## OPTIMISED PHOTOCATALYTIC DEGRADATION OF CIPROFLOXACIN USING METAL-DOPED TITANIUM DIOXIDE NANOPARTICLES

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### Abstract

This flat display shaped by ciprofloxacin pharmaceuticals among water sources remains a potential threat to the ecosystems aversive to environmental and health effects save for decommissioning. This research focuses on determining the enhanced photocatalytic removal of ciprofloxacin through metal-doped TiO2 nanocomposite particles. Several metal dopants such as, silver, iron and copper metal ions were investigated on the visible light photocatalytic activity of TiO2. Thus, parameters of the influences on which the reaction rate allows for the optimisation of experimental conditions, namely pH level, the dosage of a catalyst, and the initial concentration of ciprofloxacin were comprehensively investigated. In these experiments, the enhancement of degradation efficiency has clearly shown that the metal-doped TiO2 nanoparticles are more efficient in the degradation process; here the highest degradation rate is achieved by Ag-doped TiO2. Pseudo-first-order kinetic analysis of the data further substantiated the above observation. Hence this research reveals the possibility of using metal-doped TiO2 nanoparticles for efficient wastewater treatment.

### INTRODUCTION

Many pharmaceuticals have been detected in aquatic systems worldwide because they are persistent and are known to have negative impacts on the environment and the health of humans and animals. Because of the widespread use of drugs in water bodies especially the extensively used antibiotics, there are questions as regards the ecological impact of the residue and human health impact through ingestion of water or consumption of food products containing the residue. A frequently present antibiotic in surface water, groundwater and treated drinking water is Ciprofloxacin; the antibiotic is not fully removed in conventional wastewater treatment steps. This antibiotic, like most pharmaceuticals, is highly stable in conventional treatment processes and may therefore persist in aquatic environments (Pascariu, Gherasim and Airinei, 2023).

Since the use of traditional treatment processes has not been fully successful in the removal of recalcitrant compounds, AOPs have been eyed as suitable technologies for the degradation of pharmaceutical compounds in water. AOPs produce strongly reactive radicals such as hydroxyl radicals which can decompose organic pollutants into harmless by-products. Of all the AOPs, Photocatalysis has been considered to be the most effective strategy for environmental biotreatment because photocatalysts activate in the presence of sunlight to effectively degradation of hazardous pollutants (Akhter et al., 2022).



Figure 1(Source of Water Contamination (Checcucci, Trevisi et al. 2020)

Titanium dioxide (TiO2) is still one of the most attractive photocatalyst materials owing to its advantages: chemical stabilities, no toxicity concerns and relatively low cost; the photocatalytic activity towards the formation of reactive species under UV light. This photocatalytic process of TiO2 usually involves the use of ultraviolet light that excites the valence band to release electrons that form the electron-hole pairs. These excited electrons can then move to the surface of the catalyst where they participate in oxidation reactions that minimizes the concentration of ciprofloxacin and other organic pollutant. However, the application of TiO2 for photocatalytic degradation comes into some questions because the wide band gap ( $^{\sim}3.2$  eV) only enables reaction under ultraviolet light ageing, natural light, which mainly is visible light ageing (Ahmadpour et al., 2024).

In extending these limitations, efforts have been made to improve the photocatalytic activity of TiO2 which includes metal doping among others. Metal ions doping on TiO2 results in changes in its electronic structure - the bandgap narrows down allowing the photocatalysts to capture light waves in the visible region. Copper (Cu), silver (Ag) and iron (Fe) have been considered to be potent dopant elements to enhance the photocatalytic behaviour of TiO2. These metal dopes can effectively narrow the bandgap of TiO2 and therefore, the material can be used to photo-catalyse under sunlight or visible light (Khalil et al., 2024). Also, metal doping can eliminate the recombination of electron-hole pairs, which is a major disadvantage of photocatalytic reactions. This reduction of recombination further increases the efficiency of the photocatalytic degradation process of organic pollutants including ciprofloxacin (Ravi, Bhan and Golder, 2025).



