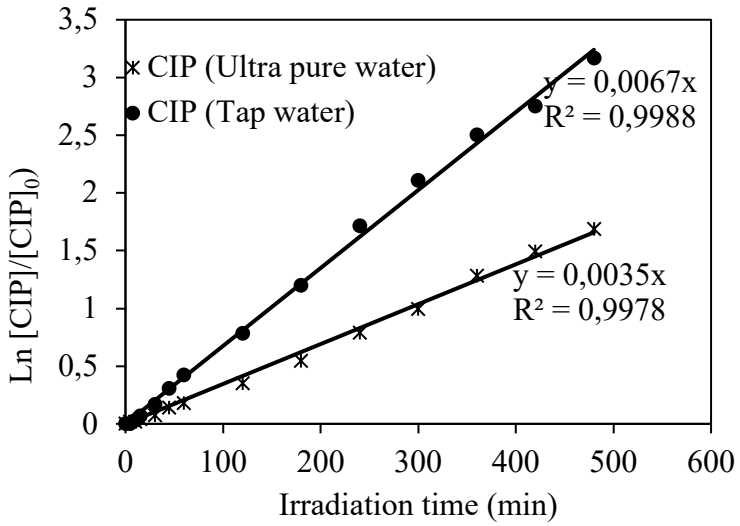

Figure 3: Evolution of ciprofloxacin rate equations in ultrapure water and tap water

3.1.2. Spectrum UV visible of ciprofloxacin

The visible UV spectrum of ciprofloxacin intercepts the UVA wavelength **(Figure 4)**. This interception with the length of 365 nm shows that the CIP absorbs in this wavelength region and therefore could be degraded by photochemical reactions. The photochemistry of FQs is known to be essentially a photochemistry in the triplet state in an aqueous medium (Sturini *et al.*, 2015). Once populated, this excited state reacts in three main ways (Schmitt *et al.*, 2017). This excited state promotes the rupture of the functions of the ciprofloxacin chain (Niu *et al.*, 2018). There is a gradual disappearance of the degradation of the ciprofloxacin molecule by photolysis in water. Excited triplet states are important intermediates in the photochemistry of organic molecules (Schmitt *et al.*, 2019). It should be noted that the extinction of the excited triplet states of the selected photosensitizers caused by bicarbonate ions can be considered relatively low under the conditions of aerated water, which is the case for most sunny surface waters (Yang *et al.*, 2022). In the case of steady-state irradiation, such as solar lighting, a reduction in the lifetime of the excited triplet state quantitatively corresponds to a reduction in the concentration of the excited triplet state, and consequently in the velocity constant for the transformation induced by the triplet state of a hypothetical trace contaminant (Bhat *et al.*, 2022; Ben Salem *et al.*, 2014).

