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Treatment of Malachite Green Dye-Contaminated Wastewater via Photolysis Treatment Process

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A photodegradation experiment was performed in a batch photoreactor, and concentration reduction and degradation efficiency were calculated from absorbance values obtained using an ultraviolet-visible (UV-Vis) spectrophotometer. The effects of different operational parameters were studied. The effects of various UV wavelengths were investigated using different types of UV irradiation, UV-A, UV-B, and UV-C. UV-C, which has the shortest wavelength and therefore the highest energy, was the most effective UV irradiation to degrade malachite green (MG) molecules, resulting in 88% degradation after 3 h of irradiation. Increasing the dye's initial concentration resulted in reduced degradation rates. The highest degradation was at 20 ppm (92.2%), while the lowest was at 100 ppm (61.9%). The photodegradation rate was better at neutral pH (95.6%) compared to acidic pH (84.2%). Longer irradiation time resulted in increasing degradation efficiency of MG. Due to the incomplete mineralisation of the dye after photolysis, COD and TOC content decreased only by 3.7% and 8%, respectively. Meanwhile, BOD analysis increased after photolysis, proving that photolysis is an efficient pre-treatment method before biological treatment. Reaction kinetic studies indicated that all experiments conformed to first-order kinetics, and the degradation rate constants were between 0.0054 min^{-1} and 0.0171 min^{-1}, with correlation coefficients ranging between 0.9286 to 0.9938.

Keywords: Photolysis; malachite green; UV irradiation; photodegradation; degradation efficiency

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Water is vital for all living things and is fundamental to maintain the sustainability of the earth's ecosystem. With the growth of industrialization and the world's population, contamination caused by organic pollutants in the environment is becoming a great concern worldwide. In Europe, an estimated 700 occurring pollutants, originating from contaminants such as petroleum, textiles, personal care products, and pesticides, are regularly reported in the aquatic environment [1]. Many of these industries have also been discharging untreated sewage into nearby water bodies. Industrial wastewater is one of the major contributors to water pollution. Thus, the contaminated wastewater must be treated before it can be safely disposed [2, 3].

The textile industry is highly water-intensive, producing large volumes of effluents with coloured water. Producing 1 kg of textile is estimated to require approximately 200 litres of water [4]. During the dyeing process, about 10-15% of dyes may be released from the discharge point into the wastewater stream [5]. The discharge of effluent from textile and dyestuff industries is one of the primary sources of water contamination. It is estimated that about 700,000 tons of dyestuffs are produced yearly worldwide, while 280,000 tons of textile dyes are discharged into water basins as textile effluent [6-8].

Discharging dyes has so many negative impacts for both toxicological and aesthetic reasons. According to past research, the pollution of water resources from dyes is very high in toxicity and can harm aquatic organisms, flora, and fauna [9]. Malachite green (MG) dye is a water-soluble cationic triphenylmethane dye that appears as a dark green and crystalline solid [10]. Conventionally, MG is extensively used for dyeing paper, silk, cotton, leather, and wool [11, 12]. MG is also utilised as a biocide in the aquaculture sector, where it is highly efficient against fungal and protozoal infections [13]. The discharge of MG-based effluent imposes destructive consequences for both toxicological and aesthetic reasons. MG is one of the most contentious dyes due to the toxicity concerns associated with carcinogenesis, mutagenesis, teratogenicity, and multi-organ tissue damage [14].

Photolysis is the use of photon energy directly in the breakdown of pollutants, and it is described as a chemical-less process because it only uses photon energy. Because photolysis treatment can only degrade pollutants that can absorb photon energy, the effectiveness of degradation is heavily determined by a pollutant's absorptivity and the light source's wavelength and intensity [15]. Photolysis is a process that uses UV irradiation without the presence of oxidants and catalysts to break down contaminants into smaller molecules. Photolysis has been recognised as a pre-treatment technique before biological treatment. The biodegradation of dyes is often less efficient because modern dyes are synthetically engineered to resist weathering and are typically non-biodegradable. Khezrianjoo et al. [16] applied photolysis in the degradation of Direct Yellow 11 before they proceeded with the mineralisation of the dye with biological treatment.

In this study, the application of photolysis on the degradation of MG in simulated wastewater was investigated. Quantifying the BOD, COD, and TOC analysis of pre- and post-treatment studies were conducted to determine the effectiveness of the treatment. The photolysis experiment was performed in a batch photoreactor. Effects of different types of UV irradiation (UV-A, UV-B, and UV-C), initial concentration (20-100 ppm), pH (pH 3-7), and contact time (15-180 min) on the photolysis process were also investigated. A UV-Vis spectrophotometer was used to determine the dye's percentage removal, thus to evaluate the photolytic activity of the MG dye in the simulated wastewater.

MATERIALS AND METHODOLOGY

Materials

Malachite green oxalate powder (CAS: 2437-29-8; MW: 463.50) was purchased from Sigma-Aldrich and used without further purification. Hydrochloric acid (HCl) (37%) and sodium hydroxide (NaOH) (≥98%) for pH adjustment were purchased from Fisher Scientific and Sigma-Aldrich, respectively. Distilled water was used for experimental and dilution purposes.

Apparatus and Instruments

An ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Cary 3500) was used to measure absorbance in a quartz cell with a path length of 1 cm. pH determination and adjustment of solutions were carried out using a pH meter (Eutech pH 700). Other apparatus used were a beaker (Schott), a volumetric flask (Pyrex), a pipette, a retort stand, a magnetic stirrer, a stir bar, a lamp sheath, and lamps. The lamps used as the radiation sources for this study were 9W UVA (365 nm) lamp from Sylvania, 9W UVB (311 nm) lamp from Philips, and 9W (Pro UV, 254 nm) UVC lamp also from Philips (Model: TUV PL-S 9W/ 2P 1CT).

Preparation of Stock Solution

A 1000 mg/L stock solution was prepared by dissolving 1 g of MG dye in 1 L of distilled water. MG solutions with different concentrations for specific experiments were prepared by diluting the MG stock solution with distilled water.

Calibration of Instruments

The dye's maximum wavelength was obtained using a UV-Vis spectrophotometer, and the maximal absorbance of MG dye was analysed within the wavelength range of 610–630 nm. The dye solution was injected into the sample cell and the spectrophotometer scanned through the whole visible light spectrum (800-400 nm). The wavelength at which the sample absorbed the best was shown by the peak of the curve displayed by the spectrophotometer. The spectrophotometer was calibrated using distilled water in both sample cells and reference. Then, the absorbance of the dye sample was measured by placing it into a sample cell instead of distilled water [17]. The pH meter was calibrated using buffer solutions (pH = 4.00, 7.00, 10.00) before determining the pH of the samples [11].

Photolysis Experiment

The photolysis degradation experiments were performed in a batch photoreactor. The temperature was kept constant and any interference from ambient light was kept to minimal. A low-pressure mercury lamp with three different radiations was used as the source of photons: UV-C, λ= 254 nm; UV-B, λ = 311 nm; and UV-A, λ= 365 nm. Figure 1 depicts the experimental setup for the photolysis experiment. The lamp was placed in quartz lamp sheets and fitted at the centre of the beaker. Before the beginning of each experiment, the lamp was switched on for 20 min to reach its operating temperature and to ensure stable light emission [18, 19]. The experiments were carried out with a 500 mL mixture of dye solution in a 1000 mL beaker under continuous stirring at room temperature. The pH of the solution in each experiment was adjusted with 0.1 M NaOH and HCl [5, 20,21]. The effects of different operational parameters were studied by changing the type of UV irradiation, initial dye concentration, pH of the solution, and contact time. The experiments were run by changing one variable while keeping the others constant. Every set of experiments was conducted three times, each for 3 h, with a sample extracted every 15 min to obtain the concentration using a syringe and transferred into a vial through a syringe filter (Whatman membrane filter).

