DOXYCYCLINE PHOTOCATALYTIC DEGRADATION USING MESOPOROUS CARBON NITRIDE (MCN) UNDER VISIBLE LIGHT

Azzahra Hanggararas Sasdika [1)], Ervin Nurhayati [1)], Isni Arliyani [1)],
Muchammad Tamyiz [2)], Adhi Yuniarto [1)], Yu Syuan Liou[3)], Checia Hu[3)]
[1)] Department of Environmental Engineering, Faculty of Civil, Planning and Geo-Engineering, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia
[2)] Department of Environmental Engineering, Faculty of Engineering, Universitas Nahdlatul Ulama Sidoarjo, Sidoarjo 61218, Indonesia
[3)]Department of Chemical Engineering and Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 70101, Taiwan
[*)]E-mail:* ervin@enviro.its.ac.id

Abstract

Antibiotic contamination in aquatic environments has become a global concern due to its potential contribution to antimicrobial resistance and adverse impacts on aquatic ecosystems. Photocatalysis using carbon nitride-based semiconductor materials has emerged as a promising approach for the removal of antibiotic pollutants. This study aimed to evaluate the performance of Mesoporous Carbon Nitride (MCN) for the degradation of DOX under visible-light irradiation at initial concentrations of 0.5, 5, 20, and 50 mg/L. Photocatalytic experiments were conducted in a laboratory-scale reactor equipped with a magnetic stirrer to maintain solution homogeneity. DOX concentration was determined using UV–Vis spectrophotometry, while ammonia (NH_3-N) analyses were performed to investigate compound transformation during the degradation process. The results demonstrated that both irradiation time and initial DOX concentration significantly influenced the degradation performance. The highest degradation efficiency was achieved at an initial concentration of 50 mg/L, reaching 36.51% after 150 min of visible-light irradiation, whereas the degradation efficiency at 20 mg/L was 12.29%. Degradation rate analysis revealed maximum values of 0.103 mg L^{-1} min^{-1} and 0.514 mg min^{-1} g^{-1} at 50 mg/L. Changes in ammonia concentration indicated that the photocatalytic process not only promoted DOX degradation but also facilitated the transformation of nitrogen-containing compounds during the reaction. Meanwhile, the apparent negative degradation efficiencies observed at 0.5 and 5 mg/L were attributed to analytical limitations associated with UV–Vis measurements at low concentrations. These findings demonstrate the potential of MCN as a visible-light-responsive photocatalyst for the treatment of antibiotic-contaminated wastewater.

Keywords: Antibiotic; Doxycycline ; Mesoporous Carbon Nitride ; Photocatalysis ; Visible light

1. INTRODUCTION

The presence of antibiotic residues in aquatic environments has become a critical environmental issue due to their persistence and potential to induce antimicrobial resistance. These contaminants originate from various sources, including domestic wastewater, agriculture, and pharmaceutical industries, leading to their continuous discharge and accumulation in water bodies. Among them, *Doxycycline* (DOX) is frequently detected due to its widespread use and low biodegradability, making it a significant contaminant of emerging concern.

Conventional wastewater treatment processes are generally ineffective in removing antibiotic compounds, resulting in their persistence even after treatment. Therefore, advanced treatment methods are required. Photocatalysis has attracted considerable attention as it can degrade complex organic pollutants into simpler and less harmful substances. However, commonly used photocatalysts such as graphitic carbon nitride (g-C_3N_4) still face limitations, particularly low surface area and rapid recombination of electron–hole pairs.

To overcome these limitations, *mesoporous carbon nitride* (MCN) has been developed with improved structural properties, including higher surface area and enhanced photocatalytic activity. Despite its potential, studies on DOX degradation using MCN are still limited, especially in terms of process optimization and interaction between operational parameters.

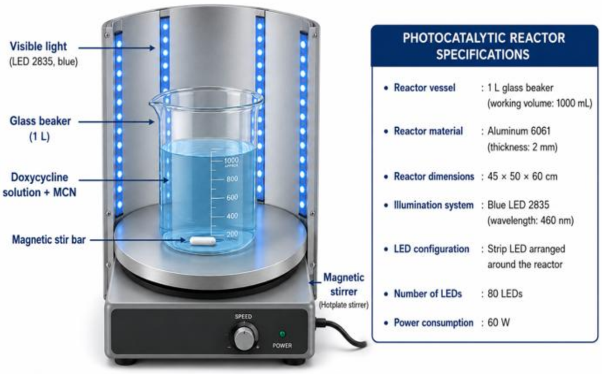
Based on these gaps, this study This study aims to evaluate the effect of initial doxycycline concentration on the photocatalytic degradation performance of Mesoporous Carbon Nitride (MCN) under visible light irradiation and to assess the associated changes in ammonia (NH_3–N).

2. MATERIALS AND METHODS

This study was conducted to evaluate the performance of Mesoporous Carbon Nitride (MCN) as a photocatalyst for the degradation of doxycycline (DOX) under visible-light irradiation. Artificial wastewater was prepared by mixing DOX and ammonia to simulate a wastewater matrix containing both antibiotic contaminants and nitrogen-containing compounds commonly found in domestic and livestock wastewater. Nitrogen contained in feed protein is not completely utilized by livestock; therefore, approximately 50–80% of the consumed nitrogen is excreted back into the environment. The excreted nitrogen is then subjected to microbial decomposition, during which organic nitrogen compounds are converted into ammonia, leading to its accumulation in livestock wastewater.