Fig. 1.2:Source of Sustainable Energy (Lin, Yang et al. 2022)

Therefore, it is a major concern when there are pharmaceutical contaminants in aquatic environments, however, the degradation of these pollutants can be addressed through the following oxidation processes: Photocatalysis advanced especially the use of TiO2 and Metals doped TiO2. The alteration of TiO2 through metal doping improves its photocatalytic activity in addition to making photocatalytic reactions possible under visible light. Further investigations into enhancing methods of metal doping, and the discovery of other new photocatalysts, are vital as a means of enhancing the efficiency and applicability of the technologies in combating pharmaceutical pollution of water (Giram, Shrivastava and Das, 2024).

### 2. Literature Review

The problem of pharmaceuticals entering water sources and polluting water systems is a current environmental problem which is particularly alarming since compounds such as antibiotics are scarcely biodegradable and could pose serious health risks. Ciprofloxacin (CIP), a fluoroquinolone antibiotic, is frequently isolated in wastewater and various aquatic systems and is recalcitrant to biodegradable through traditional sewage treatment processes. The removal of such pollutants by applying the photocatalytic activity of titanic or titanium dioxide (TiE<sub>2</sub>) nanoparticles has become quite popular because of its stability, non-toxicity and high oxidation power (Kovačević et al., 2024). Nonetheless, TiE<sub>2</sub> has a great band gap of, 3.2 eV meaning that its photocatalytic reactivity is restricted to under UV light only. To avoid this limitation, doping of TiE<sub>2</sub> with various metals has been attempted, with the view of increasing photocatalytic efficiency, especially under visible light. This review is especially concerned with metal-doped TiO<sub>2</sub> in photocatalytic degradation of ciprofloxacin, including optimization of parameters and possible mechanisms (Lin et al., 2024).

### 2.1 Titanium (IV) Oxide as a Photocatalyst

Among the peRs, TiO<sub>2</sub> in the anatase phase is one of the most explored photocatalysts for organic pollutants degradation because of its low cost, chemical inertness, and environmental benignancy. The TiO<sub>2</sub> photocatalyst can upon exposure to UV light produce electron-hole pairs that transfer redox reactions and generate ROS such as  $\bullet$ OH and O<sub>2</sub> $\bullet^$ which are capable of degrading organic pollutants (Krakowiak et al., 2021).

Nonetheless, the largest disadvantage of  $TiO_2$  is that its band gap of the material is large, and therefore can only accommodate wavelengths of light in the ultraviolet portion of the electromagnetic spectrum. This has engendered plenty of research in altering  $TiO_2$  through permissiveness with metals to expand the range of light absorption, separation efficiency of electron-hole pairs and photocatalytic reactions (Vanlalhmingmawia, Lee and Tiwari, 2023).

### 2.2 Metal Doping of TiO<sub>2</sub>

The present method of doping TiO<sub>2</sub> by various metal ions has been found to enhance its photocatalytic activities due to the reduction in band gap energy, the shift of the absorption edge in the visible region of the electromagnetic spectrum, and a decrease in recombination rate of electron-hole pairs. Some of the investigated metals are noble metals (Ag Au), transition metals (Fe Cu Ni) and other metal oxides (Chauhan, Agnihotri and Vasundhara, 2024).

### 2.2.1 Noble Metal Doping (Ag, Au)

Silver (Ag) Doping: Silver is one of the most investigated dopants for TiO<sub>2</sub> materials. The incorporation of Ag destabilizes the TiO2's surface Plasmon resonance (SPR), thus increasing its photocatalyst activity under visible light. However, the photoinduced electrons reduce the recombination rate because silver nanoparticles can also work as electron collectors (Zhao et al., 2020). Research has revealed that Ag-doped TiO<sub>2</sub> has a activity higher photocatalytic in degrading ciprofloxacin; in this case, Ag works as an electron acceptor, thus extending the photocatalytic energy (Din and Khalid, 2023).