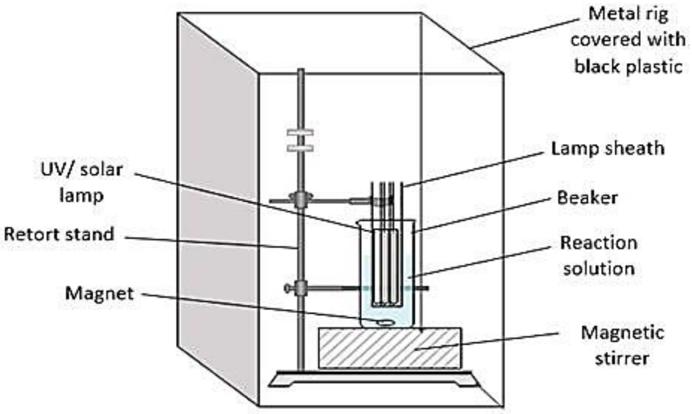

Figure 1. Experimental setup of batch photoreactor (Source: Joseph *et al*. [19]).

The 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 used. The initial concentration of the dye solution of 40 ppm and pH 5 (natural pH of MG dye in water) were chosen as constant parameters to show the effect of different irradiation wavelengths. During the photodegradation process, 5 mL of sample was extracted from the beaker to be analysed using a UV-Vis spectrophotometer every 15 min for 3 h.

The Effect of Initial Concentration of Dye

To study the effect of initial concentration of dye, one set of experimental runs was performed with initial concentrations of 20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm, while keeping the other parameters constant, such as irradiation of UV-C and its natural pH. 5 mL of sample was extracted to be analysed every 15 min for 3 h.

The Effect of pH of Solution

The pH of the simulated wastewater was adjusted to the desired value by adding drops of 0.1 M of NaOH or HCl [5,20, 21]. The effect of pH of solution was studied by varying the pH at pH 3, 5, and 7. The initial dye concentration of 40 ppm and UV-C were used in the experiment. 5 mL of sample was extracted to be analysed every 15 min for 3 h.

The Effect of Contact Time

Contact time was investigated using the initial dye concentration of 40 ppm, pH 5, and UV-C irradiation. 5 mL of sample was extracted and filtered to obtain the concentration at predetermined intervals of 15, 30, 45, 60, 75, 90, 105, 120, 135, 150 and 180 min.

Degradation Studies

The concentration of MG dye at different time intervals was obtained with a measurement value of absorbance at λmax= 616 nm using a UV-vis spectrophotometer. The concentration was determined based on Beer-Lambert's law, which was established by relating the known concentration of dye solutions to the absorbance. Equation 1 was used to calculate the percentage of degradation efficiency of the MG solution. 3 mL of the solution was extracted and the absorbance was obtained every 15 min for 5 h.

$$\text{Degradation efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

Where, C_0 is the initial concentration of MG at t = 0 min and C_t is the concentration of MG at t min.

Analysis of Water Quality Parameters

The environmental aspect of photolysis degradation of MG dye was evaluated using the water quality parameters (BOD, COD, and TOC) to evaluate the treatment's effectiveness. BOD refers to the amount of oxygen required by bacteria and other microorganisms while decomposing organic matter under aerobic (with oxygen) conditions at a specific temperature [22]. The BOD method is based on detecting the amount of dissolved oxygen (DO) before and after incubating a sample for a set of time intervals at the temperature of 20ºC [23]. The BOD analysis was done using BOD5 according to the standard APHA 5210 B, 2012 method. COD is the quantity of a certain oxidant that reacts with a sample, and the amount of oxidant consumed is measured in units of oxygen equivalency. COD analysis was done using the COD digestor according to the standard method of HACH 8000 to obtain the difference in the amount of organic matter before and after photolysis. TOC is a measure of organic carbon in a sample. The decrease in TOC content can be used to evaluate dye degradation. TOC measurements were made using a TOC analyser before and after the photolysis experiment.

Reaction Kinetics

Previous studies on the photolysis of MG follow the first-order kinetics [11, 24, 25]. Thus, it is the best model of kinetics to explain the degradation of MG dye solution. The first-order constants were determined by regressing concentration against time (t) data according to Equation 2:

$$ln \frac{C_t}{C_o} = -kt \qquad (2)$$

Where, C_t is the concentration of MG at time t (mol L^{-1}), C_o is the initial concentration of MG (mol L^{-1}), k is the first order rate constant (min^{-1}), and t is the time lapsed (min).

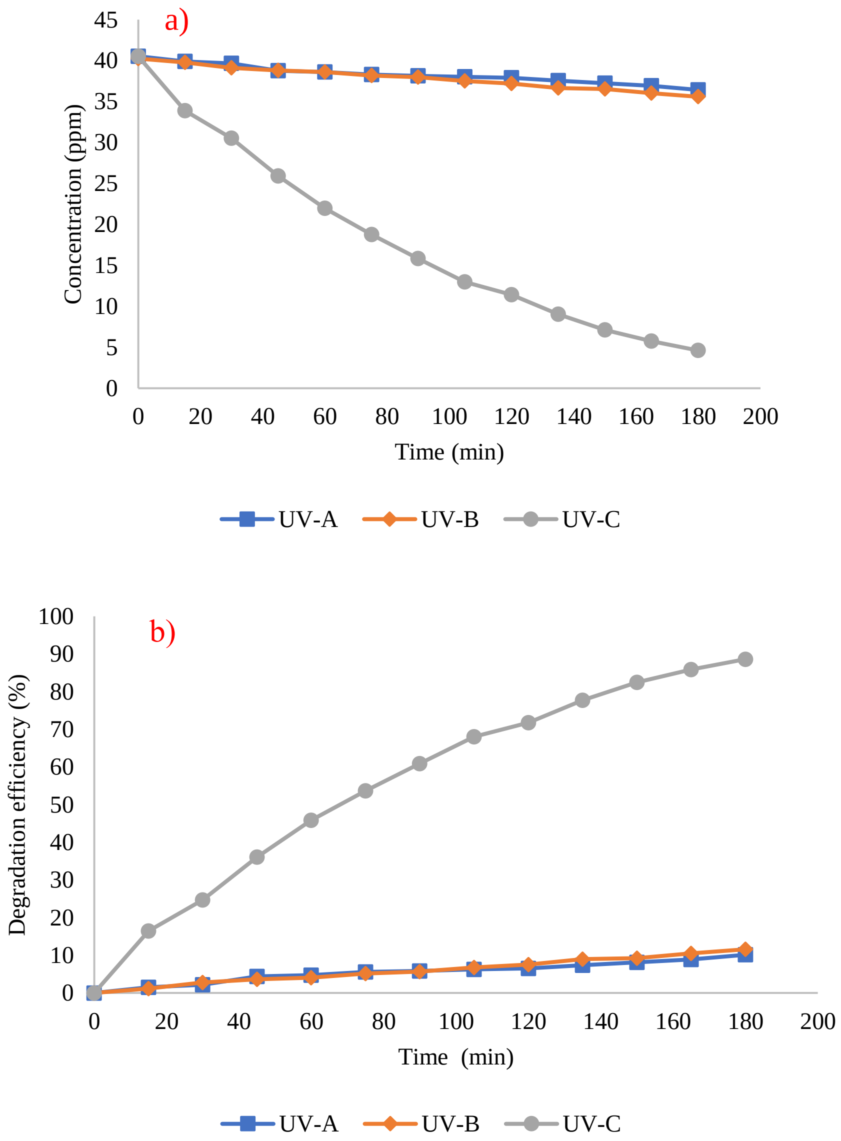

Figure 2. (a) Graph of concentration of MG against time for different types of irradiation. (b) Graph of degradation efficiency of MG against time for different types of irradiation. [Experimental conditions: 500 mL of 40 ppm MG at its natural pH].