Ammonia was intentionally added to represent nitrogen compounds frequently present in livestock wastewater and was maintained at a constant concentration throughout all experiments. Therefore, ammonia was not treated as an independent variable, and this study focused on evaluating the photocatalytic degradation of DOX in the presence of ammonia as a co-existing pollutant rather than investigating ammonia removal. The selected ammonia concentration was intended to create a more realistic wastewater environment and to assess photocatalytic performance under complex wastewater conditions.

The initial DOX concentrations used in this study were 0.5, 5, 20, and 50 mg/L. Photocatalytic degradation experiments were carried out using a photocatalytic reactor equipped with a blue LED lamp (460 nm) and a magnetic stirrer to maintain solution homogeneity throughout the reaction. The photocatalyst dosage was fixed at 0.2 g/L for all experiments. The data obtained were analyzed descriptively based on the effect of irradiation time and initial concentration on the degradation efficiency of DOX using MCN. The illustration of photocatalytic reactor can be seen in Figure 1.



PHOTOCATALYTIC REACTOR SPECIFICATIONS

• Reactor vessel	: 1 L glass beaker (working volume: 1000 mL)
• Reactor material	: Aluminum 6061 (thickness: 2 mm)
• Reactor dimensions	: 45 × 50 × 60 cm
• Illumination system	: Blue LED 2835 (wavelength: 460 nm)
• LED configuration	: Strip LED arranged around the reactor
• Number of LEDs	: 80 LEDs
• Power consumption	: 60 W

Figure 1. Schematic Illustration of the Visible-Light Photocatalytic Reactor for DOX Degradation

Prior to the photocatalytic experiments, MCN was synthesized using melamine and ammonium chloride (NH_4Cl) as precursors at a mass ratio of 1.00 g and 0.01 g, respectively. The precursors were thoroughly mixed in a porcelain crucible and subsequently calcined in a furnace at 550 °C for 180 min. After naturally cooling to room temperature, the obtained material was washed several times with deionized water followed by ethanol to remove residual impurities. Finally, the material was dried in an oven to obtain the final MCN photocatalyst.

The degradation performance was evaluated by quantifying DOX concentrations using UV–Vis spectrophotometry. The maximum absorption wavelength (λmax) of DOX was determined to be 366 nm, and all measurements were performed at this wavelength. A calibration curve was established using 15 standard solutions with concentrations of 0.5, 1, 3, 5, 7, 9, 10, 12.5, 15, 20, 25, 30, 40, 50, and 60 mg/L. Linear regression analysis yielded the equation $y = 0.0242x + 0.0218$ with a coefficient of determination (R^2) of 0.9952. The high R^2 value indicates excellent linearity between concentration and absorbance, confirming the suitability of the calibration curve for subsequent DOX quantification. The UV–Vis calibration curve of DOX is shown in Figure 2.

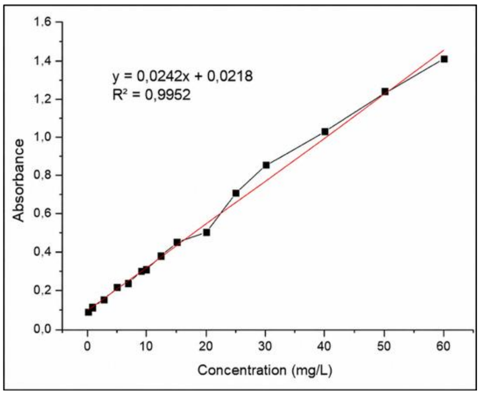


Figure 2. Calibration Curve of DOX

Determined by UV–Vis Spectrophotometry

In addition to DOX degradation, the transformation of nitrogen-containing compounds during the photocatalytic process was evaluated by measuring ammonia (NH_3–N) concentrations. Ammonia analysis was performed using the Nessler spectrophotometric method. The maximum absorbance peak was observed at 412 nm; therefore, all measurements were conducted at this wavelength.

Furthermore, the physicochemical properties of MCN were characterized to investigate its structural, optical, and surface characteristics. Crystal structure analysis was performed using a Rigaku MiniFlex 600 X-ray diffractometer (XRD) with a scanning range of 5–60° (2θ). Optical properties were analyzed using UV–Diffuse Reflectance Spectroscopy (UV–DRS) with a UV–Vis spectrophotometer equipped with an ISA-220 Integrating Sphere Accessory over a wavelength range of 200–800 nm. Surface area analysis was conducted using a NOVA 800 surface area analyzer with N_2 as the adsorbate.

3. RESULT AND DISCUSSION

Characterization of Mesoporous Carbon Nitride (MCN)

Characterization of the MCN was conducted to determine the physical and structural properties of the synthesized material. In this study, the characterization methods employed included X-ray Diffraction (XRD), Brunauer–Emmett–Teller (BET), and UV–Visible Diffuse Reflectance Spectroscopy (UV–DRS) analysis.

XRD analysis was conducted to determine the crystal structure of MCN, while BET analysis was performed to confirm the mesoporous characteristics of MCN. Meanwhile, UV–DRS analysis was carried out to determine the band gap energy of MCN in relation to the energy of the light source used in the photocatalytic process.