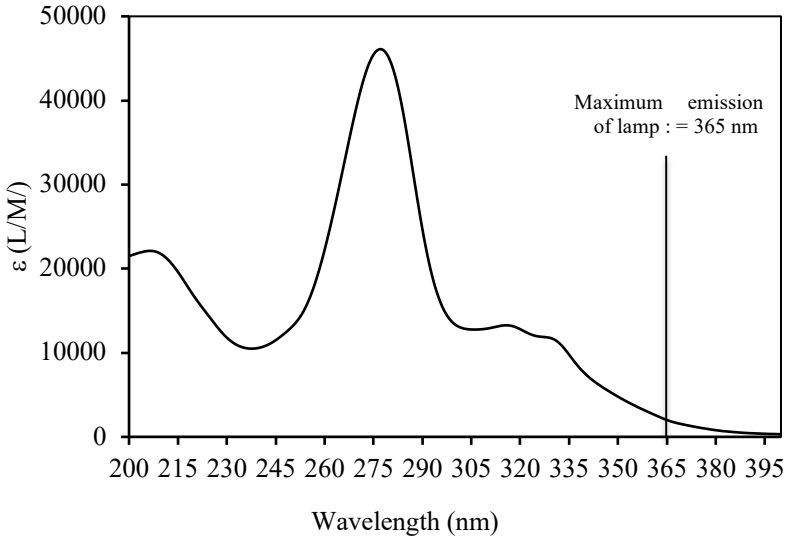

Figure 4: Visible UV spectrum of ciprofloxacin, pH = 6, [CIP] = 20 mg/l

3.2. Photocatalysis of ciprofloxacin

3.2.1. Effect of TiO_2 concentrations

The effect of TiO_2 concentration on ciprofloxacin degradation was investigated in solutions of ultrapure water and tap water doped with 20 mg/l of ciprofloxacin **(Figure 5 and 6)**. In ultrapure water doped, ciprofloxacin degraded faster at concentrations of 0.1 and 0.5 g/L of TiO_2. However, for 1 g/L of TiO_2, there was a decrease in the rate of ciprofloxacin degradation, possibly due to a screening effect that prevented photon penetration into the solution. Titanium dioxide is a photocatalyst that can be used to degrade organic pollutants in water through a process known as photocatalysis. When TiO_2 is irradiated with UV light, it generates reactive oxygen species (ROS) that can break down organic molecules such as antibiotics like ciprofloxacin (Manasa *et al.*, 2021).

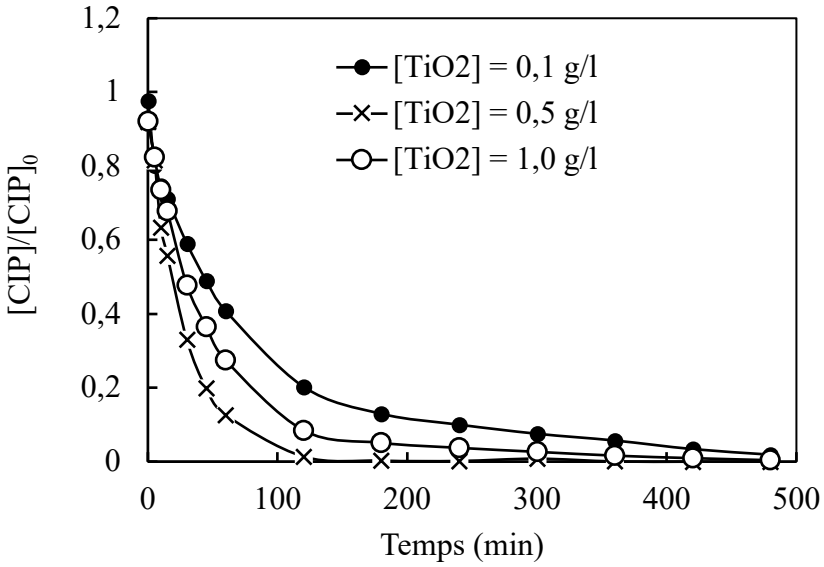

Figure 5: Degradation kinetics of ciprofloxacin TiO_2 in ultrapure water matrices

The concentration of TiO_2 can affect the rate of ciprofloxacin degradation because the availability of TiO_2 will determine the number of active sites for photocatalysis to occur (Malakootian et al., 2020). Generally, increasing the concentration of TiO_2 will increase the rate of

ciprofloxacin degradation, up to a certain point where further increases in TiO_2 concentration may not result in significant improvement (Hu et al., 2020). On the other hand, in tap water, better degradation was observed. At 1 g/L of TiO_2, the rate of ciprofloxacin degradation followed the evolution of TiO_2 concentrations, indicating a synergistic effect between water quality and process improvement. This synergistic effect improved the rate of ciprofloxacin degradation through a combination of photolysis and photocatalysis processes in tap water matrices. The values of k_{app} ranged from 1.10-2 to 2.3.10-2 min-1 for 0.1; 0.5 and 1 g/l.