RESULTS AND DISCUSSION

The effect of Different Types of UV Irradiation

Degradation efficiency is heavily determined by a pollutant's absorptivity and the light source's wavelength and intensity [15]. The effect of type of UV irradiation with different wavelengths were studied for 3 hours by varying the UV lamps, which were UV-C, λ= 254 nm; UV-B, λ = 311 nm; and UV-A, λ= 365 nm, with 40 ppm of initial dye concentration at its natural pH. Figure 2(a) shows MG concentration against time and Figure 2(b) shows degradation efficiency of MG against time for the three different types of irradiation. All three types of UV irradiation showed decreased MG concentration, meaning MG degradation occurred. 88% of MG was degraded within 3 h using UV-C irradiation, whereas the degradation efficiency of MG using UV-A and UV-B was only 10.1% and 11.5%, respectively, within the same duration. The degradation observed after the UV exposure of the dye is most efficient using UV-C light than UV-B, which also has a higher degradation than UV-A. UV-C wavelengths have strong degradation ability because their photons have enough energy to allow radicals to form. The low degradation of UV-A irradiation is due to the low interaction between UV-A emission and the dye absorption bands, as UV-A has a low photon energy level [26]. Lowering the wavelength of UV irradiation increases the energy of photons, which will give higher dye degradation efficiency [19]. A few studies of photolysis degradation of dyes also support this result. According to Cortés et al. [26], in the photolysis of acid blue 9, no degradation occurred after 3.5 h irradiation with UV-A. Whereas 12% degradation with UV-B irradiation and 58% degradation with UV-C irradiation within the same duration. Photolysis degradation of three triphenylmethane dyes, which were acid fuchsin, basic fuchsin, and gentian violet dye, was also found to have higher degradation with UV-C than UV-A irradiation [27]. Joseph et al. [19] also reported that UV-C irradiation has the highest degradation efficiency compared to UV-A and UV-B after 1 h for methylene blue (MB) dye. They reported the degradation efficiency of UV-C, UV-B, and UV-A irradiation as 80%, 38.24%, and 12.07%, respectively. Other than dyes, photolysis of organic contaminants like triclocarban has been reported to have almost 100% degradation with UV-C irradiation compared to under simulated solar light (λ= 365 nm) and natural sunlight (λ= 365 nm), which showed no difference [28].

The Effect of Initial Concentration of Dye

The effect of initial dye concentration was studied by varying the initial concentration between 20 to 100 ppm. Figure 3 shows that lower dye concentration has greater degradation efficiency than higher dye concentration. The photodegradation rate of the dye decreases with increasing initial concentration of the dye. Irradiation of MG solutions with initial concentrations of 20, 40, 60, 80, and 100 ppm for 180 min resulted in 92, 88, 82, 77 and 62% degradation efficiency, respectively. The degradation efficiency for the initial concentration of 20 ppm reached the highest efficiency of 92.2% within 3 h, whereas 100 ppm has only 61.9% degradation efficiency within the same duration of irradiation. This can be explained by the penetration of photons entering the solution diminishes at high concentrations, resulting in an inner filter effect. Lower photon penetration causes less photons to be absorbed by MG [29-31]. The opposite effect occurs when the initial concentration is low, where MG absorbs more photons.

Moreover, 100 ppm has the lowest degradation efficiency compared to the other concentrations because at a high initial concentration, insufficient free radicals cause some of the molecules not to oxidise. At high concentrations, the light penetration of the system decreases, which results in less generation of hydroxyl radicals [19]. A similar result was also reported by Ghime et al. [32] for photolysis of MG which they found that 81% of MG was decolourised for 100 ppm compared to higher concentrations in the range of 150-200 ppm, where the decolourisation fell to 60-70%. The effect of initial dye concentration on the photodegradation of MG with similar results has also been reported by previous studies [33-35]. Ghodbane & Hamdaoui [30] reported that photolysis entirely degraded acid blue 25 (AB25) of an initial concentration of 10 mg/L compared to the highest concentration, which was 150 mg/L, which only reached 7% of degradation efficiency.