Based on the X-ray diffraction (XRD) analysis, the diffraction pattern of the sample exhibited characteristics typical of graphitic carbon-based materials. The obtained data revealed the presence of a dominant main diffraction peak at approximately 2θ = 26–27°, along with a weak peak around 2θ = 13°. The crystal structure characterization results obtained from XRD analysis are presented in Figure 3.

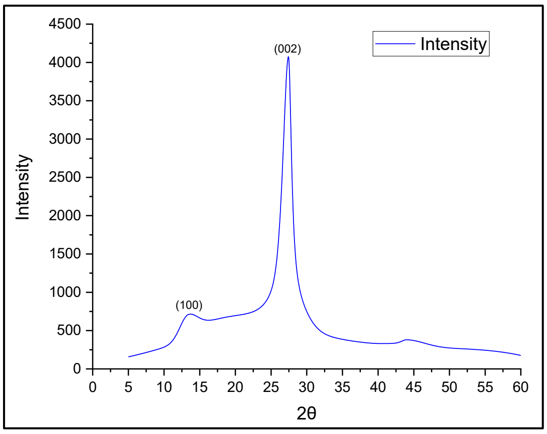


Figure 3. X-ray Diffraction (XRD) Analysis Results of Mesoporous Carbon Nitride (MCN)

The strong peak within the range of 2θ = 26–27° was associated with the (002) crystal plane, which represents the interlayer stacking of graphitic carbon nitride (g-C_3N_4) or graphitic carbon structures. This indicates the presence of a layered structure (Nunna et al., 2024). Meanwhile, the peak around 2θ = 13° corresponded to the (100) plane, indicating the in-plane structural packing of tri-s-triazine units, which are the primary building blocks of g-C_3N_4 (Zhao et al., 2015).

The surface texture characteristics of the MCN composite material were analyzed using nitrogen adsorption–desorption isotherms. The obtained isotherm curve exhibited a tendency resembling type IV isotherms, in which type IV isotherms represent mesoporous materials. However, the formed hysteresis loop was not clearly observed and was not completely closed, indicating that the material did not exhibit an ideal mesoporous pattern according to the IUPAC (International Union of Pure and Applied Chemistry) classification. The nitrogen adsorption–desorption isotherm BET results characterization results obtained from BET analysis are presented in Figure 4.

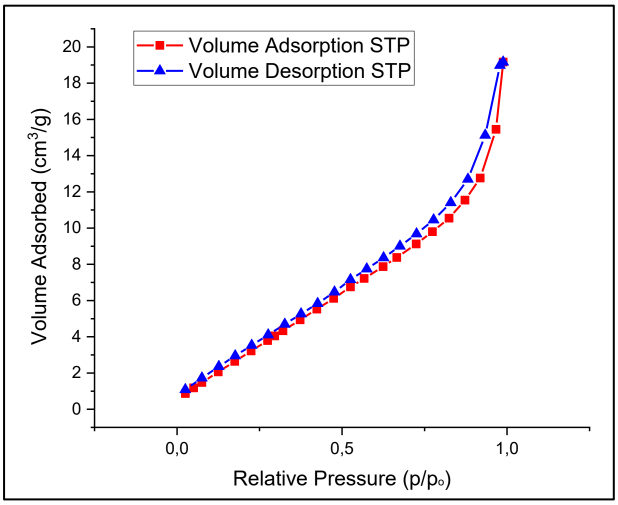


Figure 4. Nitrogen Adsorption–Desorption Isotherm BET Results of MCN Material

Nevertheless, the BET analysis revealed that the material possessed an average pore diameter of approximately 3.22–3.24 nm with a pore volume of about 0.128 cm^3/g, which still falls within the mesoporous range (2–50 nm). This result confirms that the material has a mesoporous structure with a relatively narrow pore size distribution. The specific surface area obtained from the multipoint BET method was 77.322 m^2/g, indicating that the material possesses a relatively large active surface area. This value is relatively higher than that of bulk g-C_3N_4 generally reported in the literature, where previous studies showed that g-C_3N_4 samples synthesized without template addition only exhibited a surface area of approximately 7.3 m^2/g.

UV–Visible Diffuse Reflectance Spectroscopy (UV–DRS) characterization was also conducted to evaluate the light absorption capability and determine the band gap energy of the MCN material. The band gap value is an important parameter in photocatalytic materials because it determines the minimum energy required for electrons to transition from the valence band to the conduction band during light irradiation.

The determination of band gap energy was carried out using the Tauc plot method based on UV–DRS data. In general, the Tauc equation describes the relationship between the absorption coefficient (α) and photon energy (hν) as follows:

$$(\alpha hv)^n = A(hv - Eg) \qquad (1)$$

where:

α = absorption coefficient,

hν = photon energy,

A = proportionality constant,

Eg = band gap energy,

n = constant depending on the type of electronic transition in the material.

The Tauc plot curve produced a linear equation of y = 1.3765x − 3.5749 with a coefficient of determination (R^2) value of 0.9934, indicating an excellent fitting linearity. The band gap energy (Eg) value was obtained from the intersection point of the fitted line with the photon energy axis (hν) at y = 0. Based on the Tauc plot analysis, the band gap energy of the MCN material was determined to be 2.60 eV. This value indicates that the material can be excited at a maximum wavelength of approximately 477 nm, which still lies within the visible light region.