• Gold (Au) Doping: There are also improved photocatalytic properties of gold-doped TiO<sub>2</sub> because of the SPR effect of gold nanoparticles and better light absorption in the visible light range as well as better charge separation. Unlike silver, studies of Audoped TiO<sub>2</sub> have illustrated higher efficiency in the destruction of organic compounds (Yasar and Kadhem, 2024).

# 2.2.2 Doping of Transition Metal such as Fe, Cu and Ni

• **Iron (Fe) Doping:**  $TiO_2$  doped with iron is one of the most investigated materials in an attempt to make the material suitable for utilization in solar spectra. The fat-soluble iron ion (Fe<sup>3+</sup>) in TiO<sub>2</sub> can also be used as a redox mediator for boosting the production of hydroxyl radicals (•OH) and superoxide radicals (O<sub>2</sub>•<sup>-</sup>). Previous studies have established that photocatalytic degradation of ciprofloxacin can be done using Fe-doped TiO<sub>2</sub>, and this photocatalyst exhibits a faster degradation rate compared to TiO<sub>2</sub> (Manea et al., 2021). • **Copper (Cu) Doping:** Copper-doped TiO<sub>2</sub> also improves the photocatalytic oxidation of any kind of pollutants contained in organic compounds. Copper ions may change the structure of TiO<sub>2</sub>, decrease the band gap, and increase the number of active sites for the adsorption of organic pollutants. In addition, the doping of copper enhances the efficiency of charge carrier separation while increasing ROS production and enhancing the degradation efficiency of ciprofloxacin (Pascariu et al., 2022)

• Nickel (Ni) Doping: Most of the reports have pointed out that doping of Nickel in TiO<sub>2</sub> has the potential to enhance photocatalytic degradation, especially under visible light. Nickel ions were found to enhance the generation of hydroxyl radicals as well as the separation of the electron and hole which enhances the ability of the photocatalyst to degrade ciprofloxacin. The dopant concentration is vital in determining the highest photocatalytic activity of the sample (Patidar et al., 2024)

### 2.3 Processes of Photocatalytic Reactions

The mechanism of photocatalytic degradation involves several key steps:

• Excitation of TiO<sub>2</sub>: When TiO<sub>2</sub> is illuminated, electrons in its valence band get promoted to the conduction band and thus form electron and hole pairs.

• Formation of ROS: The photo-generated electrons (e<sup>-</sup>) reduce dissolved oxygen to form superoxide anions ( $O_2 \bullet^-$ ), while the holes (h<sup>+</sup>) oxidise water or hydroxide ions to generate hydroxyl radicals ( $\bullet$  OH). These two reactive species are rather oxidative and are capable of degrading organic pollutants ciprofloxacin among them.

• **Degradation of Ciprofloxacin**: Hydroxyl radicals and superoxide anions reduce the molecular of ciprofloxacin into smaller conjugate fragments including carbon dioxide, water and inorganic ions (Yan et al., 2024)

• Charge Separation and Recombination: Thus, metal doping is found to be supremely significant in the aspect of charge separation. The dopant metal also consumes the photogenerated electrons and holes to improve the photocatalytic performance of the photocatalyst. Consequently, understanding the factors that influence photocatalytic degradation can be of paramount importance, as will be explained in the following section.

Several factors influence the efficiency of photocatalytic degradation of ciprofloxacin using metal-doped TiO<sub>2</sub>:

• **Doping Concentration:** From the above results, it can be seen that the concentration of the metal dopant plays a decisive role in the photocatalytic efficiency. A small concentration of metal dopant can improve the photocatalytic efficiency, whereas a high concentration of dopant may cause metal particles to aggregate or generate new recombination sites, thus negatively affecting the photocatalytic process (Wang et al., 2021).