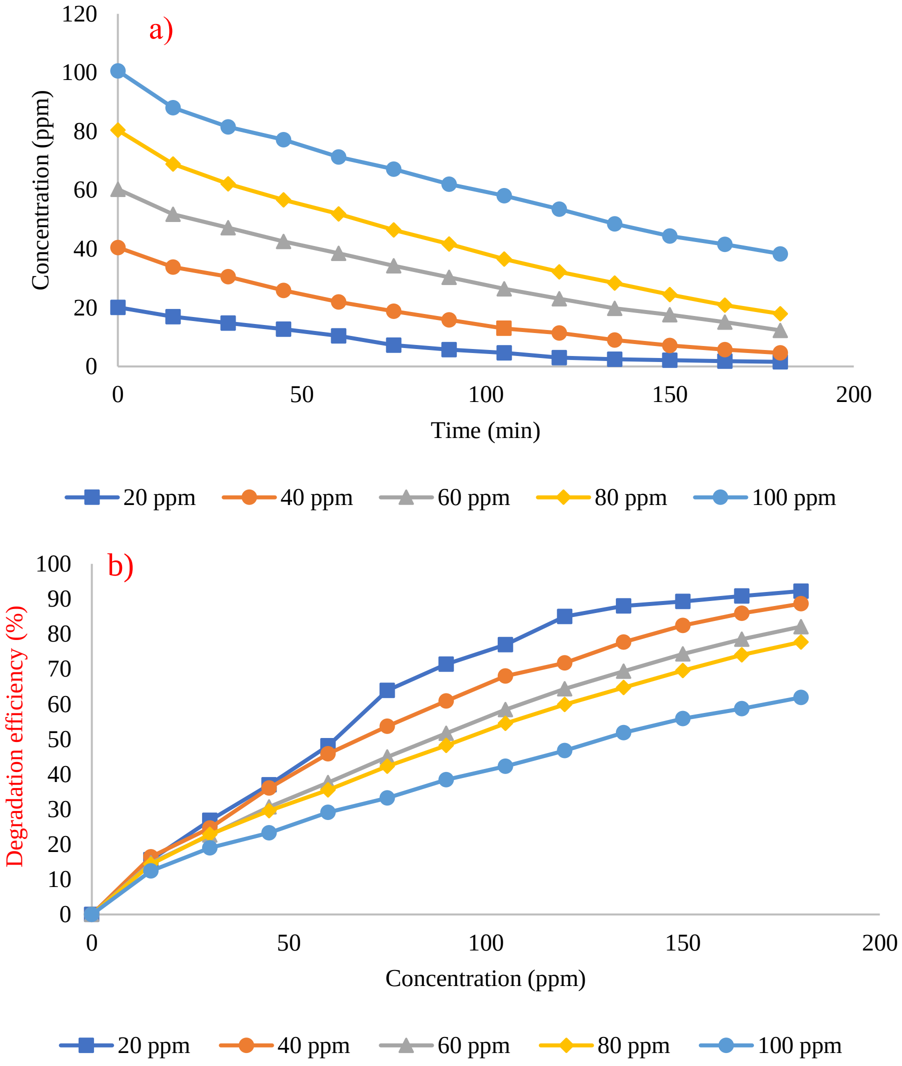

Figure 3. (a) Graph of concentration of MG against time for various initial dye concentrations (The experimental conditions: 500 mL at its natural pH with UV-C). (b) Graph of degradation efficiency of MG against time for various initial dye concentrations [Experimental conditions: 500 mL at its natural pH with UV-C).

The Effect of pH on Structural Properties of MG

The chemical structure of MG, as shown in Figure 4, is known to be pH-dependent. The natural pH of MG is pH 5. MG can exist in two forms in an aqueous solution: the cationic dye and the colourless carbinol form. The ionisation constant (pKa) of MG is 6.9, and it is completely protonated at pH 4.0. Most of the molecules are deprotonated at pH 10, and the solution is colourless [14, 33]. The balance between these two forms and the pH is essential in the analysis of MG, which pH can influence the structural stability of MG and the intensity of its colour. Thus, with blank MG solutions with an initial concentration of 40 ppm at its natural pH of 5, the influence of initial pH was investigated. Following pH adjustment, a solution is maintained for 1 hour in a dark place before the absorbance is determined. Based on Figure 5, the colour was stable throughout the pH range of 3–7 [33, 34].

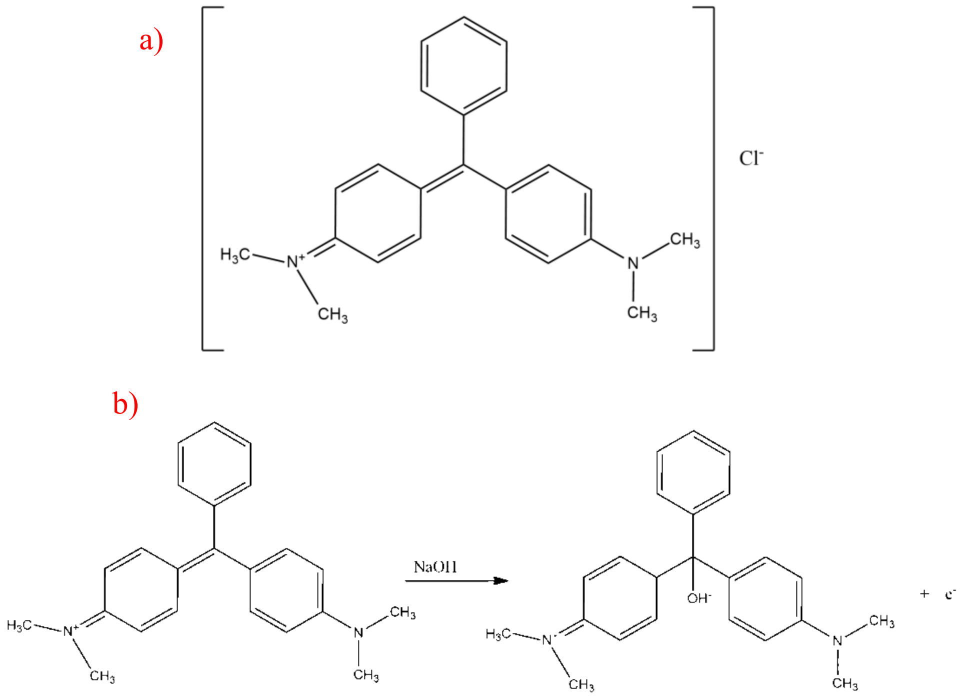

Figure 4. (a) Chemical structure of MG. (b) MG salt reacts with NaOH to form carbinol base MG.

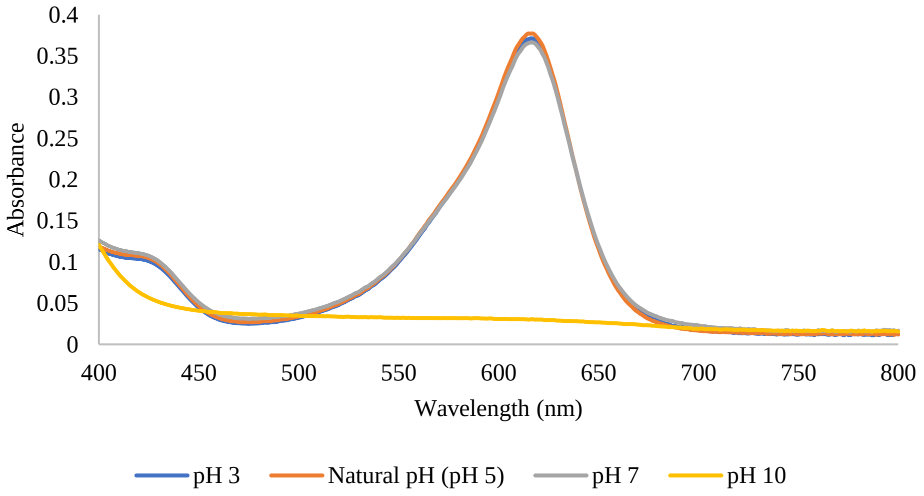

Figure 5. Evolution of UV-visible spectra of MG at different pH values after 1 hour, with the initial concentration of 40 ppm.

The change of colour from blue-green to colourless was observed with pH 10. This can be explained by the fact that in the absence of light, a hydroxyl ion attacks the ionic form of MG (blue-green coloured) and releases an electron and water, changing it to its carbinol form (molecular colourless form) [27]. As shown in Figure 4(b), when an OH- is bonded to the middle carbon, the conjugation between the benzene rings is disturbed, and the molecule becomes colourless [11]. The cation is converted to a carbinol base when sodium hydroxide (NaOH) is added. Figure 6 shows the UV-Vis spectra of the MG solution of pH 10 with the initial concentration of 40 ppm before and after the addition of NaOH. Samples were extracted every 5 minutes and the absorbance was obtained to see the colour evolution. The visible range spectra showed that the maximum absorption is reduced with time, which explains the colour lost in the solution. There was a slight peak shift in the range of 200-300 nm, which may the evidence of structural changes of MG.