Tauc plot curve UV-DRS characterization results of MCN Material are presented in Figure 5.

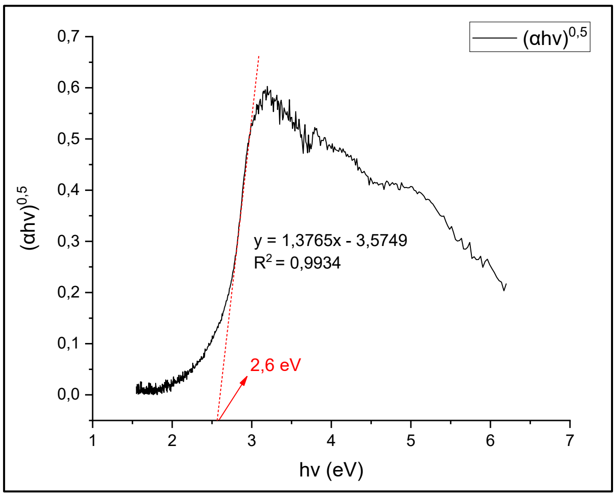


Figure 5. Tauc Plot Curve UV-DRS Results of MCN Material

The use of a 460 nm LED lamp in the photocatalytic process was therefore compatible with the optical characteristics of the material. This is because the photon energy of the 460 nm light source (2.70 eV) is higher than the band gap energy of MCN (2.60 eV), allowing electrons within the material to be effectively excited during the irradiation process.

These results of characterization indicate that the synthesized MCN material has favorable structural, textural, and optical properties for visible-light-driven photocatalytic degradation processes.

Effect of Photocatalytic Degradation Using Mesoporous Carbon Nitride (MCN) on Doxycycline Transformation

The study begins with the evaluation of DOX photodegradation using MCN as a photocatalyst at initial concentrations of 0.5, 5, 20, and 50 mg/L. The experiments were conducted in a photocatalytic reactor equipped with a magnetic stirrer to maintain solution homogeneity throughout the irradiation process. The results demonstrated that irradiation time significantly influenced the degradation performance of DOX. In general, longer irradiation periods led to higher degradation efficiencies due to the enhanced generation of Reactive Oxygen

Species (ROS), such as hydroxyl radicals (•OH) and superoxide radicals ($•O_2^-$), during the photocatalytic process.

This phenomenon is closely related to the photocatalytic mechanism of MCN as a semiconductor material capable of utilizing light energy to generate electron–hole (e^-/h^+) pairs. Upon light irradiation, electrons in the valence band are excited to the conduction band, producing charge carriers that subsequently participate in ROS generation. The photogenerated electrons can react with dissolved oxygen to form superoxide radicals ($•O_2^-$), while the holes in the valence band can react with water molecules or hydroxide ions to produce hydroxyl radicals (•OH). These reactive species possess strong oxidative capabilities and play a crucial role in the degradation of antibiotic compounds into simpler molecules (Wang et al., 2020).

The MCN photocatalyst employed in this study exhibits characteristics similar to those of graphitic carbon nitride (g-C_3N_4), a metal-free semiconductor known for its ability to efficiently generate ROS under visible-light irradiation. Through a series of oxidation reactions involving hydroxyl radicals, superoxide radicals, and photogenerated holes, DOX molecules can be progressively degraded into simpler intermediate compounds and subsequently mineralized into CO_2 and H_2O (Esfandiaribayat et al., 2024). Therefore, increasing the irradiation time generally enhances ROS generation, thereby improving the photocatalytic degradation efficiency of DOX. Photocatalytic Degradation of DOX Using MCN at Various Initial Concentration can be seen in Table 1.

Table 1. Photocatalytic Degradation of DOX Using MCN at Various Initial Concentrations

Initial DOX Concentration (mg/L)	Process Stage	Time (min)	Degradation Efficiency (%)
50	Before Treatment	0	0.00%
	Adsorption Stage	30	2.04%
	Photocatalytic Treatment	90	26.10%
	Photocatalytic Treatment	120	33.93%
	Photocatalytic Treatment	150	36.51%
20	Before Treatment	0	0.00%
	Adsorption Stage	30	2.73%
	Photocatalytic Treatment	90	4.10%
	Photocatalytic Treatment	120	4.64%
	Photocatalytic Treatment	150	12.29%

At an initial concentration of 50 mg/L, the photocatalytic process exhibited the highest degradation performance, achieving a degradation efficiency of 36.51% after 150 minutes of irradiation. Meanwhile, in a lower degradation efficiency of 12.29% was obtained at an initial concentration of 20 mg/L. The increase in degradation efficiency with prolonged irradiation time indicates that the ROS generated during the photocatalytic process effectively decomposed DOX molecules into simpler compounds. This finding is consistent with the study reported by Zhang et al. (2021), which demonstrated that longer irradiation times enhanced antibiotic degradation due to the increased generation of ROS throughout the photocatalytic reaction. The effect of irradiation time on DOX degradation at different initial concentrations can be seen in Figure 6.

