

Photocatalytic Degradation and Kinetics of Malachite Green Using UV-TiO₂ System

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ABSTRACT

Untreated effluents may also contain dyes, especially in discharges from textile and fabric industries. Synthetic dyes have an adverse effect on all forms of life when discharged directly into the environment. This study investigates the photodegradation of Malachite Green (MG), a triaryl methane dye and the influence of initial dye concentration, pH, catalyst dose, reaction time on the overall photodegradation process. Photoreactor technique utilized was the slurry method; the photoreactor was equipped with a 15 W UV light and the photocatalyst used was nano titanium dioxide (80% anatase and 20% rutile). The results obtained showed that variation in the physical parameters influenced the efficiency of photodegradation. Kinetic study indicated that MG photodegradation follow the pseudo-first-order kinetics; 10 ppm MG gave the highest-first-order rate constant, followed by 30 ppm MG while 50 ppm MG gave the least rate constant; implying that better degradation was obtained at low MG concentration. Impact of Cu²⁺ ions on MG degradation was also investigated and results indicated an inhibitory effect.

KEYWORDS: Photodegradation, synthetic dye, malachite Green, titanium dioxide, kinetics

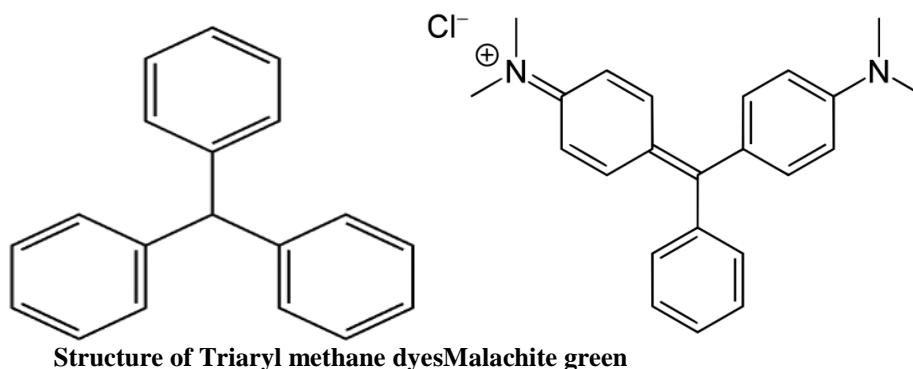
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I. INTRODUCTION

Dyes and pigments are the most important colorants used to add color or to change the color of something (Gurses et al., 2016). They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. Untreated effluents may also contain dyes, especially in discharges from textile and fabric industries. Synthetic dyes have an adverse effect on all forms of life when discharged directly into the environment. For instance, the chemical aniline, which forms the basis for azo dyes is considered a deadly poison since it gives off carcinogenic amines (Anon, 1996). Macron and Ames, 1983, reported that some groups of aromatic amines are established mutagens in the standard mutagenicity assay. Kant, 2012 stated that the presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals collectively make the textile effluent highly toxic. The colloidal matter present along with colors and oily scum increase the turbidity, give the water a bad appearance and foul smell and prevent the penetration of sunlight necessary for the process of photosynthesis (Vijaraghavan, 1999). This, in turn, interferes with the oxygen transfer mechanism at air-water interface, which in turn, interferes with marine life and self-purification process of water. If this effluent is allowed to flow in the fields, it clogs the pores of the soil resulting in loss of soil productivity (Kant, 2012). Furthermore, if the effluent is allowed to flow into drains and rivers, it affects the water quality making it unfit for human consumption. Thus, it is important to remove these pollutants from the waste waters before their final disposal.

Malachite green dye has the triaryl methane chromophoric group with the molecular formula C₂₃H₂₅ClN₂ and molecular weight 364.911 g/mol. Its IUPAC name is 4-[[4-dimethylamino)phenyl]methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride. MG is used in aquarium as antibacterial, antifungal & antimicrobial agent. It is also used as a dye for silk, leather, paper etc.



Photocatalysis refers to a catalytic process that is initiated by light. Invariably, it means that the photocatalytic process cannot be carried out in the absence of light. It is an effective method in water treatment because it leads to a complete chemical transformation of the pollutants into non toxic or less toxic products. Fujishima and Honda, 1972, discovered that water can be split into hydrogen and oxygen through photocatalytic process. Further studies by Fox & Dulay, 1993, found that irradiated semiconductor particles could catalyze a lot of interesting and useful reduction-oxidation reactions of organic and inorganic compounds. Thus, this research is an investigation of the photocatalytic degradation of malachite green using titanium dioxide as the photocatalyst in the presence of UV light.