• **pH of the Solution:** pH impacts the charge distribution and adsorption of ciprofloxacin on the TiO<sub>2</sub> surface. Thus at acidic or near neutral pH, ciprofloxacin can be seen to adsorb more on the TiO<sub>2</sub> surface thus increasing the degradation process.

• Light Source: The intensity of the light and the wavelength used are knobs which determine the activation of TiO<sub>2</sub>. Although TiO<sub>2</sub> is photo catalytically active under UV only, doping by metals can shift the absorption edge into the visible light region, more appropriate for photocatalytic solardriven degradation (Mokhtari et al., 2022)

• **Catalyst Dosage:** This study reveals that there is a correlation between the concentration of TiO<sub>2</sub> in the reaction and the photocatalytic activity. The amount of catalyst enhanced the number of active sites for the degradation of the pollutant, although large quantities were likely to hinder illumination and thus lower photocatalytic degradation (Yin et al., 2022)

• **Reaction Time:** The degradation rate is most often a function of time, which rises to a certain point and then levels off when the pollutant is no longer appreciably altered by continued exposure. For that reason, one must ensure that the time spent on the reaction is sufficient enough to increase the amplitude of degradation at a higher level.

### 2.4 Optimization Strategies

• **Composite Materials**: Doping titanium dioxide with metals and compounding it with other materials like graphene, carbon nanofibres and polymer, can even improve the photocatalytic efficiency. This material can enhance the charge carrier mobility, surface area and also the light absorption to visible range (Zhou et al., 2018).

• Surface Modification: Changing the surface of  $TiO_2$  to include defects or other chemical groups can improve the adsorption pattern of ciprofloxacin and also improve the photocatalytic degradation efficiency.

• **Experimental Design:** To achieve an optimal degradation performance, various optimization methods including response surface methodology (RSM) and others are employed to determine the best balance of metal doping concentration, pH, catalyst dosage, and light intensity (Anucha et al., 2022)

3. Materials and Methods

The TiO2 nanoparticles were produced through the sol-gel method of preparation which is regularly preferred method because of its efficiencies and ease of preparation of high-quality nanoparticles. Reflected by this process, the titanium precursor that is often used is titanium isopropoxide, Ti [OCH (CH3)2]4, which was first dissolved into a solvent and then water and a catalyst, usually an acid or base, were added to promote hydrolysis and condensation reactions. The obtained sol is gelled to form a solid-like network of TiO2 and again heated to different high temperatures to achieve the required crystalline phase of TiO2 nanoparticles.

To improve the photocatalytic behaviour of TiO2, the metal doping technique was incorporated by including different concentrations of Ag, Fe, and Cu. The doping was done by a process of incorporating metal ions, like AgNO3, FeCl3, and Cu (NO3)2 by dissolving the salts in the sol before the gelation. By doping TiO2 with metal ions, the amounts of metal dopants per mole of TiO2 were changed to evaluate their impact on the photocatalytic performance of TiO2. Further, after doping the TiO2 nanoparticles were subjected to temperature treatment at high temperatures between (400-500°C) to facilitate the entry of the metal ions into the TiO2 lattice and also ensure that all the

TiO2 only has negligible defects and in crystalline form (Suwannaruang et al., 2020).



The structural and morphological characteristics of the synthesized metal-doped TiO2 nanoparticles were thoroughly analyzed using various characterization techniques:

• X-ray diffraction (XRD): The detailed structure and phase of the synthesized TiO2 nanoparticles were determined by X-ray diffraction analysis. This functional use of the diffraction patterns was used for the formation of anatase phase TiO2 and for analyzing the influence of metal doping within that material. The incorporation of metal ions into the TiO2 lattice was assumed if the peaks shifted or were intensified or reduced in intensity.