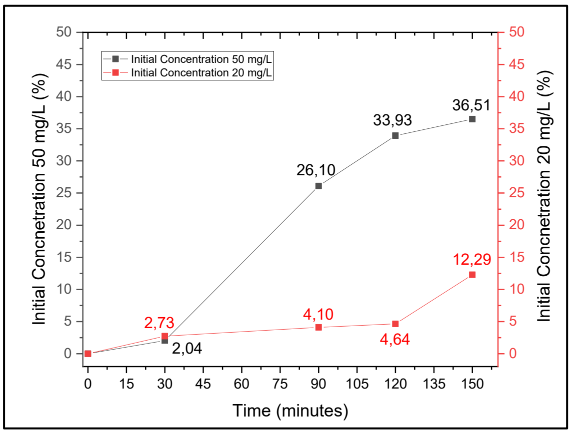


Figure 6. Effect of Irradiation Time on DOX Degradation at Different Initial Concentrations

The experiments that conducted at initial concentrations of 0.5 and 5 mg/L exhibited apparent negative degradation efficiencies, where the measured DOX concentration increased during the irradiation process. This phenomenon does not indicate an actual increase in pollutant concentration within the solution but rather suggests potential analytical limitations associated with measurements at low concentrations. This behavior may be attributed to the reduced sensitivity of the UV-Vis spectrophotometer when absorbance values approach the instrument's detection limit, making small concentration changes more susceptible to measurement fluctuations. Analytical interference may also arise from the formation of intermediate degradation products containing chromophoric groups that absorb at wavelengths close to that of DOX, thereby contributing to the detected signal during analysis.

Similar observations have been reported by González et al. (2022), who demonstrate that the photocatalytic degradation of antibiotics can generate intermediate compounds that remain detectable during spectrophotometric measurements, potentially affecting the interpretation of residual pollutant concentrations. Furthermore, Skoog et al. (2018) reported that UV–Vis measurements at low concentrations generally exhibit higher uncertainty due to absorbance signals approaching the instrumental detection limit, as well as the influence of light scattering caused by suspended particles. Therefore, the results obtained at 0.5 and 5 mg/L in the present study are more likely attributable to analytical limitations and measurement interference rather than an actual increase in DOX concentration during the photocatalytic process.

The relatively low degradation percentage observed in this study was most likely caused by using artificial wastewater designed to resemble domestic wastewater. Therefore, the system did not only contain DOX as the target antibiotic pollutant but also included ammonia as an additional component.

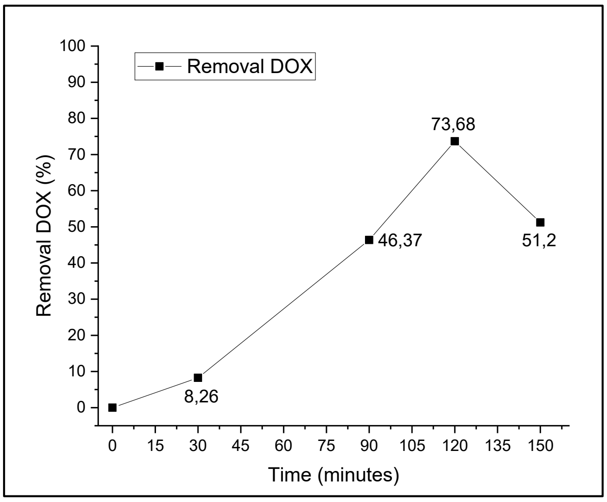


Figure 7. Effect of Irradiation Time on DOX Degradation in Pure Solution at 50 mg/L Initial Concentration

This assumption was supported by a control experiment using a pure DOX solution, as presented in Figure 7. The control study was conducted at an initial concentration of 50 mg/L, which previously showed the highest degradation performance. The results demonstrated that the degradation percentage could reach approximately 73% at 120 minutes of irradiation. However, a slight decrease in removal efficiency was observed at 150 minutes, indicating the possible occurrence of desorption, namely the release of compounds that had previously been adsorbed onto the catalyst surface back into the solution.

In photocatalytic systems, adsorption and desorption processes occur dynamically; therefore, compounds attached to the catalyst surface do not always remain permanently adsorbed. Changes in system conditions, such as catalyst surface saturation or weakened interactions between DOX and the catalyst surface, may cause the adsorbed compounds to be released back into the solution. This observation is consistent with previous studies reporting that photocatalytic systems are commonly conditioned under dark conditions prior to irradiation in order to approach adsorption–desorption equilibrium. Therefore, the increase in concentration observed at the final reaction time in this study was likely associated with the desorption process (Taher et al., 2025).

The low DOX removal efficiency observed under several experimental conditions may also be influenced by reaction competition between DOX and other compounds present in the system, particularly ammonia. During the photocatalytic process, reactive species such as hydroxyl radicals (•OH), superoxide radicals ($\bullet O_2^-$), and photogenerated holes (h^+) act as the primary oxidizing agents responsible for degrading organic pollutants. However, these reactive species do not exclusively react with DOX; they may also react with ammonia and other compounds present in the solution. Consequently, the number of reactive species available for DOX degradation decreases, leading to lower removal efficiency (Zhao, 2025).

In addition, the presence of other compounds in the solution may result in competition for active sites on the photocatalyst surface. Coexisting substances within the water matrix can compete with antibiotics for adsorption onto the active sites of the photocatalyst, thereby affecting the degradation efficiency of the antibiotic. Furthermore, García-Prieto et al. (2022) reported that ammonia can react with hydroxyl radicals (•OH) during the photocatalytic process, causing part of the reactive species to be consumed for ammonia oxidation. As a result, DOX degradation becomes less effective because the generated reactive oxygen species (ROS) must be shared among multiple simultaneous reactions (García-Prieto et al., 2022).