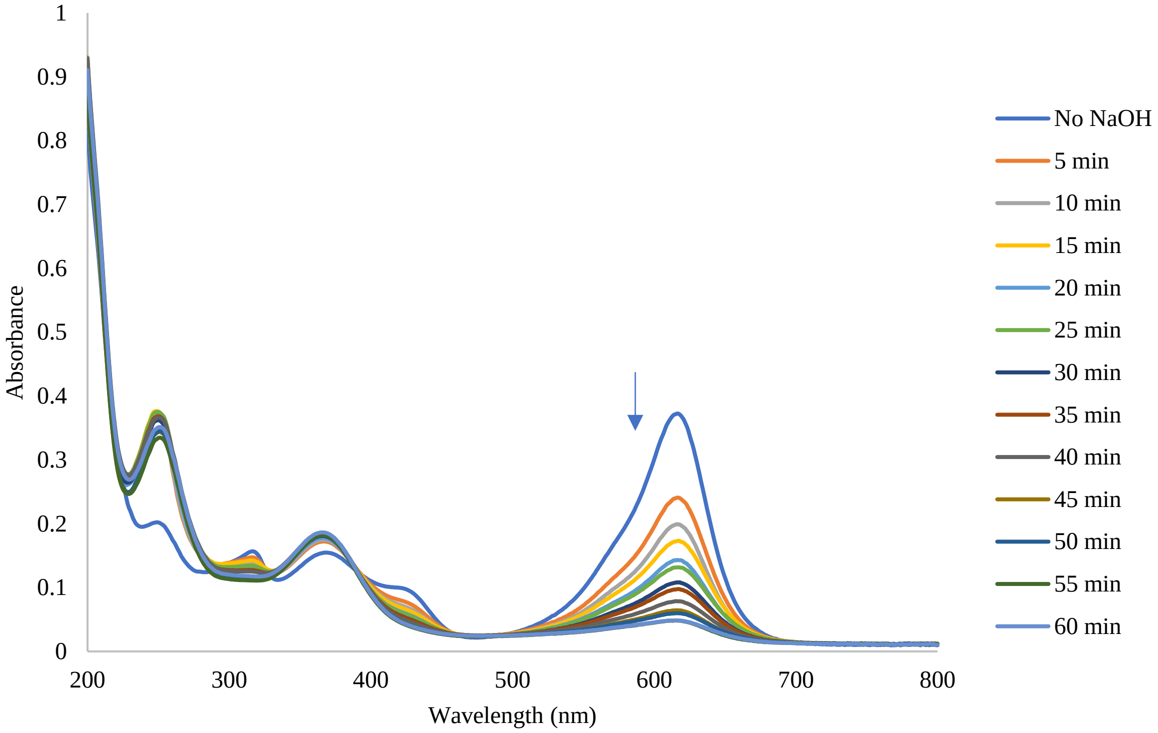

Figure 6. Experimental UV-Vis spectra at pH 10, at 40 ppm of MG.

The Effect of pH on Photolysis Process

Experiments were carried out at different solution pH values in the pH range of 3-7 to study the effect of pH on the photolytic degradation of MG. Figure 7(a) shows the degradation of MG at different pH values. In each of the experiments, a decrease in concentration was observed. The degradation efficiency of MG was found to increase slightly as the pH increased. Figure 7(b) shows the graph of degradation efficiency of MG against time for different pH. The higher degradation efficiency of MG at pH 7 (95.6%) is because it can produce more hydroxyl radicals compared to acidic pH (84.2%) and the natural pH of MG, pH 5 (88.6%). The hydroxyl radicals, the most prevalent oxidation species in an alkaline medium, enhance the ability to degrade dyes [35]. Another reason for the higher efficiency may be that MG is a cationic dye, and its degradation is favoured at alkaline pH values [19]. A slight decrease was observed for pH 3, where HCl was added to adjust the pH. The lower degradation efficiency in the acidic medium is attributable to the amount of added conjugated base, Cl-, as reported by Mitrovic et al. [36]. As shown in Equation 3, a chlorine ion reacts with a hydroxyl radical to form an inorganic radical ion, hypochlorite radical ion, which is less reactive than hydroxyl radicals. Due to the presence of competing anionic species, the hydroxyl radicals are less prone to be involved in the dye degradation process.

$$Cl^- + {}^{\bullet}OH \rightarrow ClHO^{\bullet-} \qquad (3)$$

The obtained results are consistent with the works that have been published. Putri et al. [35] reported that photodegradation of MG at pH 7 is higher at 60% compared to pH 5 at 49%. Another example is that 95% of allura red dye was degraded at pH 12, and the degradation efficiency decreased as the pH value decreased [37]. Wen et al. [38] reported that MB degradation increases as the solution's pH increases.

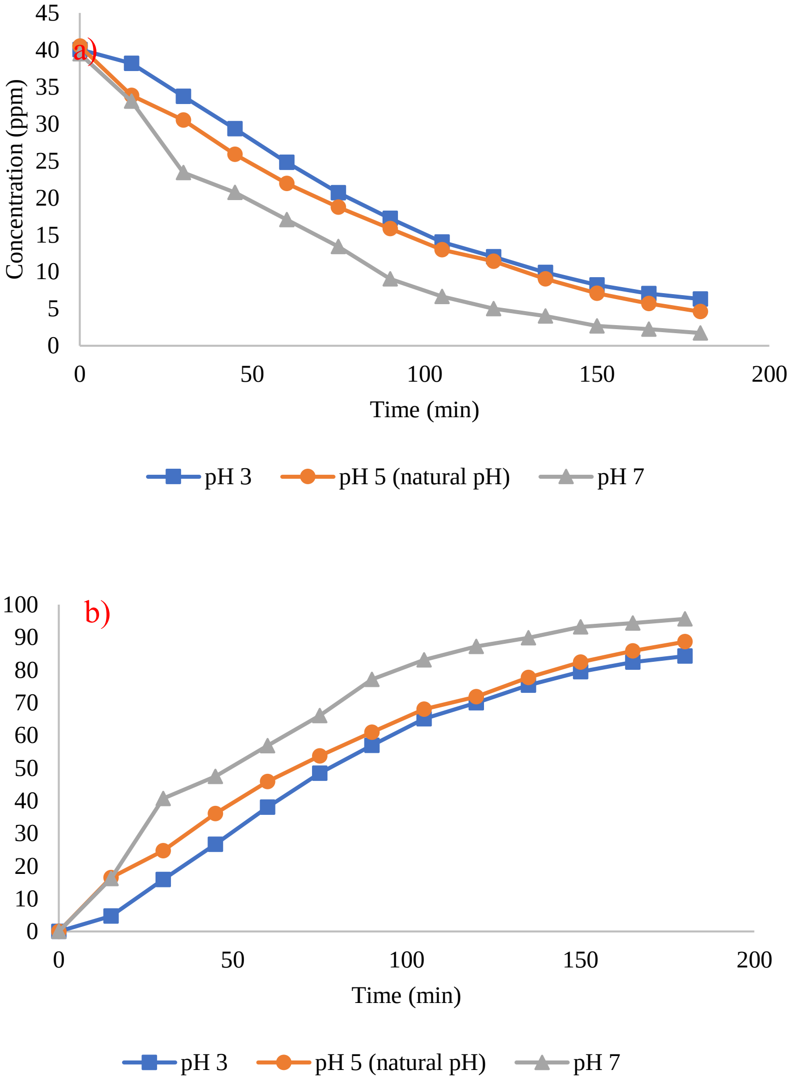

Figure 7. (a) Graph of concentration of MG against time for different pH. (b) Graph of degradation efficiency of MG against time for different pH.