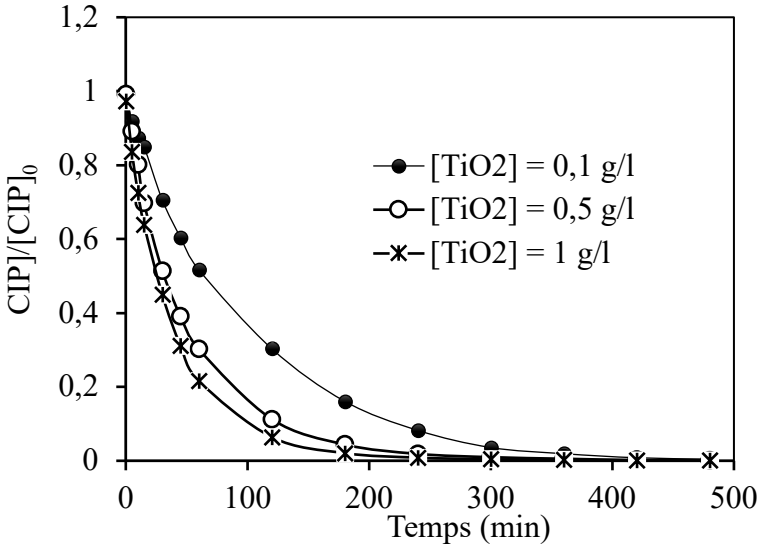

Figure 6: Effect of TiO_2 concentrations in tap water

These values were lower than that obtained at 0.5 g/L in ultrapure water but still indicated a positive evolution **(Figure 7).** Although hydrogen carbonates (HCO_3^-) and carbonate ions (CO_3^{2-}) can inhibit $OH^\bullet$ radical catalytic activity, their abundance could participate in the photolytic activity, leading to a combination of the two processes. On the contrary, a slight difference was observed at high concentrations of TiO_2 during the degradation of ciprofloxacin in this matrice water (Mirzai *et al*., 2020).

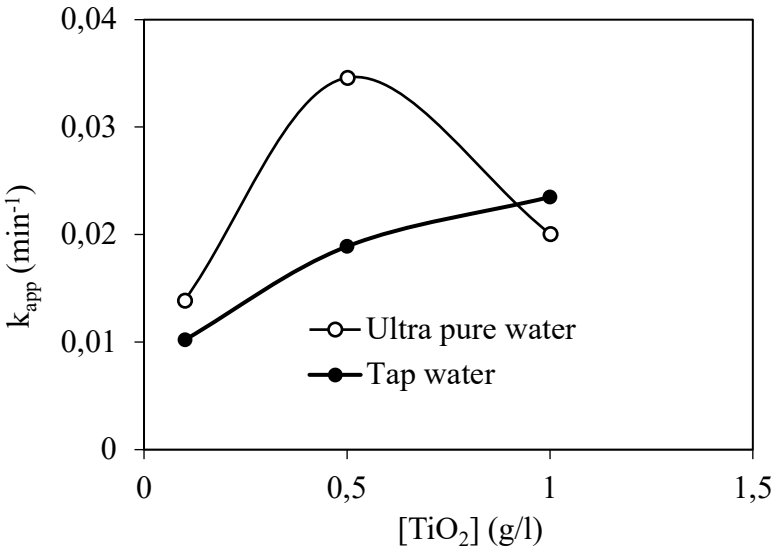

Figure 7: Evolution k_{app} in ultrapure water and tap water

3.2.2. Effect of dilution matrices

The water taken from the outlet of the treatment plant underwent the same treatment process and conditions **(Figure 8)**. The degradation rate was halved in tap water ($k_{app} = 1.10^{-2}$ min^{-1}) and reduced by a quarter in wastewater ($k_{app} = 2.10^{-2}$ min^{-1}) compared to ultrapure water ($k_{app} = 5.10^{-2}$ min^{-1}) (Table 2). These results emphasize the physical and chemical quality of the water matrices. This slowdown in degradation may be attributed to the presence of carbonate or hydrogen carbonate ions in tap water and nitrate (NO_3^-), ammonium (NH_4^+), or chloride (Cl^-) ions in treated wastewater. These ions have a strong affinity with hydroxyl radical degradative activities (Pereira *et al.*, 2013; Sheng *et al.*, 2013), leading to competition with ciprofloxacin ions for $OH^\bullet$ radicals (Wang *et al.*, 2015).

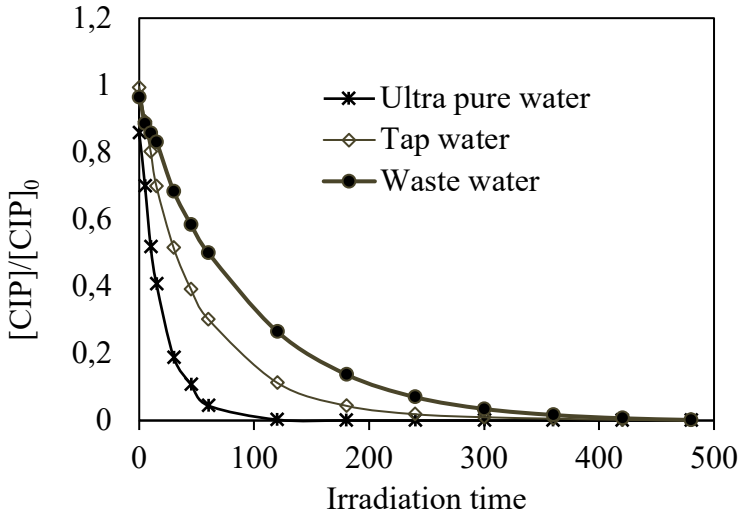

Figure 8: Degradation of ciprofloxacin in treated water, [CIP] = 20 mg/l, [TiO_2] = 0.5 g/l