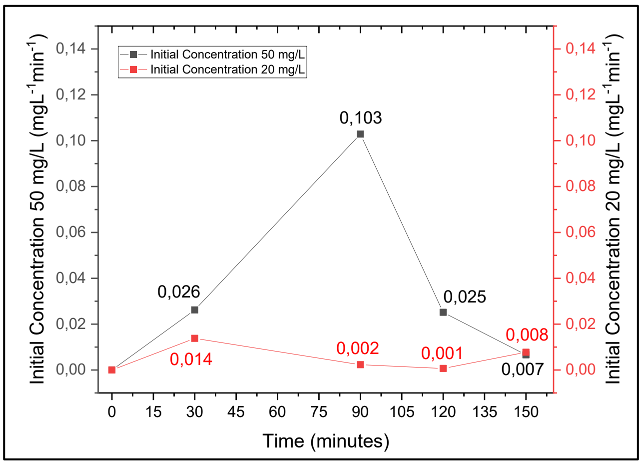


Figure 8. Degradation Rate of DOX as a Function of Irradiation Time

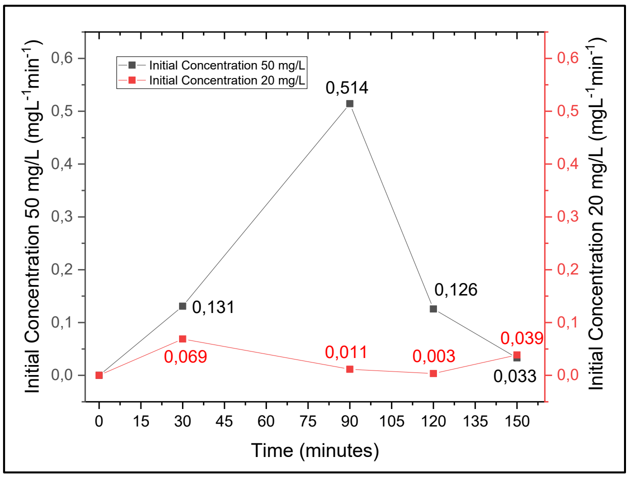


Figure 9. Specific degradation rate of DOX as a function of irradiation time

To further evaluate the photocatalytic performance of MCN, the degradation rate was calculated based on the solution volume (mg/L/min) and catalyst mass (mg/min/g). The results are presented in Figure 8 and Figure 9.

As shown in Figure 8, the highest degradation rate was achieved at an initial DOX concentration of 50 mg/L, reaching 0.103 mg/L/min at 90 minutes of irradiation. Meanwhile, the degradation rate at 20 mg/L was significantly lower, with a maximum value of only 0.069 mg/L/min during the adsorption stage and decreasing thereafter. This result indicates that a higher initial DOX concentration provided more pollutant molecules available for interaction with the active sites of the photocatalyst and the generated Reactive Oxygen Species (ROS), thereby enhancing the overall degradation process. Similar observations have been reported by Chong et al. (2010), who noted that increasing pollutant concentration within an optimum range can improve photocatalytic degradation due to a higher probability of contact between pollutants and catalyst active sites.

The degradation rate at 50 mg/L increased markedly from 0.026 mg/L/min at 30 minutes to 0.103 mg/L/min at 90 minutes, corresponding to the period in which ROS generation and photocatalytic activity were most effective. After 90 minutes, the degradation rate decreased to 0.025 mg/L/min at 120 minutes and further declined to 0.007 mg/L/min at 150 minutes. This reduction suggests that a substantial portion of DOX had already been degraded, resulting in fewer remaining molecules available for oxidation. In addition, intermediate compounds formed during degradation may compete with the parent compound for the available ROS, leading to a gradual decline in the degradation rate (Mills & Le Hunte, 1997).

A similar trend was observed when the degradation rate was normalized by catalyst mass (Figure 8). The maximum degradation rate reached 0.514 mg/min/g at 90 minutes for the 50 mg/L solution, whereas the highest value obtained at 20 mg/L was only 0.069 mg/min/g. The significantly higher degradation rate per unit catalyst mass demonstrates that MCN utilized its active sites more effectively at higher DOX concentrations. With a greater number of pollutant molecules adsorbed onto the catalyst surface, electron transfer reactions and ROS generation could be utilized more efficiently, resulting in enhanced photocatalytic degradation performance (Herrmann, 1999).

Overall, the degradation rate analysis supports the degradation efficiency results discussed previously. The 50 mg/L concentration not only exhibited the highest degradation efficiency but also showed substantially greater degradation rates in both volumetric and catalyst-normalized calculations. These findings indicate that, under the experimental conditions applied in this study, an initial DOX concentration of 50 mg/L provided more favorable conditions for maximizing the photocatalytic activity of MCN.