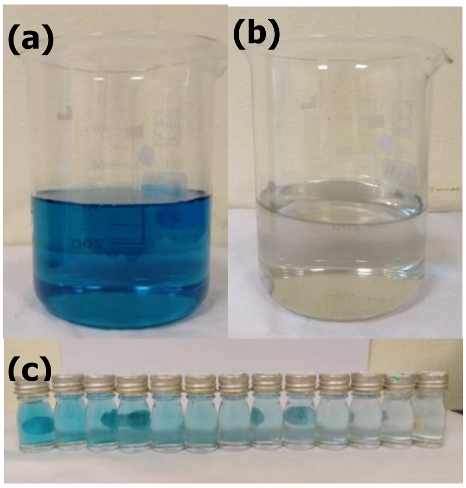

Figure 8. Colour changes of MG before and after irradiation for 3 h with UV-C and initial concentration of 40 ppm. (a) Before irradiation, (b) after irradiation, and (c) colour changes throughout the experiment every 15 min.

The Effect of Contact Time

MG concentration decreased with increasing contact time, indicating MG is degraded under UV irradiation. By the end of the irradiation, the intensity of the blue-green colour of MG was reduced (Figure 8). Fischer et al. [25] and Putri et al. [35] have reported that the degradation percentage of MG increases along with increasing irradiation time. It can be explained that MG can absorb more photon energy with much more prolonged exposure to UV irradiation. Moreover, as irradiation time increases, more hydroxyl radicals are produced. In the photolysis process, the production of hydroxyl radicals is important because they oxidises organic contaminants to simpler intermediates [19].

Photolytic Degradation of MG

Changes in molecular and structural characteristics of MG caused by photolytic degradation can be proved by observing the UV-visible spectral changes of the dye solution as a function of contact time at 15 min intervals. Based on Figure 9, as the irradiation time of photolysis increased, absorption bands decreased in intensity, and their spectral shape changed, indicating the dye's degradation. The maximum absorption of the visible band at 616 nm decreased; this rapid decrease specifies the elimination of the dye's conjugate structure, and a small hypsochromic shift was observed with increasing irradiation time. The maximum absorption wavelength shifted from 616 nm to 597 nm at 180 min irradiation time. The hypsochromic shift, or blue shift, may be caused by an N-demethylation process [33, 35]. As a result, it is concluded that MG degradation occurs through two processes, which are N-demethylation and conjugated structure degradation. The loss of colour observed during irradiation suggests that MG was reduced to its leuco-form [33, 35], as shown in Figure 10.

The major photodegradation mechanisms of MG in numerous different photodegradation processes have been reported as N-demethylation of the MG molecule and cleavage of the conjugated structure to create benzophenone derivatives (BPD) [11, 24, 39]. N-demethylation reaction is when OH• attacks the N,N-dimethyl position, which reduces the polarity of MG molecules, leading to MG degradation mechanism via photolysis that can be explained by MG molecules undergoing photochemical reactions, in which by absorbing light, the molecules are broken down into smaller ones [19, 40].

The absorption of light energy causes the transformation of MG to intermediates or by-products:

$$\text{MG} + h\nu \rightarrow \text{By-products} \qquad (4)$$

UV-C, which has a wavelength of 254 nm, is equivalent to a photon energy of 6.7 eV, greater than the bond dissociation energy (BDE) of water molecules (5.21 eV). Thus, it can dissociate water to generate hydroxyl radicals [19]. The light energy required to dissociate the water molecules during photolysis is ~2.76 eV [41]. The water molecules will be cleaved under UV irradiation to form hydrogen and hydroxyl radicals:

$$H_2O + h\nu \rightarrow {}^{\bullet}OH + H \qquad (5)$$

Further degradation of MG occurs by the reaction of hydroxyl radicals generated with the dye molecules:

$$\text{MG} + {}^{\bullet}OH \rightarrow \text{Products} \qquad (6)$$

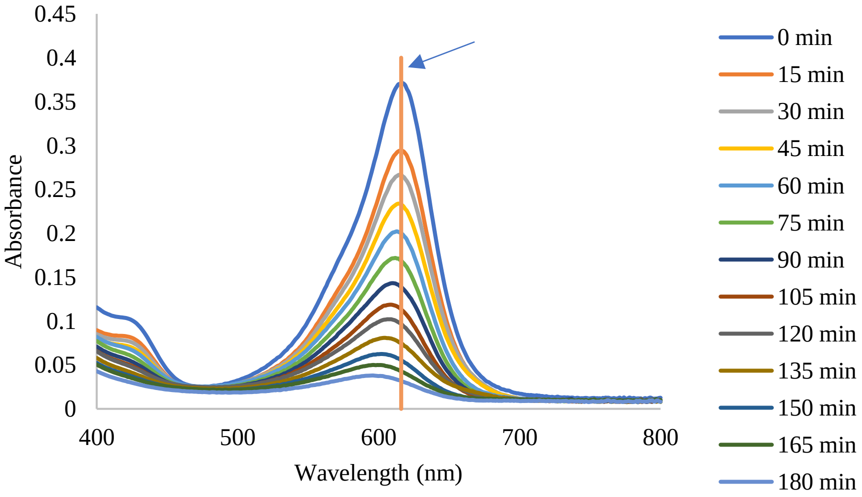

Figure 9. Absorption spectra of degradation of MG by photolysis with concentration of 40 ppm at its natural pH using UV-C.

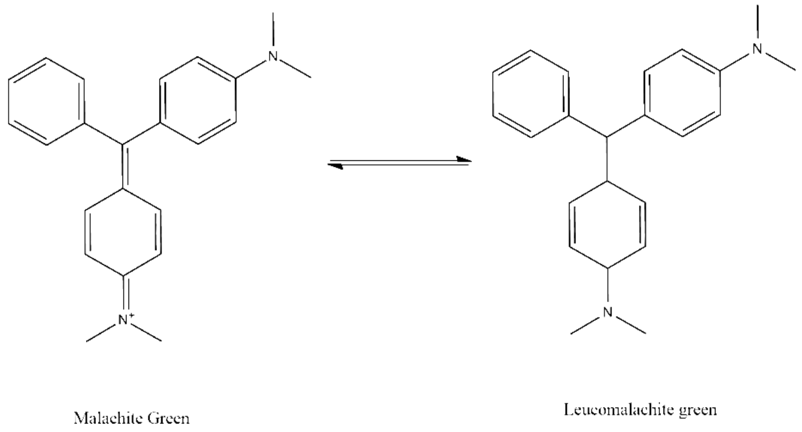

Figure 10. Mechanism of MG reduction forming Leucomalachite green.

Table 1. Results of analysis of water quality parameters before and after treatment.

Parameter	Before treatment	After treatment
BOD_5, mg/L	5.06	7.17
COD, mg/L	27	26
BOD/COD	0.19	0.28
TOC, mg/L	4.39	4.04

Analysis of Water Quality Parameters

The environmental aspect of photolytic degradation of MG dye was evaluated using the water quality parameters, BOD, COD, and TOC, to evaluate the treatment's effectiveness. These parameters were compared before and after the photolysis experiment with a contact time of 3 h using an initial concentration of 40 ppm and UV-C at its natural pH. Table 1 shows the results for the parameters before and after the treatment.

