In-Situ Removal of Residual Antibiotics (Tetracycline) in a Recirculating Aquaculture System using a Photolysis Treatment Process

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The treatment of wastewater and recirculating water in aquaculture systems prior to its release into the environment is critical to ensuring regulatory compliance. Many mechanical systems, employing different biological and chemical protocols, have been developed over the years. Antibiotics are applied routinely in aquaculture to mitigate risks posed by biological agents such as viruses, bacteria, fungi, and parasites. However, these have detrimental effects on aquatic life and can cause infection in humans. The removal of excessive and persistent antibiotics from wastewater is a key stage in the treatment of effluent from aquaculture systems. This study aimed to evaluate the efficacy of the photolysis process for the in-situ removal of the antibiotic tetracycline (TC) from a recirculating aquaculture system. Three distinct forms of ultraviolet (UV) light, UV-A, UV-B, and UV-C, were used to study the effects of different radiation wavelengths. Ultraviolet-visible (UV-Vis) spectrophotometry was used to monitor the degradation of the antibiotic in a batch photoreactor by measuring absorbance values and computing the attenuation of concentration. The impact of different operational parameters on degradation efficiency was investigated. It was observed that increasing the initial concentration of the antibiotic led to a decrease in the degradation rate. At 3 ppm, the degradation efficiency was 81.3 %, while at 15 ppm, it decreased to 63.6 %. UV-C was shown to be the most efficient wavelength for breaking down TC molecules, resulting in a degradation of 63.6 % after 2 hours of exposure. The photodegradation rate of TC was proven to be higher at a basic pH (89.6 %) than in an acidic medium (66.9 %). Increasing irradiation time led to a higher TC degradation efficiency, where it reached 41.7 % after 60 minutes of irradiation and 63.6 % after 120 minutes. The levels of COD and TOC were observed to decrease by only 15.8 % and 6.6 % respectively, likely due to the formation of intermediates following photolysis. However, the change in BOD_5 was negligible. The BOD_5/COD ratio for the degradation of TC was found to have increased from 0 to 0.05, demonstrating a slight improvement in biodegradability of the organic residues. The reaction kinetics studies revealed that all experiments followed pseudo-first-order kinetics, with correlation coefficients (R^2) ranging from 0.9945 to 0.9981. The environmental impact of the photolysis byproducts, though potentially less harmful than the parent compound, remains unclear and necessitates comprehensive investigation.

Keywords: Photolysis; ultraviolet A, B, C irradiation; tetracycline; antibiotic

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Aquaculture has been projected to account for 62 % of the world's total production of aquatic species by 2030, as the global population continues to rise. According to a report in 2018, aquaculture contributed 46 % of the overall production of marine and freshwater species. Considering the prevailing favourable patterns, there is a potential for substantial production growth in the future [1]. The recirculating aquaculture system is an innovative approach to aquaculture that employs multiple water treatment stages to process and recycle wastewater from tanks. The recirculating aquaculture system provides advantages in terms of water conservation, land

conservation, energy efficiency, and greenhouse gas emissions. These benefits result from innovative advancements in aquaculture equipment [2].

Antibiotics are of crucial significance in the management and prophylaxis of bacterial infections as well as the facilitation of growth in aquaculture. The environmental implications associated with antibiotic contamination, arising from the improper use of antibiotics and inadequate removal of antibiotic residue in aquaculture, have been widely reported [3]. The use of antibiotics remains prevalent in numerous areas, especially in underdeveloped countries, due to the absence of stringent statutory regulations [4]. According to the State of World Fisheries and Aquaculture, 2018 [5], China has implemented restrictions on antibiotics in recent times, emphasizing the need for aquaculture biosecurity and aquatic animal health management. However, addressing biosecurity requires significant resources, strong political will, and coordinated international action and cooperation. This report also highlighted that China played a crucial role in global aquaculture production, contributing to over 60 % of the total output.

The utilization of antibiotics within the aquaculture sector is influenced by a multitude of factors, encompassing governmental legislation and regulations, the status of the host disease, the specific pathogen in question, and ecological parameters. The application of antibiotics within the aquaculture sector is contingent upon the adherence to country-specific regulatory frameworks. In certain countries, the use of antibiotics is subject to rigorous regulations that permit only a restricted number of approved antibiotics for use within the aquaculture sector. This is particularly observed in Japan, North America, and Europe [6]. The National Pharmaceutical Regulation Authority (NPRA), a division of the Malaysian Ministry of Health, is responsible for drug regulation in Malaysia [7]. In a study, it was found that tetracyclines, quinolones, and sulfonamides were the most detected classes of antibiotics among the 23 antibiotics identified in aquaculture facilities in Malaysia [8]. This finding indicates a significant prevalence of antibiotics in these facilities. Despite Malaysia's ban on chloramphenicol and nitrofurans in aquaculture, the Food and Drug Administration (FDA) of the United States has consistently detected these residues in Malaysian seafood [9]. According to the FDA's report in 2018, there were 44 such cases detected between 2009 and 2018. Furthermore, an uptick in the use of antibiotics within the aquaculture sector is anticipated, due primarily to the rapid expansion of emerging economies. Hence, it is crucial to underscore the scientifically sound application of antibiotics and advocate for the effective regulation of antibiotics residues in the aquaculture sector, rather than enforcing a blanket prohibition on their usage [4]. Further, non-compliance with the statutory limits set by importing countries can lead to restrictions on imports from the entire country, which would cause significant economic losses.

Tetracycline (TC) antibiotics have a longstanding presence in the field of medicine. These antibiotics are not only used for human therapy, but also for veterinary and agricultural purposes [10]. They are the second most commonly used class of antibiotics in the world due to their efficacy against a wide variety of bacteria that cause diseases in humans and animals, their good bactericidal characteristics, and affordability [11, 12]. However, they can potentially lead to the widespread development of antibiotic resistance if used without control [13]. To date, there is limited information available regarding the usage of TC antibiotics specifically in recirculating aquaculture systems.