Effect of Photocatalytic Degradation Using Mesoporous Carbon Nitride (MCN) on Ammonia Transformation

Since the results obtained at initial concentrations of 0.5 and 5 mg/L did not exhibit a reliable degradation trend, subsequent analyses were focused on the 20 and 50 mg/L samples to evaluate changes in ammonia (NH_3-N) concentrations. Based on the laboratory results, distinct ammonia transformation patterns were observed between the two concentrations. At 20 mg/L, the ammonia concentration generally decreased during the initial stage of the process and showed only a slight increase toward the end of the irradiation period. This trend suggests that DOX degradation occurred; however, the cleavage of nitrogen-containing functional groups was relatively limited due to the lower number of DOX molecules present in the solution. Ammonia concentration changes at different DOX initial concentration can be seen in Table 2.

Table 2. Ammonia (NH_3–N) Concentration During DOX Photodegradation at Different Doxycycline Initial Concentrations

Sample Code	Ammonia (mg/L)
Initial Concentration 20 mg/L	
Minutes 0	53.13
Minutes 30 (Dark phase)	48.19
Minutes 90 (Irradiation phase)	46.58
Minutes 120 (Irradiation phase)	41.74
Minutes 150 (Irradiation phase)	46.47
Initial Concentration 50 mg/L	
Minutes 0	93.87
Minutes 30 (Dark phase)	87.78
Minutes 90 (Irradiation phase)	90.11
Minutes 120 (Irradiation phase)	99.60
Minutes 150 (Irradiation phase)	90.65

More pronounced increase in ammonia concentration was observed at an initial concentration of 50 mg/L throughout the irradiation process. This increase indicates that the degradation process proceeded more intensively, resulting in the release of a greater amount of nitrogen-containing groups from DOX into the solution in the form of ammonia. Furthermore, the decrease in ammonia concentration observed after 120 min of irradiation suggests the possible occurrence of further oxidation reactions, in which ammonia was transformed into other nitrogen species such as nitrite or nitrate during the photocatalytic process. This observation implies that the degradation process not only generated ammonia as an intermediate product but also progressed toward further mineralization. This interpretation is supported by the findings of Esfandiaribayat et al. (2024), who reported that the reactive oxygen species (ROS) generated by carbon nitride-based materials can promote not only antibiotic degradation but also the transformation of intermediate compounds into simpler products during photocatalysis. Consequently, the ammonia formed during degradation may undergo subsequent oxidation reactions, leading to a reduction in its concentration at later stages of the process.

Table 3. Ammonia (NH_3–N) Concentration During Photocatalytic Treatment Without DOX

Time (minutes)	Ammonia (mg/L)
0	39.91
30	30.69
90	26.14
120	21.86
150	21.60

To further evaluate the behavior of ammonia during the photocatalytic process, a control experiment containing only ammonia solution without DOX was conducted, as presented in Table 3. The results showed a gradual decrease in ammonia concentration from 39.91 mg/L to 21.60 mg/L during the irradiation period. This trend indicates that ammonia can also undergo photocatalytic oxidation in the presence of MCN under visible light irradiation. Ammonia concentration changes during photocatalytic treatment without DOX can be seen in Table 3.

Compared to the system containing DOX, the control experiment exhibited a more consistent decrease in ammonia concentration without significant fluctuations. This observation suggests that the increase in ammonia concentration observed in the DOX-containing system was likely associated with the degradation of DOX molecules, particularly the cleavage of nitrogen-containing functional groups that released ammonia into the solution. In contrast, in the absence of DOX, the reactive oxygen species generated (ROS) were primarily utilized for ammonia oxidation, resulting in a continuous decrease in ammonia concentration throughout the process.

These findings support the assumption that ammonia in the photocatalytic system may act both as an intermediate degradation product and as a competing compound that can subsequently undergo further oxidation reactions during irradiation.

Overall, the findings indicate that both the initial DOX concentration and irradiation time played important roles in determining the effectiveness of photocatalytic degradation using MCN. The 50 mg/L sample exhibited superior degradation performance compared with the other tested concentrations, as reflected by its higher degradation efficiency and distinct ammonia transformation pattern. These results suggest that the photocatalytic process not only contributed to DOX degradation but also promoted the conversion of nitrogen-containing intermediates during the reaction.

4. CONCLUSION

The results of this study demonstrate that Mesoporous Carbon Nitride (MCN) can degrade DOX under visible-light irradiation. The degradation performance was influenced by both irradiation time and the initial DOX concentration, with the 50 mg/L sample exhibiting superior degradation performance compared to the other tested concentrations. Prolonged irradiation enhanced the generation of Reactive Oxygen Species (ROS), which played a crucial role in the photocatalytic degradation of DOX. The different ammonia transformation patterns observed at 20 and 50 mg/L indicate that the photocatalytic process not only reduced DOX concentration but also affected the transformation of nitrogen-containing compounds during the reaction. The increase in ammonia concentration at certain stages suggests the cleavage of nitrogen-containing functional groups from the DOX structure, whereas the subsequent decrease in ammonia concentration may indicate further oxidation processes associated with mineralization.

Nevertheless, the apparent negative degradation efficiencies observed at low concentrations (0.5 and 5 mg/L) suggest the presence of analytical limitations, potentially arising from measurement interference associated with the UV–Vis method. Therefore, further studies are required to provide a more comprehensive understanding of the degradation mechanism, including the identification of intermediate degradation products and the analysis of other nitrogen species, such as nitrite and nitrate, formed during the photocatalytic process.