Based on the results, the BOD5 value increased from 5.06 mg/L to 7.17 mg/L after photolysis. It can be explained that photolytic oxidation enhances biodegradability by converting non-biodegradable organic substrates into more biodegradable compounds [42]. Smaller degradable intermediates formed after photolysis are more biodegradable and easier to be metabolised by microorganisms than the parent compounds before the treatment [43, 44]. Other than the BOD5 value, pollutants' biodegradability can be estimated by evaluating the resulting BOD5/COD ratio, also known as the "biodegradability index" [45]. Wastewater is considered biodegradable when the ratio is more than 0.4 [16, 46]. Based on the BOD5 and COD results, the BOD5/COD ratio for degradation of MG increased from 0.19 to 0.28, which can be considered partially biodegradable [16]. The same pattern was seen in a research by Kusic et al. [44], where the authors studied nine reactive triazine dyes (reactive blue 198, reactive blue 2, reactive blue 49, reactive red 45, reactive red 195, reactive red 120, reactive green 8, reactive brown 2 and reactive yellow 3), and the BOD5 values increased after the photodegradation treatment. The increases are explained to correlate with the decreasing aromaticity in the structure of the dyes. The presence of aliphatic structures among created by-products, which are typically regarded as more biodegradable than aromatic ones, was identified in all cases of the dyes. Furthermore, Khezrianjoo [16] reported that the BOD5 also increased for the photodegradation of direct yellow 11 after 120 min irradiation, by which they decided to proceed with the mineralisation of the dye with biological treatment. Photodegradation of methylparaben also enhances the biodegradability, which the solution's BOD5/COD ratio was found to increase after the treatment process, as reported by Zúñiga-Benítez & Peñuela [47]. The biodegradability index (BOD5/ COD) for most of the dye solutions when total discolouration is obtained. It implies that photolysis tends to enhance the biodegradability of dye-containing solutions. Thus, this technique could be used as a pre-treatment step for conventional biological wastewater treatment.

The COD value was reduced by 3.7% (Table 1). The low COD removal is due to the formation of intermediates or by-products that could still contribute to the COD value [19]. A complete decolourisation indicates colour disappearance, which only signifies that the chromophore group responsible for the dye's colour is destroyed, which does not mean the complete removal of organics [27]. Thus, the dye is not directly mineralised but changed into intermediates products. The results showed only 8% reduction in TOC under irradiation of UV-C (Table 1). This result implies that even though 88% of the degradation could be achieved within 3 h with the UV irradiation, the organic compound of MG did not completely mineralise.

Traditional water treatment processes such as coagulation, filtration, and chlorination frequently fail to adequately remove new pollutants, such as dyes. Recalcitrant dyes can also be removed using several physical processes, including ion exchange, adsorption and membrane filtering methods. However, they have the disadvantage of increasing sludge formation volume [48]. It is essential to use advanced oxidation processes, such as photolysis, to separate contaminants from water. Conventional methods, as aforementioned, are incapable to treat persistent pollutants such as dyes. Moreover, conventional methods incur high costs and operational problems. The data summarised in Table 2 illustrate the removal efficiencies of photolysis process aimed at abating dyes.

Reaction Kinetics

Kinetic studies indicate the information on the optimum conditions for degrading dyes. Due to the concentration of MG molecules dropping exponentially, as in a first-order reaction, the degradation in this study was explained in terms of first-order reactions [11, 24, 25]. On the assumption that the concentration of MG represents a first-order reaction, the rate constant (*k*) was determined by regressing against time (*t*) data according to Equation 2. All experiments with varying parameters conformed to first-order kinetics according to the results. Figure 11 and Table 3 show the rate constants (*k*) and regression correlation for the effect of different types of UV irradiation. The rate of degradation of MG was highest under UV-C irradiation (0.0113 min-1), followed by UV-B (0.0007 min^{-1}) and UV-A (0.0006 min^{-1}). As the rate constant is in decreasing order from UV-C to UV-A, a significant correlation can be made between irradiation wavelength and rate constant. The shorter the irradiation wavelength, the higher the rate constant, giving higher degradation efficiency [31].

Table 2. Photolysis process for the degradation of various dyes.

Reference	Pollutant	Experimental condition	Results
[19]	Methylene blue	UV lamps (UV-A, UV-B, UV-C)	COD removal: 83.3% achieved after 60 min (UV-C) 96.7% degradation of MB after 5 h (UV-C)
[49]	Reactive red 120 (RR120)	Low pressure mercury lamp, [Fe+3]0 = 0.25–2.75 mM, [MB]0 = 100–200 mg/L, initial pH 1–11	92% colour of the dye was removed in 55 min under conditions of Fe3+ concentration, 2.35 mM, pH 3.6, and initial dye concentration of 170 mg/
[50]	Orange II (OII)	8 W UV mercury lamps	Exhibited an inverse relationship with initial OII concentration, while it was directly proportional to optical power intensity and temperature in the UV/NO_3^--I^- system
[51]	Fuchsine Dye	Natural pH, 6.4 under UV-A light	Acidic medium is favoured to decolourise this dye at pH 4.6 and the efficiency of photoreaction increases from 73.75% to 89.63% at 70 min
[37]	Allura red	UV light (254 nm)	63.29% decolourisation after exposure to 6 h UV illumination

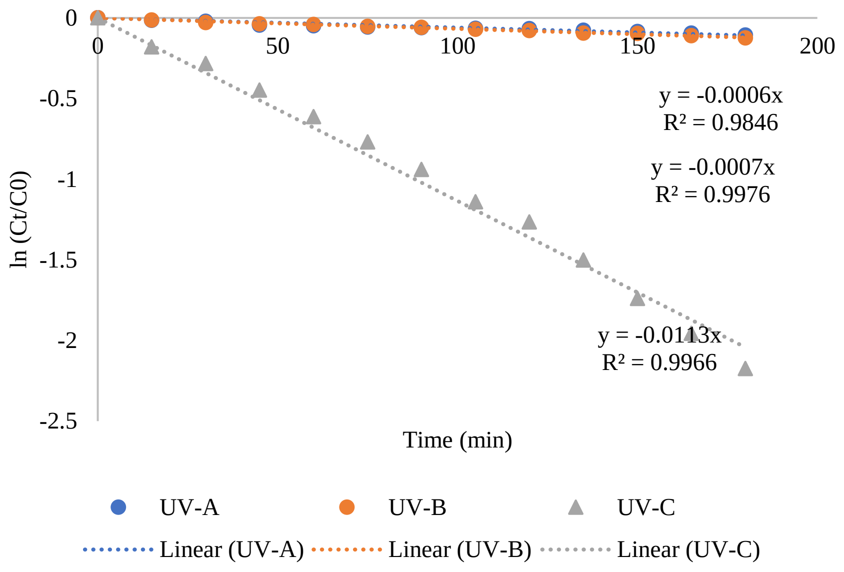

Figure 11. Plot of $ln\frac{C_t}{C_o}$ versus time for the photolytic degradation of MG under different types of UV irradiation.

Table 3. Rate constants and regression correlation (R^2) for the effect of different types of UV irradiation.