• Scanning electron microscopy (SEM): The shape and surface characteristics of nanoparticles, which were synthesized in this work were analyzed using scanning electron microscopy. This technique was found useful in the identification of the particle

size, shape and surface morphology of the metaldoped TiO2 nanoparticles. These images were useful for identifying any inclination of aggregation, or changes in the distribution of particles due to doping. (Majumder et al., 2020)

• UV-Vis diffuse reflectance spectroscopy (DRS): In this study, the DRS combined with spectroscopic ellipsometry were used to analyze the optical properties of synthesized metal-doped TiO2 NPs. From the obtained diffuse reflectance spectra it is then possible to analyze the absorption characteristics of the photocatalyst in the UV-visible light region most effective for its application. Shifts of the position of the absorption edge to the visible region indicated the success of the formation of the desired reduced bandgap of TiO2 with incorporation of metal elements, showing good photocatalytic activity under visible-light illumination (Petronela et al., n.d.)

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3.1 Experiments on the Photocatalytic Degradation The photocatalytic degradation activities were investigated under visible light illumination to assess the performance of various metal-loaded TiO2 nanoparticles in the photodegradation of ciprofloxacin, a frequently identified PPCP. The degradation experiments were performed in a batch reactor where the TiO2 nanoparticles were dispersed in a ciprofloxacin-containing aqueous solution. A lamp emitting visible light was used to treat the system, and the rate of disappearance of ciprofloxacin was followed over time.

Several experimental variables were optimized to achieve the best photocatalytic performance:

• **PH** (3-9): Photocatalytic degradation of ciprofloxacin was investigated with varying pH of the solution, where necessary, by adding appropriate acids or bases. The pH is a constraint because it affects the charge of the TiO2 nanoparticles, the ionization state of ciprofloxacin in solution and the formation of reactive oxygen species during the photocatalytic process (Mao et al., 2024).

• Catalyst Dosage (0.1-1.0 g/L): Catalyst concentration was also taken into consideration to compare the degradation rate while increasing the amount of the metal-doped TiO2 nanoparticles added. More amounts of the catalyst can increase the available active sites for the photocatalytic reaction

but at the same time can increase the particle agglomeration or light scattering. After analysing these factors, the best dosage was established to consider to achieve maximum degradation efficiency.

• Initial Ciprofloxacin Concentration (10-50 mg/L): The influence of the initial concentration of ciprofloxacin on the degradation process was investigated by adding different concentrations of the pollutant in the solution. Concentrations of ciprofloxacin above 5 mg/L, can cause slower degradation rates since the degradation time will be longer and there is photocatalytic inactivity as a result of the fully occupied active sites on the catalyst. The concentration range was selected because environmental pharmaceutical levels are usually in that range (Amigun et al., 2022).

In the degradation experiments, the amount of ciprofloxacin used was determined by taking samples of the solution at different time points. The concentration of the remaining ciprofloxacin was also determined using a UV-Vis spectrophotometer where the absorbance spectrum of ciprofloxacin was used to calculate for concentration of the antibiotic in the solution. The photocatalytic degradation efficiency was then determined using the initial and final concentration of the ciprofloxacin after which the photocatalytic degradation rate was given as the percentage degradation over time.

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### 4. Results and Discussion

### 4.1. Characterization of Metal-Doped TiO2

The structural, morphological and optical characterization of the synthesized metal-doped TiO2 nanoparticles was carried out using various characterization techniques to validate the synthesis of nanoparticles and to determine their potential for photocatalytic application.

X-ray Diffraction (XRD): XRD results identified that TiO2 nanoparticles have not altered the anatase phase which is highly effective in the photocatalytic process. The diffraction reveals that the XRD patterns of the obtained material comply with the pure anatase TiO2 phase, the peaks located at 25.3°, 37.8°, 48.0°, and 54.4° with (101), (004), (200), (105) crystal facets respectively. No new peaks related to the metal dopants Ag, Fe, and Cu were identified in the patterns, however, implying that the dopants were indeed incorporated into the TiO2 lattice without causing an alteration in crystallinity. A peak shift of 0.025-0.038° and changes in peak intensities were observed, lifting the evidence of interaction of the metal ions with the TiO2 lattice and the modification of crystal structure due to doping.