According to Ahmed and Turchini, [14], the recirculating aquaculture system (RAS) is widely acknowledged as a viable substitute for the traditional system. Sha et al. [4] found that the utilization of a land-based aquaculture approach is a key characteristic of the RAS. This system incorporates a range of water treatment units, including ultraviolet disinfection, biological filters, and other related applications. The closed-loop configuration of the system enables the optimal utilization of antibiotics and the effective removal of residues, which are of minimal significance [15]. It is crucial for the water treatment unit to swiftly eliminate residual antibiotics to prevent the accumulation of antibiotics in the water and the subsequent development of resistance genes in other microbes via the process of horizontal gene transfer. This is essential to ensure the safety and quality of aquatic products as well as to protect the bacteria in the biofilter unit [4]. Previous studies have reported that photocatalysis is an effective method for the photodegradation of antibiotics [11, 16]. Therefore, for this research project, a photolysis-based advanced oxidation process (AOP) was selected to eliminate antibiotic residues from RAS. AOPs have been proven to have an exceptional ability to degrade recalcitrant components by producing highly reactive and oxidizing free radicals [17, 18].

Photolysis treatments are a type of AOP that relies on energy supplied by radiation, with sunlight being the most abundant and environmentally friendly source [19]. According to Cuerda-Correa et al. [20], photolysis is a chemical-free treatment with comparatively low maintenance and operating costs. Furthermore, UV has demonstrated its adaptability and ability to facilitate the cleavage of chemical bonds in a broad range of refractory compounds. This approach was found to be efficient in removing antibiotics from aquaculture water [21]. The ease of installation and operation of these ultraviolet (UV)-based AOPs (UV-AOPs) makes them stand out for practical use [22]. Additionally, the efficacy of photolysis differs among antibiotics and is affected by factors such as water quality, light intensity, wavelength and pH [4]. Photolysis has a specific impact on the removal and degradation of antibiotics, which is a higher removal rate from RAS than constructed wetlands [23]. The process of photolytic pollutant

degradation in water involves the use of radiation as an energy source to facilitate the breakdown of chemical compounds. This energy is absorbed by various molecules, which subsequently attain excited states and undergo diverse chemical reactions [20]. Radiant energy is absorbed by molecules through the intake of quantized units known as photons. This absorption of energy causes specific electrons to become excited, resulting in the formation of free radicals. These free radicals subsequently undergo a sequence of chain reactions, ultimately leading to the production of the intended reaction products. The absorption of photons from light energy sources induces physical and chemical transformations in molecules, whereby the photochemical alteration can occur either directly or indirectly [24].

MATERIALS AND METHODOLOGY

1. Chemicals and Materials

The antibiotic, TC, was purchased from Sigma-Aldrich and used without further purification. HCl and NaOH were also utilized for pH adjustments without further modification. 0.1 g of TC was dissolved in 1 L of distilled water to produce a 100-ppm stock solution. The solution was further diluted with distilled water to produce 3, 6, 9, 12, and 15 ppm standard solutions.

2. Apparatus and Instruments

An ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Carry 3500) equipped with a 1 cm path length quartz cell, was used to measure the absorbance. A pH meter (Eutech pH 700) was used to measure and modify the pH of the solutions. The photoreactor was a batch system (Fig. 1) made by a beaker enclosed in a cabinet to avoid interference from natural light and temperature fluctuations [25]. The radiation sources used for this study were a 9W UV-A (365 nm) lamp (Philips PL-S 9W/2P BLB), a 9W UV-B (311 nm) lamp (Philips), and a 9W Pro UV (254 nm) UV-C lamp (Philips TUV PL-S 9W/2P 1CT). The irradiance from each lamp, as supplied by the manufacturer's specification, was 10 mW/cm^2. The total radiating surface area was 91.7 cm^2 for each UV lamp. Each lamp was mounted inside a quartz lamp sheath which was immersed in the centre of the reactor beaker

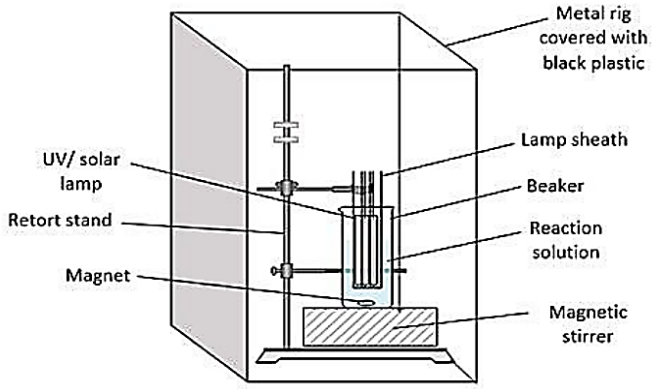

Figure 1. Schematic diagram of batch photoreactor [26].

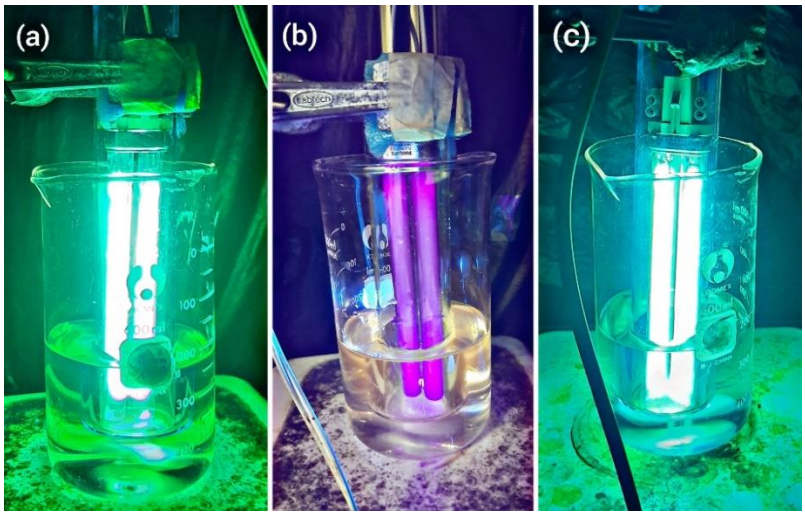

Figure 2. Batch photoreactor setups for (a) UV-C, (b) UV-A, and (c) UV-B.