Acknowledgement

The authors would like to express their sincere gratitude to the Department of Environmental Engineering, Faculty of Civil, Planning and Geo-Engineering, Institut Teknologi Sepuluh Nopember, and LPDP Scholarship for supporting. This research was made possible through the scholarship support provided by LPDP.

REFERENCES

Journal Chong, M. N., Jin, B., Chow, C. W. K., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: A review. Water Research, 44(10), 2997–3027. https://doi.org/10.1016/j.watres.2010.02.039

Journal Esfandiaribayat, Milad, Mojtaba Binazadeh, Samad Sabbaghi, Milad Mohammadi, Samaneh Ghaedi, and Hamid Rajabi. 2024. "Tetracycline Removal from

Wastewater via G-C3N4 Loaded RSM-CCD-Optimised Hybrid Photocatalytic Membrane Reactor." Scientific Reports 14(1). doi:10.1038/s41598-024-51847-5

Journal García-Prieto, J. C., González-Burciaga, L. A., Proal-Nájera, J. B., & García-Roig, M. (2022). Kinetic Study and Modeling of the Degradation of Aqueous Ammonium/Ammonia Solutions by Heterogeneous Photocatalysis with TiO2 in a UV-C Pilot Photoreactor. Catalysts, 12(3).https://doi.org/10.3390/catal12030352

Journal González, M., Rodríguez, S. M., Santos, A., Romero, A., & Pérez, J. (2022). Photodegradation of DOX in water induced by TiO_2-MCM-41: Kinetics, TOC evolution and reusability. Results in Engineering, 16, 100677. https://doi.org/10.1016/j.rineng.2022.100677

Journal Mills, A., & Le Hunte, S. (1997). An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 108(1), 1–35. https://doi.org/10.1016/S1010-6030(97)00118-4

Journal Nunna, Guru Prakash, Pitcheri Rosaiah, Sambasivam Sangaraju, Gopal Ramalingam, Ahmad Jwuiyad, Sreedhar Adem, and Tae Jo Ko. 2024. "Mesostructured Graphitic carbon nitride Composites with Silver Nanoparticle Decoration as the Best Visible-Light-Driven Photocatalysts for Dye Degradation and H2 Production." Colloids and Surfaces A : Physicochemical and Engineering Aspects 680. doi:10.1016/j.colsurfa.2023.132615.

Journal Taher, T., Maharani, P., Muhtar, S. A., Munandar, A., Sidiq, A. N., & Rianjanu, A. (2025). High Surface Area Ortho-Nb2O5 as Bifunctional Adsorbent and Photocatalyst for Efficient Removal of Tetracycline Antibiotics from Wastewater. Science and Technology Indonesia, 10(3), 916–923. https://doi.org/10.26554/sti.2025.10.3.916-923

Journal Wang, X., et al. (2021). Efficient photocatalytic degradation of DOX by coupling α-Bi_2O_3/g-C_3N_4 composite and H_2O_2 under visible light. Environmental Research, 197, 110925. https://doi.org/10.1016/j.envres.2021.110925

Journal Yan, X., Qian, J., Pei, X., Zhou, L., Ma, R., Zhang, M., Du, Y., & Bai, L. (2021). Enhanced photodegradation of DOX (DOX) in the sustainable $NiFe_2O_4$/MWCNTs/BiOI system under UV light irradiation. Environmental Research, 199, 111264. https://doi.org/10.1016/j.envres.2021.111264

Journal Zhang, X., Chen, J., Jiang, S., Zhang, X., Bi, F., Yang, Y., Wang, Y., & Wang, Z. (2021). Enhanced photocatalytic degradation of gaseous toluene and liquidus tetracycline by anatase/rutile titanium dioxide with heterophase junction derived from materials of Institut Lavoisier-125(Ti): Degradation pathway and mechanism studies. Journal of Colloid and Interface Science, 588, 122–137. https://doi.org/10.1016/j.jcis.2020.12.042

Journal Zhang, Y., Li, Y., Ruan, Z., Yuan, Y., & Lin, K. (2022). Extensive solar light utilizing by ternary C-dots/Cu_2O/$SrTiO_3$: Highly enhanced photocatalytic degradation of antibiotics and inactivation of E. coli. Chemosphere, 290, 133340. https://doi.org/10.1016/j.chemosphere.2021.133340

Journal Zhao, Zaiwang, Yanjuan Sun, Qian Luo, Fan Dong, Hui Li, and Wing Kei Ho. 2015.

"Mass-Controlled Direct Synthesis of Graphene-like Carbon Nitride Nanosheets with Exceptional High Visible Light Activity. Less Is Better." Scientific Reports 5. doi:10.1038/srep14643.

Journal Zhao, Z. (2025). Research Progress on the Photocatalytic Degradation Performance of Antibiotics by Bismuth-based Photocatalysts. In Highlights in Science, Engineering and Technology ESAET (Vol. 2025).

Journal Zhu, D., Cai, L., Sun, Z., Zhang, A., Héroux, P., Kim, H., Yu, W., & Liu, Y. (2021). Efficient degradation of tetracycline by RGO@black titanium dioxide nanofluid via enhanced catalysis and photothermal conversion. Science of the Total Environment, 787, 147536. https://doi.org/10.1016/j.scitotenv.2021.147536

Book Skoog, D. A., Holler, F. J., & Crouch, S. R. (2018). Principles of instrumental analysis (7th ed.). Cengage Learning.

COVER IMAGE