Type of UV irradiation	Rate constant, min^{-1}	R^2
UV-A	0.0006	0.9286
UV-B	0.0007	0.9909
UV-C	0.0113	0.9867

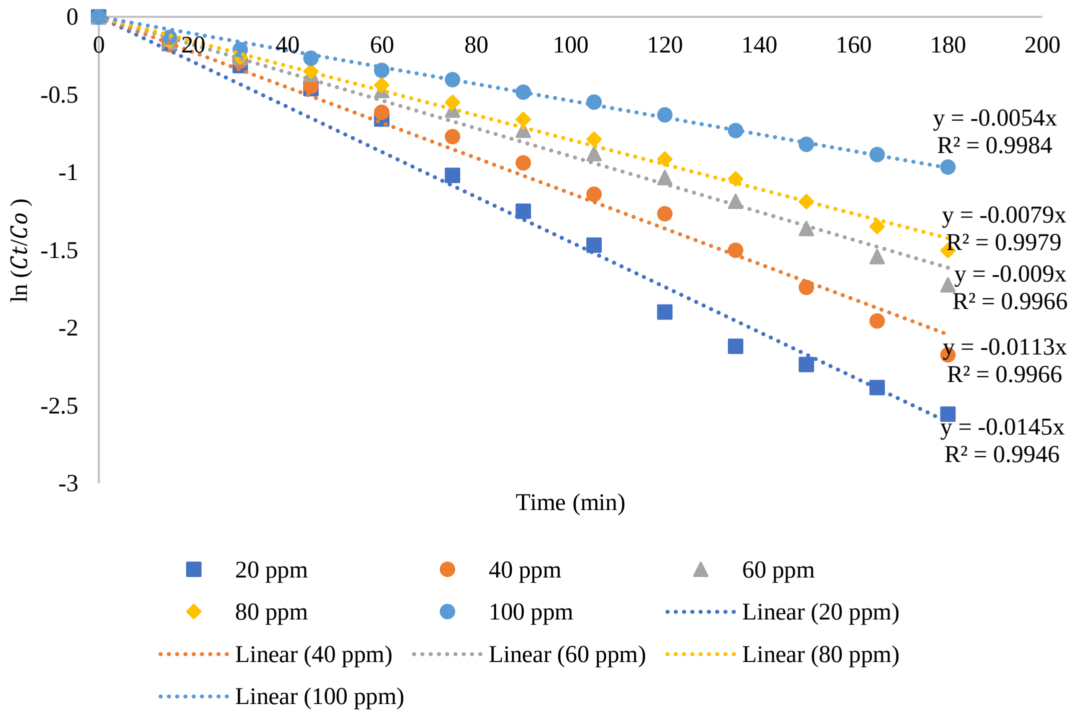

Figure 12. Plot of ln($\frac{C_t}{C_o}$) versus time for the photolytic degradation of MG at different initial concentrations of dye.

Table 4. Rate constants and regression correlation for the effect of initial dye concentration.

Concentration, ppm	Rate constant, min^{-1}	R^2
20	0.0145	0.9829
40	0.0113	0.9891
60	0.0090	0.9890
80	0.0079	0.9926
100	0.0054	0.9938

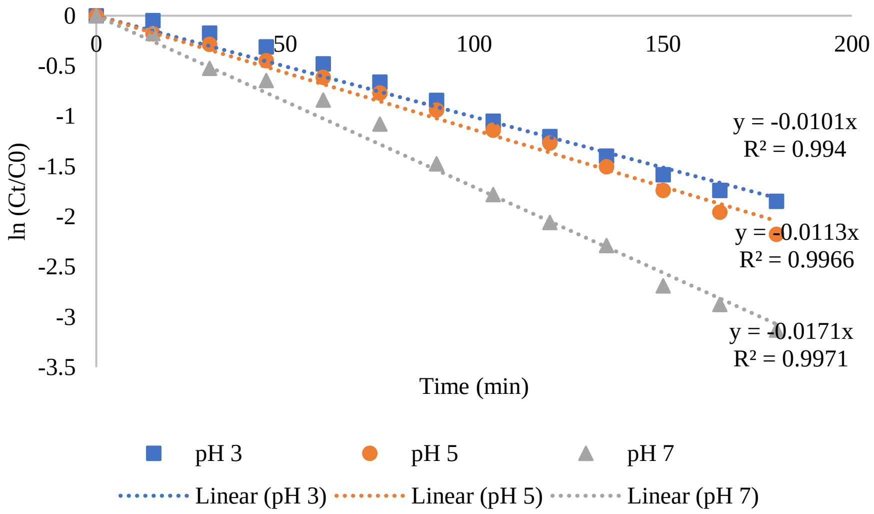

Figure 13. Plot of $\ln(C_t/C_0)$ versus time for the photolytic degradation of MG at different pH.

Table 5. Rate constants and regression correlation for the effect of pH.

pH	Rate constant, min^{-1}	R^2
3	0.0101	0.9788
5	0.0113	0.9867
7	0.0171	0.9886

The first-order rate constants (min^{-1}) for the effect of different initial concentrations were calculated from the slopes in Figure 12 and are presented in Table 4. Based on the regression correlation (R^2), all the initial concentrations of dye to study the degradation of MG match first-order kinetics. The results show that the rate constant is higher at low MG concentrations. The highest rate constant was at the concentration of 20 ppm (0.0145 min^{-1}). At the concentration of 100 ppm, the rate was the lowest as the absorption of photons by the dye decreases, thus resulting in a reduced initial degradation rate [31].

Figure 13 shows the rate constants of the effect of pH on the photolysis of MG. Based on Table 5, neutral pH had the highest rate constant (0.0171 min^{-1}). The lowest rate constant was under an acidic medium, pH 3 (0.0101 min^{-1}), followed by the rate constant for reaction at the natural pH of MG, pH 5 (0.0113 min^{-1}). The higher rate at neutral pH of MG is due to more hydroxyl radicals that can be generated in that medium compared to the acidic and its natural pH [19].

CONCLUSION

This study shows that the photolysis process can degrade MG, a triphenylmethane dye, under UV irradiation. The UV-vis spectrometry analysis proved the degradation of MG as the maximum peak of the absorption spectrum of MG disappeared over the irradiation time. The effects of different operational parameters, such as the type of UV irradiation, initial dye concentration, pH, and contact time, have been studied. UV-C irradiation had the highest degradation efficiency of 88% compared to UV-A (10.1%) and UV-B (11.5%), which was used throughout the other experiments. The degradation efficiency of the dye decreased with increasing initial concentration of dye due to the filter effect of the high concentration of dye. Higher pH has higher degradation efficiency as more hydroxyl radicals could be generated during the photolysis process. As the time of UV exposure during photolysis increased, the degradation percentage also increased. The reduction of COD and TOC values demonstrate that the amount of organic pollutants decreased after photolysis, showing the potential of photolysis in the treatment of dye-contaminated wastewater. The BOD5 increased as the smaller intermediate products produced after photolysis are more biodegradable than the dye before photolysis. UV photolysis has been recommended as a substitute for chemical additives in wastewater treatment against a wide range of environmental pollutants. The potential of photolysis as a pretreatment before biological treatment is proven as the biodegradability of MG was increased. The photodegradation process of MG obeyed first-order kinetics. The highest rate by each of the operational parameters was recorded by the initial concentration of 20 ppm (0.0145 min^{-1}), pH 7 (0.0171 min^{-1}), and UV-C (0.0113 min^{-1}). Thus, the optimum parameters were achieved at an initial concentration of 20 ppm, pH 7, and UV-C irradiation.

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