3. Experimental Procedure

All control and photodegradation experiments were carried out with a 250 mL solution that was continuously stirred at room temperature. Control experiments with 15 ppm TC were carried out in the presence of UV-C light irradiation with continuous stirring. All experiments were done in triplicate with their average values being taken and plotted into graphs. Fig. 2 shows the photo-reactor set-up using the three different light sources.

4. Effect of Type of UV Irradiation

Different types of UV irradiation (UV-C, λ= 254 nm; UV-B, λ = 311 nm; and UV-A, λ= 365 nm) were utilized. A 15 ppm solution of TC in water at its natural pH was used to demonstrate the effects of varying irradiation wavelengths. The natural pH was simply the unadjusted pH of the TC standard solution, which was around 5 even with different initial concentrations.

5. Effect of Initial Concentration of Antibiotic

To analyze the effects of the initial concentration, a set of experimental trials was conducted with initial concentrations of 3 ppm, 6 ppm, 9 ppm, 12 ppm, and 15 ppm, while maintaining other parameters such as UV-C irradiation and natural pH. 4 mL aliquots of each sample were extracted and analyzed every 15 minutes over a 2 hour period. 2 hours was chosen as it clearly showed the photodegradation trend.

6. Effect of Solution pH

The pH of simulated wastewater was adjusted to the intended value using 0.1 M hydrochloric acid (HCl) or sodium hydroxide (NaOH). The primary objective of this study was to investigate the impact of solution pH on the system through the manipulation of pH levels at 4, 7, and 10. The experimental conditions included the use of an initial TC concentration of 15 ppm alongside UV-C irradiation. Over 2 hours, a 4 mL sample was extracted every 15 minutes for analysis.

7. Effect of Contact Time

The effect of contact time was assessed using an antibiotic concentration of 15 ppm, pH 7, and UV-C irradiation. Samples of 4 mL were extracted and subjected to filtration to determine their concentrations at predetermined time intervals of 15, 30, 45, 60, 75, 90, and 120 minutes.

8. Analytical Methods

8.1. Instrumental Analysis

A sample volume of 4 mL was collected from the reactor every 15 minutes during the two-hour experiment. The sample solutions were extracted using a syringe and transferred to vials via a syringe filter (Whatman 0.45 μm membrane filter). The samples were then analyzed using UV-Vis spectrophotometry. The concentration of TC was determined at the peak absorption of 357 nm from a calibration curve determined using a linear working range of 3, 6, 9, 12, and 15 ppm. Determination of the concentration was based on Beer-Lambert's law, which relates the absorbance of an antibiotic solution to its known concentration, as in equation 1:

$$A = \varepsilon bc \quad (1)$$

where A is the absorbance of the solution, ε represents the molar absorptivity (L/mol.cm), b represents the path length (cm), and c represents the concentration (mol/L). A calibration curve was plotted using the linear equation.

Equation 2 was utilized to calculate the TC solution's degradation efficiency. Over a 5-hour period, 3 mL aliquots of the solution were extracted every 15 minutes, and the absorbance was measured.

$$Degradation\ efficiency, \% = \frac{(C_0 - C_t)}{C_0} x100 \quad (2)$$

where C_0 refers to the initial concentration of TC at t = 0 min and C_t represents the concentration of TC at t min.

8.2. Biological Oxygen Demand (BOD) Analysis

BOD refers to the quantity of oxygen consumed during the process of organic matter decomposition by microorganisms. The BOD analysis was performed using the BOD_5 procedure outlined in APHA 5210 B, 2012. BOD_5 was determined by measuring the change in dissolved oxygen (DO) levels between the initial sample and the sample after 5 days of incubation at 20 °C.

8.3. Chemical Oxygen Demand (COD) Analysis

COD refers to the amount of a specific oxidant that reacts with the sample, where the amount of oxidant consumed is measured in oxygen-equivalent units. Using a COD digestor and the HACH 8000 standard procedure, the difference between the amount of organic matter before and after photolysis was determined. In the reactor digestion procedure, a DRB200 COD reactor and a HACH DR6000 were used to ascertain the COD value.

8.4. Total Organic Carbon (TOC) Analysis

TOC measures the amount of organic carbon in a sample. The reduction in TOC content can serve as an indicator for assessing the degradation of an antibiotic. TOC measurements were conducted using a TOC analyzer before and after the photolysis experiment.

9. Reaction Kinetics

Photolytic degradation of TC generally follows pseudo-first order kinetics [27-30]. In this study, the pseudo-first order rate constant was determined from the linear fitting of a plot of $ln\,{}^{C_t}/_{C_0}$ against time (t) according to equation 3:

$$ln\,{}^{C_t}/_{C_0} = -kt \quad (3)$$

where C_t represents the concentration of TC at time t (mol/L), while C_0 is the initial concentration of TC (mol/L), and k represents the first order rate constant (min^{-1}) at time t (min). The parameter k can be determined from the slope of the graph of $ln\,{}^{C_t}/_{C_0}$ versus t.

RESULTS AND DISCUSSION

1. Control Experiments

The desired concentration of the target pollutant was set at a fixed value of 15 ppm. This concentration was selected based on Beer's Law, where the absorbance value for 15 ppm TC exceeded 0.435, which is considered the ideal value with a small degree of error [31]. It is worth noting that this value is situated between 0.2 and 0.7 absorbance units, a range that is acceptable as an accurate analytical measurement [31-33]. In addition, the degree of error is anticipated to be high at low concentrations [34] as lower concentration solutions exhibit relatively higher measurement errors. Dilute solutions such as 3 ppm are associated with low absorbance and high transmittance values. Thus, 15 ppm was chosen instead of 3 ppm throughout this study.

2. Parametric Study

2.1. Effect of Type of UV Irradiation

Degradation efficiency is significantly influenced by the wavelength and intensity of the light source, in addition to the absorptivity of the pollutant [24]. A 15 ppm TC solution at its natural pH was used to test the effect of different types of UV irradiation for 2 hours by changing UV lamps (UV-C, λ=254 nm; UV-B, λ= 311 nm; and UV-A, λ= 365 nm). The photo-degradation trends of the TC antibiotic solutions under UV light are depicted in Fig. 3 and Fig. 4. The concentrations of all three types of UV irradiation decreased, indicating that TC was degraded. UV-C irradiation degraded 63.6 % of TC in 2 hours, while UV-B and UV-A irradiation degraded TC by 30.9 % and 7.9 %, respectively, in the same period. The degradation of antibiotics observed after UV exposure was most efficient with UV-C light, compared to UV-B, which also exhibited a higher degradation rate than UV-A.