• Scanning Electron Microscopy (SEM): The morphology of the metal-doped TiO2 nanoparticles was observed using SEM as presented in the

following image FIG 2, which shows that the particles were relatively uniformly distributed with sizes in the range of nanometers. The developed doped TiO2 had a defined spherical to quasispherical morphology, particle size, and nonagglomeration and it is evident that metal doping did not cause particle agglomeration. Uniform distribution in particle size and morphology is vital to <sup>R</sup> photocatalytic function since random photocatalytic surfaces are more accessible to photocatalyst molecules.

UV-Vis Diffuse Reflectance Spectroscopy (DRS): An analysis of the optical properties of the synthesized metal-doped TiO2 samples was performed using the DRS technique. By analyzing the UV-Vis spectra, a redshift in the absorption edge of the metal-doped TiO2 relative to that of the pure TiO2 could be observed, thus giving a corresponding decrease in the bandgap of the material. This redshift was especially marked in the Ag-doped TiO2, which had a higher UV extent of visible light absorption than the uncomplicated TiO2. The metal doping has thus improved TiO2 photocatalytic ability by expanding the optical spectrum it can tap for the photocatalytic degradation function. The increased number of visible light absorption sites is one of the approaches that contribute to increasing the

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photocatalytic activity of TiO2 in the visible light range.



Fig. 4.1: FTIR spectra of TiO<sub>2</sub>

Table 4.1: Functional groups of TiO<sub>2</sub>

Table 4.1: Func	tional groups of TiO	2		
Sr.No.	Functional group	Modes of Vibration	Wavenumber (cm <sup>-1</sup> )	Reference
1	-OH	Stretching vibrations	nı & Research 3213	(Khan, Raza et al. 2024)
2	-OH	Bending vibrations	1643	(Franco, Zabisky et al. 2020)
3	Ti-O-Ti	Stretching vibrations	721	(Khadar, Behara et al.2021)
4	Ti-O-Ti	Bending vibrations	634	(Khadar, Behara et al.2021)



Sr.No.	Wavenumber (cm <sup>-1</sup> )	Functional group	Modes of Vibration	Referance
1	400-700 cm <sup>-1</sup>	Ti-O	Stretching and bending modes	(Lopes, Maria da Graça et al. 2020)
2	700-1000 cm <sup>-1</sup>	Ti-O-Ti	Bridging modes	(Rahmawati, Butburee et al. 2023)
3	450-550 cm <sup>-1</sup>	Ag-O-Ti-O	Bridging modes	(Garg, Kataria et al. 2023)
4	3421 cm <sup>-1</sup>	O-H	Stretching	(Garg, Kataria et al. 2023)

### Fig. 4.2: FTIR spectra of Ag/TiO<sub>2</sub>

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### 4.2. Photocatalytic Performance

The photocatalytic efficiency of removing ciprofloxacin, a model API, pharmaceutical was estimated as a function of the metal-doped TiO2 nanoparticles exposed to visible light. Doping was efficient in enhancing the photocatalytic degradation efficiency of TiO2 with Ag-doped TiO2 showing the highest efficiency in the degradation of CPC in aqueous solutions.

• **Degradation Efficiency**: The Ag-doped TiO2 sample underwent 92% degradation efficiency under visible light irradiation for 120 minutes, much better than the rest of the samples including untainted TiO2 and other metal-containing samples including Fe and Cu. This result shows that the Ag doping of TiO2 is a highly effective photocatalyst with associated band gap decrease and additional charge carrier separation.

Optimal Conditions: Thus, the effect of the different experimental parameters under which the photocatalytic degradation efficiency was optimized was determined. It was also observed at pH 5 that the catalyst worked at its best degradation level, so this pH can be considered optimal. Based on these results, the chosen catalyst dosage of 0.5 g/L is deemed to be optimal, in terms of generating a sufficient number of active sites for photocatalytic reactions while minimizing particle condensation. Moreover, initial ciprofloxacin concentration at 20 mg/L was established to be the most efficient in which the photocatalytic degradation process proceeded at a convenient rate but without overloading the photocatalyst and hence its capability to degrade the contaminant.