Table: Kinetic parameters of ciprofloxacin degradation in water matrices

Kinetic parameters	Ultra-pure water (pH = 6)	Ultra-pure water (pH = 7.5)	Tap water (pH = 7.5)	Wastewater (pH = 7.5)
Kinietic constant k (min^{-1})	3.4. 10^{-2}	5. 10^{-2}	2. 10^{-2}	1. 10^{-2}
Half-time $t_{1/2}$ (min)	20	14	34	64
R^2	0.99	0.99	0.99	0.99
Degradation rate (%)	99.99	99.99	99.99	99.99

3.3. Total Organic Carbon (TOC)

Figure 9 depicts the rate of disappearance and mineralization of ciprofloxacin in ultrapure water. Mineralization involves the conversion of organic carbon and other elements into inorganic form, specifically the complete oxidation of ciprofloxacin to carbon dioxide (CO_2) and water (H_2O). The results indicate a disappearance rate of over 98 %. Moreover, the complete mineralization of carbon dioxide and water along with mineral salts was observed at a rate of over 50 %. This means that more than half of the organic matter has been converted into the inorganic matter within the detection limits of the TOC meter (0.1 mg C/l).

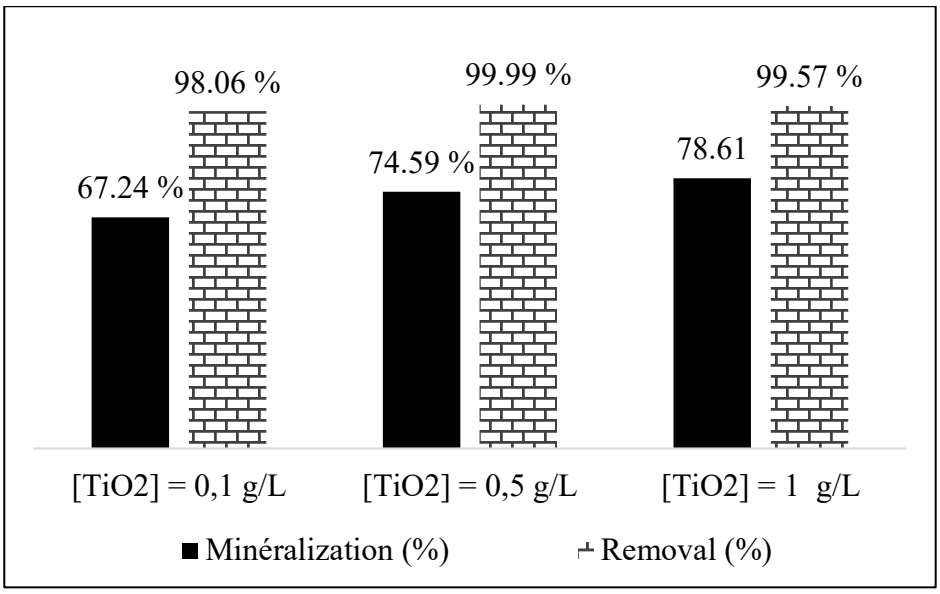

Figure 9 : Rate of disappearance and mineralization of ciprofloxacin, [CIP]=20mg/l, Ultra-pure water

Conclusion

The degradation of ciprofloxacin by UVA light was investigated in environmental matrices. The findings demonstrated that the mineralization of ciprofloxacin was enhanced by increasing the concentration of TiO_2. Moreover, it was observed that in this type of matrix, photochemistry under sunlight was an important removal pathway for these otherwise persistent anthropogenic contaminants. These results emphasized the importance of conducting further research to evaluate the actual environmental impact of such contaminants after photodegradation to different extents.

Acknowledgment: This work was supported by the Laboratory of Environmental Sciences of the Training and Research Unit in Environmental Sciences and Management of the University NANGUI ABROGOUA, Abidjan, Côte d'Ivoire.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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(2023); http://www.jmaterenvironsci.com