UV-C wavelengths have a high degradation capability because their photons have enough energy to form radicals. According to Cortés et al. [35], since UV-A radiation has a low photon energy level, there is less interaction between it and the antibiotic absorption bands, which explains why it results in less degradation. Higher photon energies at lower UV irradiation wavelengths result in a higher antibiotic degradation efficiency.

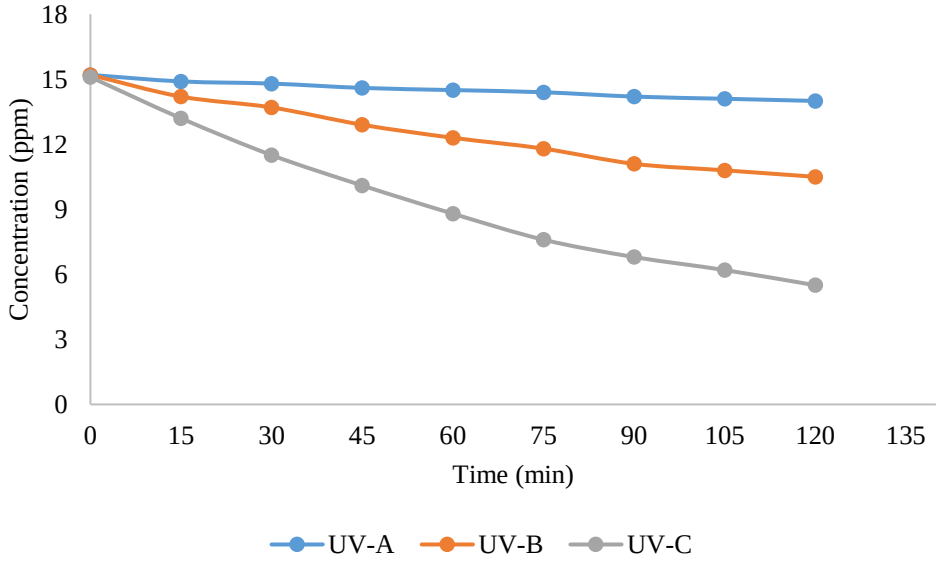

Figure 3. Concentration of TC against time for different types of UV irradiation. (The experimental conditions were 250 mL of 15 ppm TC at its natural pH).

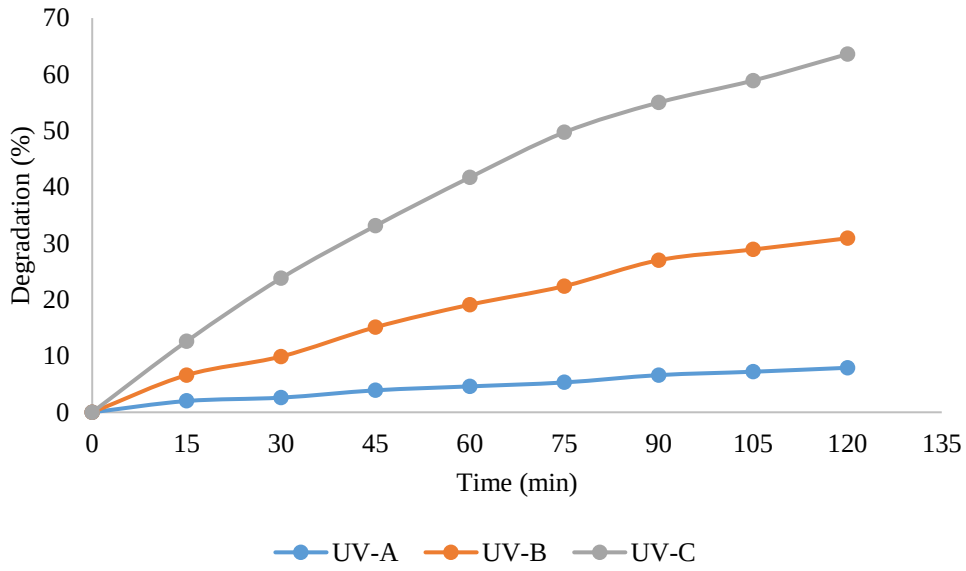

Figure 4. Degradation efficiency of TC against time for different types of UV irradiation (The experimental conditions were 250 mL of 15 ppm TC at its natural pH).

Previous studies on antibiotic photolysis degradation are consistent with this result. Despite the large variety of UV lamps available on the market, medium- or low-pressure mercury vapor lamps that emit UV-C light are the recommended choice for wastewater treatment because of their strong germicidal properties [36]. Furthermore, Ge et al. [37] studied the influence of wavelength on the ultraviolet absorption of the quinolone antibiotic sarafloxacin (SAR), and determined that the ideal wavelength range was between 250 and 280 nm. This supports the theory that UV-C is preferable for photodegradation. Additionally, Korać-Jačić et al. [38] mentioned in their study that TC was far less susceptible to UV-A or UV-B degradation at pH 5 in the absence of Fe^{3+}.

2.2. Effect of Initial Antibiotic Concentration

To investigate the impact of various antibiotic concentrations, the initial TC concentration was varied from 3 to 15 ppm at the solution's natural pH, and irradiated with UV-C. Fig. 5 and Fig. 6 show that lower TC concentrations exhibited greater degradation efficiencies. As the antibiotic's initial concentration increased, its rate of photodegradation decreased because there were enough radicals present to degrade TC under UV light [39]. Furthermore, the presence of hydroxyl radicals (·OH) increased the breakdown of intermediate products in the reaction, especially when the initial concentration of TC was higher. The degradation efficiencies of TC solutions with initial concentrations of 3, 6, 9, 12, and 15 ppm were 81.3, 77.4, 70.7, 67.8, and 63.6 %, respectively, after 120 minutes of irradiation. The degradation efficiency for an initial concentration of 3 ppm reached 81.3 % within 2 hours, whereas with 15 ppm only a 63.6 % degradation efficiency was achieved within the same duration. This shows that photon penetration into the solution had reduced, producing an inner filter effect. In other words, as the concentration increases, the solution's permeability to ultraviolet light diminishes due to this inner filter effect induced by a reduction in photon penetration [40]. This causes a reduction in the amount of hydroxyl radicals that are present in the environment. In comparison, TC absorbs a greater number of photons when its initial concentration is low.