**Kinetic Analysis**: The photocatalytic degradation process was kinetically analyzed and

revealed to follow pseudo-first-order kinetics since there was a linear relationship between ln (Co/Ct) and the irradiation time. The analysis of the performance of our Ag-doped TiO2 photocatalyst showed that the rate constant for the degradation process was 0.018 min^-1, which suggests moderate but adequate degradation activity. Based on this kinetic model, the degradation of ciprofloxacin is mainly governed by the pollutant-photocatalyst interface with rates proportional to the number of surface active sites and concentration of the catalyst used.

### 4.3. Mechanism of Degradation

The enhanced photocatalytic performance of the metal-doped TiO2 nanoparticles can be attributed to several key factors related to the electronic properties and charge dynamics of the material:

Reduced Bandgap and Inhibited Electron-Hole Recombination: Metal doping, in this case, is a viable method of reducing the bandgap of TiO2 as can be shown by the shifts to the red region of the absorption spectra. This decrease enables TiO2 to capture more of the visible light making photocatalytic actions favourable under unnatural light conditions. Furthermore, species like Ag, Fe and Cu place energy levels in the bandgap of TiO2 that can help to capture and reduce electron-hole recombination. This suppression of recombination extends the lifetime of the charge carriers, raising the prospect of them engaging in degradation processes. Generation of Reactive Oxygen Species (ROS): • Photocatalytic degradation of ciprofloxacin is considered to be mainly mediated through the formation of reactive oxygen species ROS, which is highly oxidizing and capable of degrading organic compounds. In the present study, the predominant ROS implicated in the degradation process were hydroxyl radicals (•OH) and superoxide anions (O2•-). These species are generated upon excitation of the TiO2 nanoparticles under visible light irradiation:

• • OH is highly reactive and can cause an attack on the organic contaminants leading to the formation of easily biodegradable molecules.

• Superoxide anions  $(O2 \cdot -)$  are also implicated in the oxidative breakdown of pollutants, even more so when metal dopants that enhance the electrode redox reactions are included.

The metal dopants especially Ag have a strong impact on the increase of the production of ROS due to better charge separation and improved formation of these reactive species on the surface of TiO2. This higher concentration of ROS indicates that the efficiency of degradation is higher in the Agdoped TiO2 sample prepared for the present study.

### 5. Conclusion

Therefore, there is a considerable enhancement in the photocatalytic degradation efficiency of metaldoped TiO2 nanoparticles especially in the case of Ag-TiO2 nanoparticles under visible light, and hence its applicability as a solution to contain the emission of pharmaceutical pollutants including ciprofloxacin in the wastewater is encouraged. The extension of the visible light absorption through metal doping reduces the bandgap and inhibits the electron-hole recombination, also increasing the formation of ROS for degrading the organic pollutants. The photocatalytic activity reached its highest efficiency under such conditions as pH=5, the dosage of the photocatalyst = 0.5 g/L, content of ciprofloxacin = 20 mg/L, implying the possibility of applying these catalysts to solve the problems of environmental contamination.

From this study, it is clear that metal-doped TiO2 especially with Ag doping has the potential to be used in sustainable wastewater treatment that is cheaper and environmentally friendly than the current systems used in the elimination of the recalcitrant pharmaceutical compounds. However, more work is required to examine the applicability of this technology to various pollutants, the limitation of the use of biomass to derived catalysts, and the stability in real-life conditions of the catalysts. Also for future research TiO2 photocatalytic process should be combined with other methods and technologies for water treatment to achieve the higher efficiency and reliability of the process which can lead to more effective solutions to prevent the impact of pharmaceuticals in aquatic systems.

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