2.3. Effect of Solution pH

Maximum absorption was observed at 215 nm, 270 nm, and 357 nm in the UV-vis spectra of TC, corresponding to the phenolic diketone moiety, ring A, and BCD system, respectively. At different pH values, TC dissociates in various ways. TC is an amphoteric molecule, and it exists in three different forms depending on the pH: a cationic form at pH 3.3, a zwitterionic form at pH 7.7, and an anionic form at pH 9.5 [29,38]. It has greater stability in acidic solutions compared to alkaline solutions, and it is transformed into distinct isomers in different pH solutions. Since TC is amphoteric, the dominant species in the medium varies depending on the pH. TCs^{+} is present at pH values below 4. The neutral form TCs^{0} is present at pH levels ranging from 4 to 7.5. The monoanionic form TCs^{-} is found at pH levels from 7.5 to 10.0.

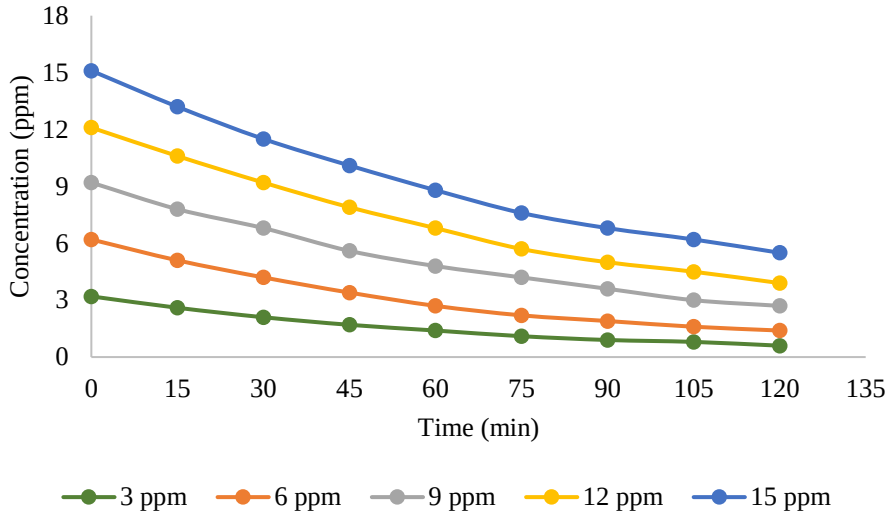

Figure 5. Concentration of TC against time for different initial concentrations of antibiotic (The experimental conditions were 250 mL at its natural pH with UV-C irradiation).

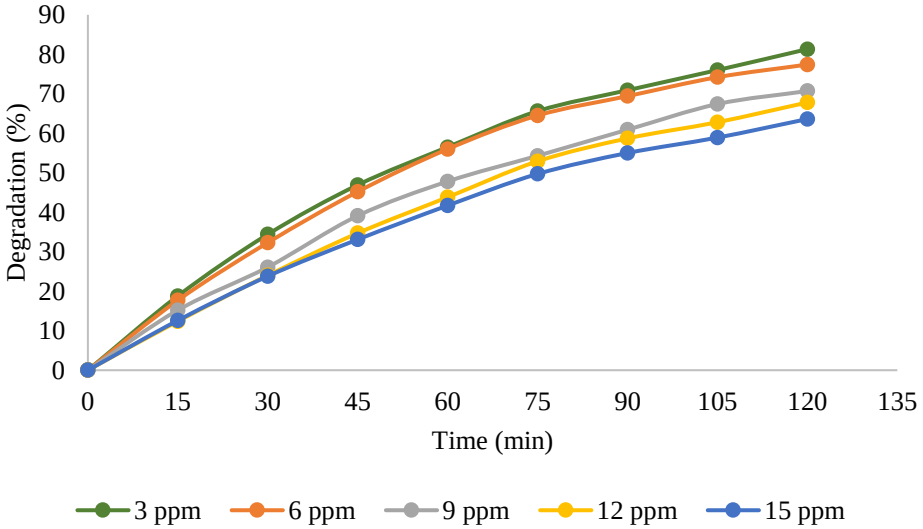

Figure 6. Degradation efficiency of TC against time for different initial concentrations of antibiotic (The experimental conditions were 250 mL at its natural pH with UV-C irradiation).

To determine how pH affects the photolytic degradation of TC, experiments were conducted on various solutions at pH 4 to 10. Fig. 7 and Fig. 8 depict the degradation of TC under varying pH conditions. A reduction in concentration was manifested in every single experiment. The degradation efficiency of TC at pH 4, pH 7, and pH 10 was 66.9 %, 75.2 %, and 89.6 %, respectively. An increase in pH was found to slightly enhance the breakdown of TC. The increased breakdown efficiency of TC at pH 10 is attributed to its higher capacity for generating hydroxyl radicals compared to pH 4 and pH 7. Hydroxyl radicals, the predominant oxidation species in an alkaline environment, have increased efficacy in breaking down the antibiotic [41]. A minor reduction in pH was detected at pH 4, which was adjusted with HCl. Mitrovic et al. [42] found that the reduced ability to degrade molecules in an acidic environment was due to the presence of higher levels of Cl- conjugated bases. These results indicate that the photooxidation process was less favourable when TCs^+ was dominant and more favourable when TCs^- was dominant. The reason for this behaviour might be attributed to the increased electronic density of TCs^- compared to TCs^+ species in the ring system, which enhances its susceptibility to attack by radical species [40]. Moreover, this is also consistent with research findings indicating that the photodegradation process of TC was reliant on pH and enhanced by alkaline conditions [38,43].

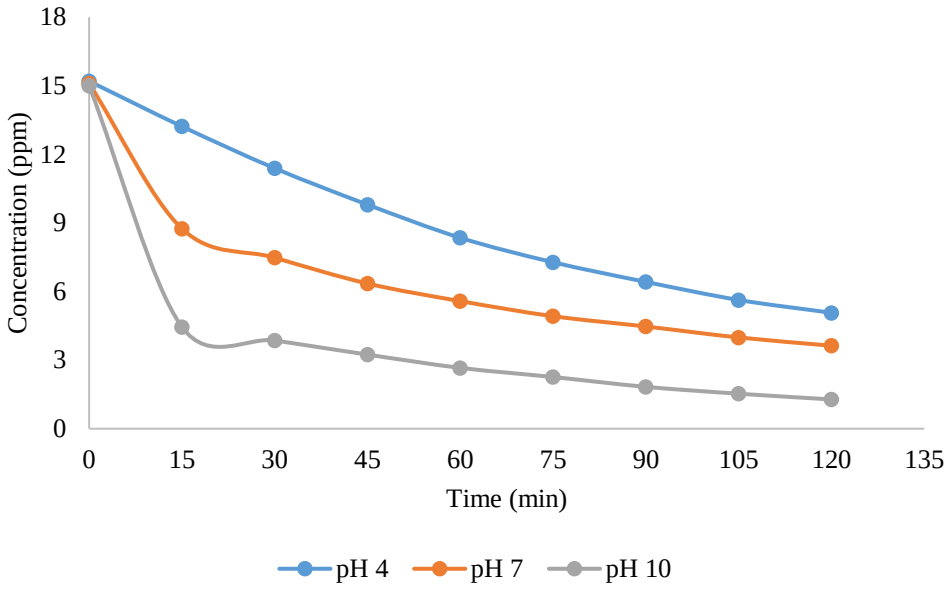

Figure 7. Concentration of TC against time under different pH conditions (The experimental conditions were 250 mL of 15 ppm TC with UVC irradiation).

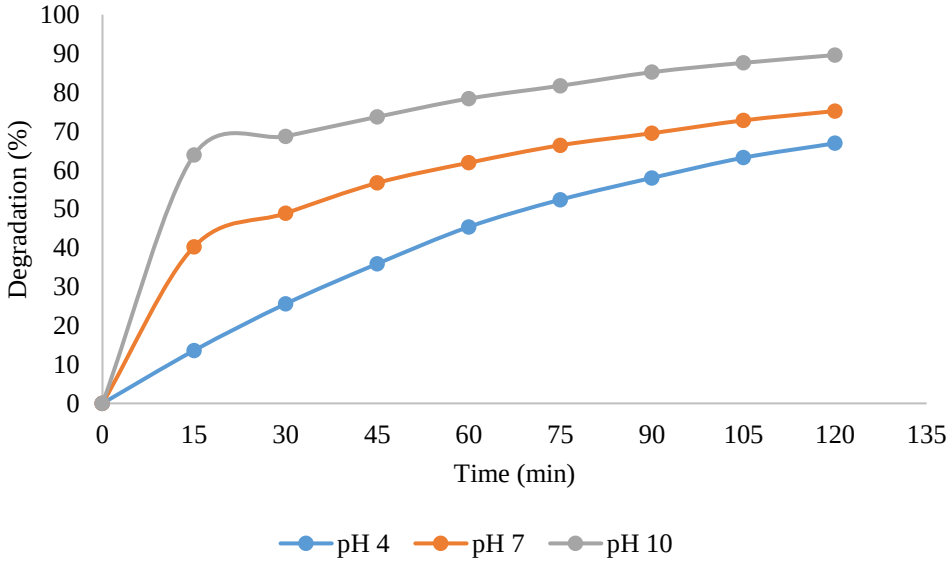

Figure 8. Degradation efficiency of TC against time under different pH conditions (The experimental conditions were 250 mL of 15 ppm TC with UVC irradiation).

2.4. Effect of Contact Time

The concentration of TC was seen to decrease as the contact time increased, demonstrating that TC underwent degradation under UV irradiation. Upon irradiation, the initially colourless TC solution transformed into a yellowish hue, as shown in Figure 9. Since TC is light-sensitive, it changed from colourless to a yellowish solution during the photolysis experiment [44, 45]. Any type of light, whether UV or natural, may cause the colour to alter over time [46]. The rise in TC degradation percentage with extended exposure to UV irradiation can be attributed to TC's ability to absorb a greater amount of photonic energy. Furthermore, with an increase in irradiation time, more hydroxyl radicals are generated. Hydroxyl radicals are produced during photolysis, which facilitates the oxidation of organic pollutants into less complex intermediates [25].

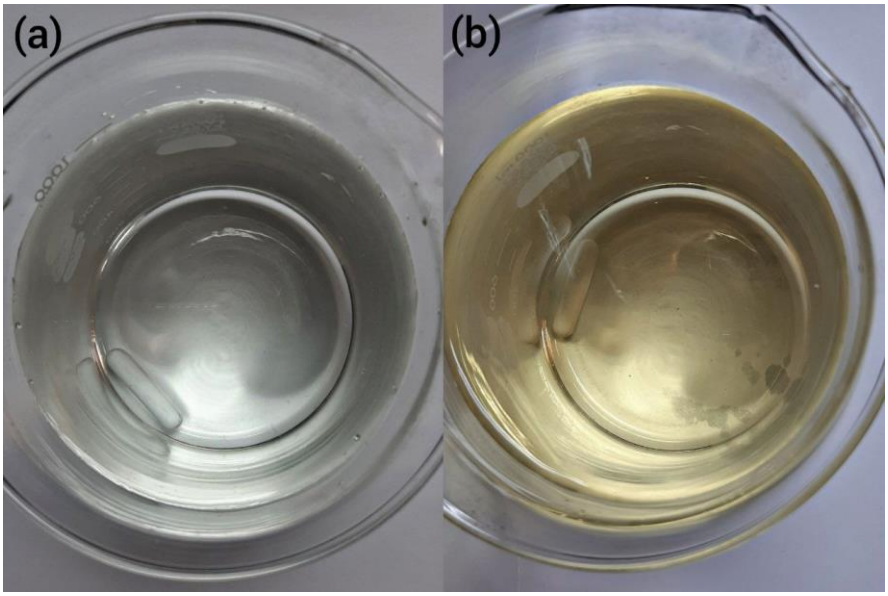

Figure 9. The change in colour of a 15 ppm TC solution after UV-C exposure for two hours. (a) Before irradiation (b) After irradiation.

3. Photolytic Degradation of TC

The molecular and structural modifications of TC generated through photolytic degradation can be detected by examination of the UV-visible spectra of the antibiotic solution recorded at 15-minute intervals. As illustrated in Fig. 10, antibiotic degradation was indicated by a reduction in the intensity of absorption bands and a modification in the spectral structure, which were the outcome of an increase in the irradiation duration during photolysis. The maximal absorption of the visible band at 357 nm decreased as the irradiation time increased, suggesting that the conjugated structure of the antibiotic was eliminated. Additionally, a hypsochromic shift (blue shift) was observed. The wavelength of maximal absorption changed from 357 nm to approximately 336 nm after 120 minutes of irradiation.

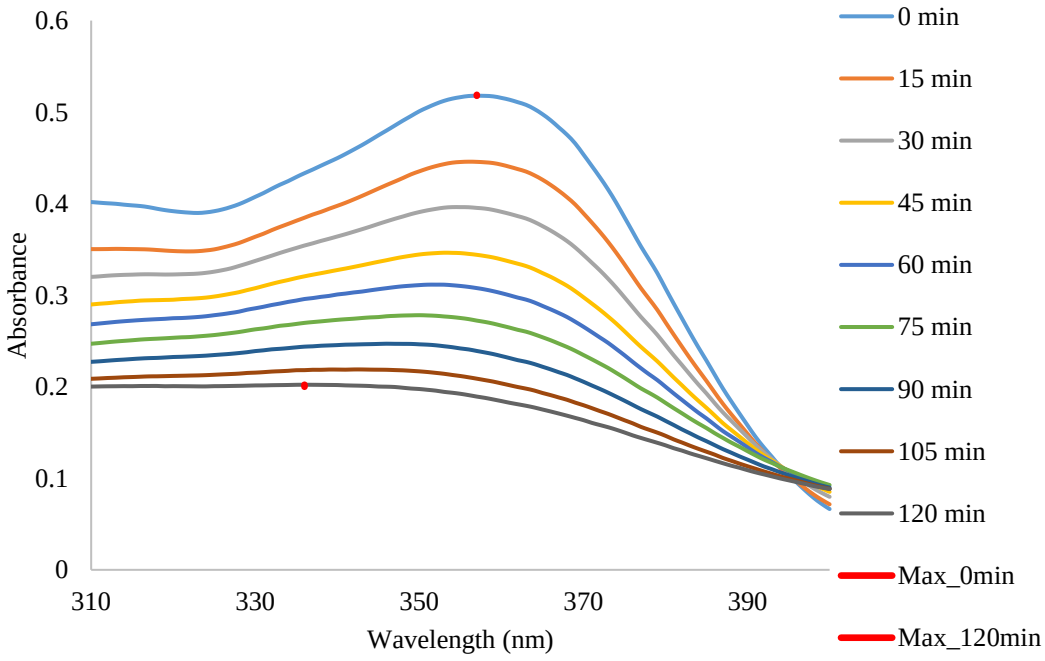

Figure 10. Absorption spectra of a 15 ppm TC solution at its natural pH degraded by photolysis with UV-C.

Table 1. Results of analysis of water quality parameters.

Parameter	Before photolysis	After photolysis	Test Method
BOD_5, mg/L	<1	1	APHA 5210 B
COD, mg/L	22.8	19.2	HACH 8000
TOC, mg/L	8.35	7.80	APHA 5310 B

Two chromophore groups are present within the TC molecule [47]. The A-ring chromophore's contribution was limited to the 250–300 nm wavelength range, while the BCD ring contributed to the 340–380 nm and 250–300 nm wavelength ranges. UV-C irradiation may selectively degrade certain chromophores while leaving others intact. The degraded chromophores contribute less to the overall UV absorption, leading to a decrease in intensity at 357 nm and a relative increase in the contribution of remaining chromophores absorbing at lower wavelengths (in this case around 336 nm), causing the observed blue shift.

The photodegradation of TC mostly encompasses demethylation, deamination, decarbonylation, dihydroxylation, hydrogen abstraction, deamidation, and ring-opening reactions [48]. Moreover, TC's principal photolysis pathways comprise ring-opening reactions and the cleavage of particular functional groups. The formation of P1 mostly resulted from the cleavage of benzene rings, wherein reactive oxygen species (ROS) targeted the C=C bond. As a result, hydroxyl, ketone, and carboxyl groups were incorporated, whereas methyl groups were concurrently eliminated [49].

4. Analysis of Water Quality Parameters

BOD, COD, and TOC were used as water quality metrics to evaluate the environmental impact of TC photolytic degradation and to identify the effectiveness of the treatments. These characteristics were compared before and after the photolysis experiment, which involved a 2-hour UV-C contact period, and an initial concentration of 15 ppm at its natural pH. The results for the parameters both before and after the treatment are displayed in Table 1.

The results of BOD_5 were <1 mg/L to 1 mg/L, which indicates the change in BOD_5 was negligible (Table 1). In addition to the BOD_5 value, the biodegradability of the pollutants can also be assessed by calculating the BOD_5/COD ratio, commonly referred to as the biodegradability index [4, 50]. The BOD_5/COD ratio for the degradation of TC increased from 0 to 0.05, demonstrating a slight improvement in the biodegradability of the organic residues [51]. Wastewater is considered biodegradable when this ratio exceeds 0.4 [52, 53]. This result supports the study by Sha et al. [4], where both the BOD_5 value and the BOD_5/COD value of the solution increased.

Oxygen consumption by oxidation is quantified analytically as COD, which can serve as an indicator of the amount of organic molecules present in water [54]. This parameter is crucial in indicating the removal of pollutants. The COD value decreased from 22.8 to 19.2 mg/L (Table 1), a reduction of 15.8 %. The limited COD removal was a result of the generation of intermediates or by-products that may also contribute to the COD [55, 26].

TOC is a supplementary parameter that can be utilized to identify the existence of impurities in water through its mineralization. This measurement provides a more precise indication of the overall quantity of organic carbon in the solution. The results showed a mere 6.6 % decrease in TOC when exposed to UV-C radiation, from the initial concentration of 8.35 mg/L (Table 1). It can thus be deduced that the organic molecules in TC did not undergo complete mineralization. The comparatively stable nature of TC's four-ring structure renders it resistant to mineralization by UV radiation, and the primary structure remains intact [29]. According to Xu et al. [30], not all four rings of the TC intermediates were fully opened, and most of them showed strong similarities to the parent structure. This also means that most of the tetracycline was broken down into by-products and only a tiny portion was turned into water and carbon dioxide [27]. The characterization of these intermediates and their toxicity to living organisms requires further study.

5. Kinetics Study

Kinetics studies provide data regarding the ideal factors for antibiotic degradation. The degradation in this study was attributed to a pseudo-first order reaction, as the concentration of TC molecules decreased exponentially [27-29,48]. Assuming the concentration of TC signified a pseudo-first order reaction, the rate constant (k) was determined using the data. The outcome of each experiment involving different parameters indicated that pseudo-first-order kinetics was observed.

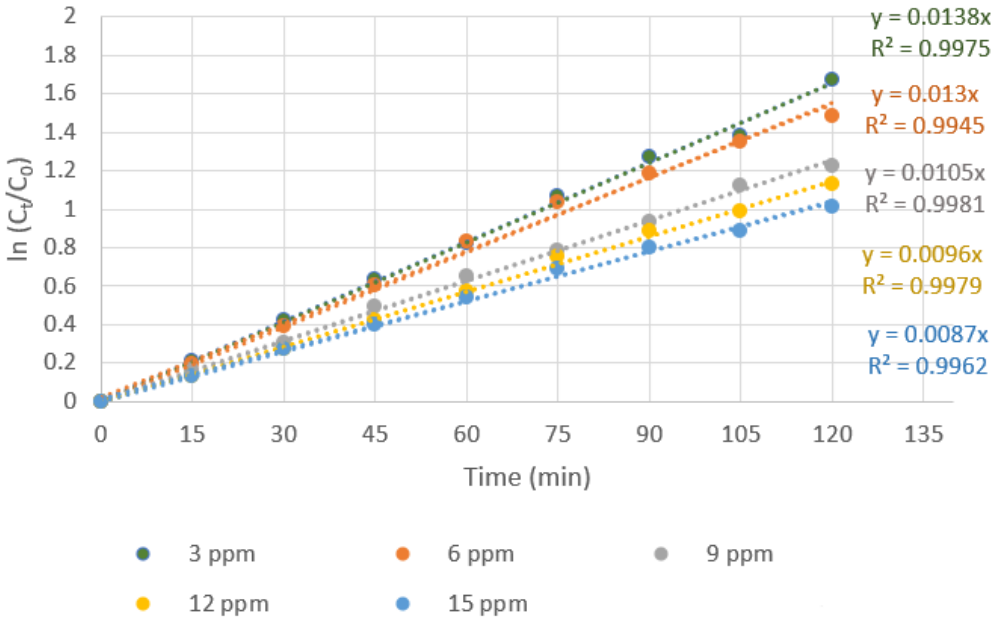

Figure 11. Time-dependent plot of $ln\,{}^{C_t}/_{C_0}$ for the photolytic degradation of TC at various initial antibiotic concentrations.

Table 2. Correlations between the rate constant and initial TC concentration as determined by regression.

Concentration, ppm	Rate constant (k), min^{-1}	R^2
3	0.0138	0.9975
6	0.0130	0.9945
9	0.0105	0.9981
12	0.0096	0.9979
15	0.0087	0.9962

From the slopes in Fig. 11, the pseudo-first-order rate constants, k (min^{-1}), for various initial concentrations were calculated and presented in Table 2. The pseudo-first-order reaction model was suitable for all the initial TC concentrations tested, as indicated by the (linear) regression correlation coefficient (R^2) values which were close to 1. The results indicate that the rate constant increased with decreasing TC concentration. At a concentration of 3 ppm, the maximum rate constant was observed (0.0138 min^{-1}). The rate of initial degradation was at its minimum at a concentration of 15 ppm, due to the antibiotic's reduced absorption of photons. There are fewer TC molecules available for photon absorption when the TC concentration decreases. As a result, fewer TC molecules compete for absorption of photons, which permits the remaining TC molecules to absorb more photons and degrade faster.

CONCLUSION

This study provides evidence that tetracycline can be degraded via photolysis when exposed to ultraviolet radiation. The degradation of TC was confirmed by UV-vis spectrometry, which showed that the maximal peak of the TC absorption spectrum diminished with increasing irradiation time. An investigation was conducted into the impact of various operational parameters, including contact time, initial TC concentration, pH, and type of UV irradiation. The degradation efficacy of UV-C irradiation was determined to be the highest at 63.6 %, surpassing that of UV-A (7.9 %) and UV-B (30.9 %). As the initial concentration of the antibiotic increased, its degradation efficiency decreased, due to the filter effect of higher antibiotic concentrations which prevented further degradation. An increased pH value corresponded to a greater efficacy in degradation due to the potential generation of hydroxyl radicals during photolysis. As the duration of UV exposure during photolysis increased, there was a corresponding increase in the percentage of degradation. The decrease in COD and TOC values indicated that photolysis resulted in the reduction of organic pollutants, thereby highlighting the potential of photolysis as a treatment method for antibiotic-contaminated wastewater. As the smaller

intermediate products generated after photolysis exhibited greater biodegradability than the antibiotic before photolysis, the BOD_5/COD ratio was elevated. Increasing the biodegradability of TC demonstrates the viability of photolysis as a pretreatment before biological treatment. The TC degradation process followed pseudo-first-order kinetics. The degradation rate of TC exhibited an exponential decrease over time, a feature of first-order processes. This implies that the residual TC concentration would progressively approach, but never actually reach, zero. To improve degradation efficiency and mineralization in a shorter time, a suitable photocatalyst may be used. Combining other AOP methods such as ozone treatment would also enhance the process.

CONFLICT OF INTEREST

The authors declare no competing interests.

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