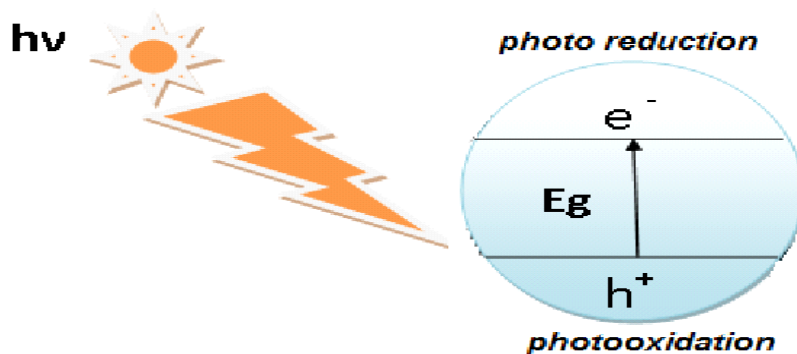


Fig. 1 Transfer of electron from valence band to conduction band in a photocatalyst

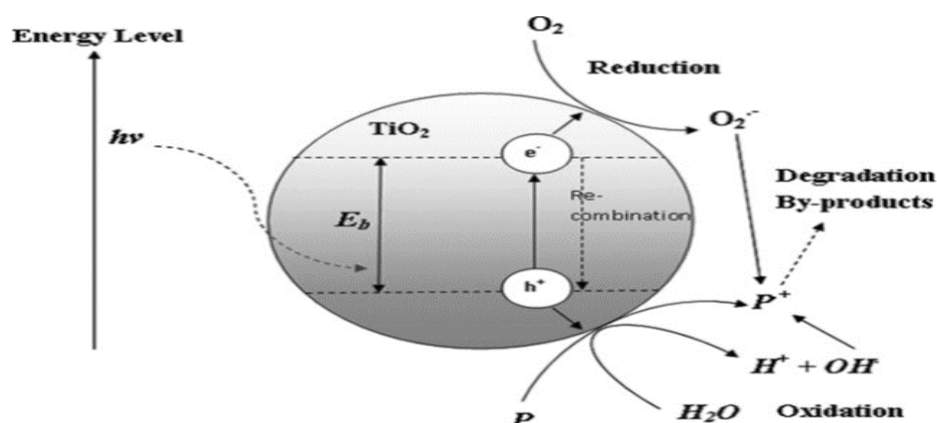


Fig. 2. The mechanism of electron-hole pair formation in a TiO₂ particle in the presence of pollutant in water

II. MATERIALS AND METHODS

The pure anatase form of titanium oxide (TiO₂) used in the experiment was purchased from US Nano Inc. The TiO₂ (80% anatase, 20% rutile) was nano sized, with a particle size < 100 nm, surface area of 200-240 m²g⁻¹, and was used for all the photocatalytic experiments without further treatment. Hydrochloric acid and sodium hydroxide used in this research were obtained from Sigma-Aldrich. All reagents were of analytical grade and were used without further purification.

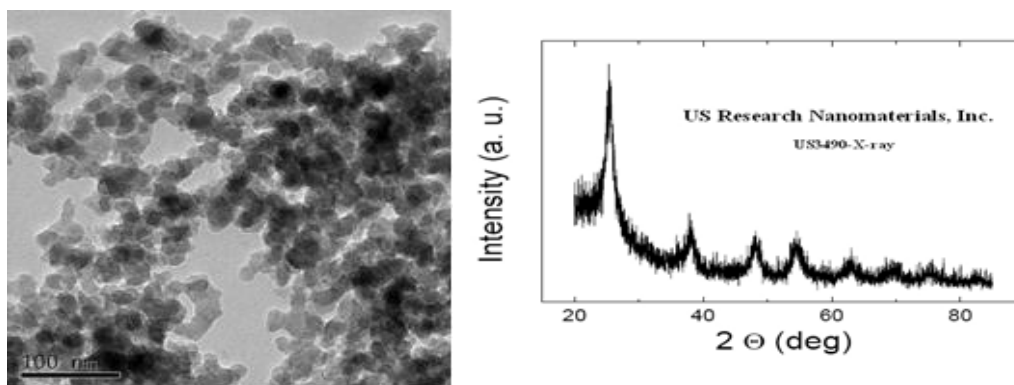


Fig. 3 Scanning Electron Micrograph of TiO₂ Fig. 4 X-ray Diffraction pattern of TiO₂

III. PROCEDURE

Photolysis test

50 ml of 30 ppm MG solution was introduced into a 100 ml beaker, placed in the photoreactor and was stirred continuously with a magnetic stirrer for 60 minutes. UV analysis of the dye was carried out for evidence of reduction in dye concentration.

Adsorption of the dye on the photocatalyst

50 ml of 30 ppm MG solution was mixed with 0.2 g of TiO₂ in a 100 ml beaker and the suspension was further mixed in the dark using a magnetic stirrer for 60 minutes. The resultant suspension was filtered and the filtrate was analyzed for any change in concentration. The difference in concentration (before and after adsorption test) was attributed to the adsorption of the dye on the photo catalyst.

Photocatalytic degradation of dye

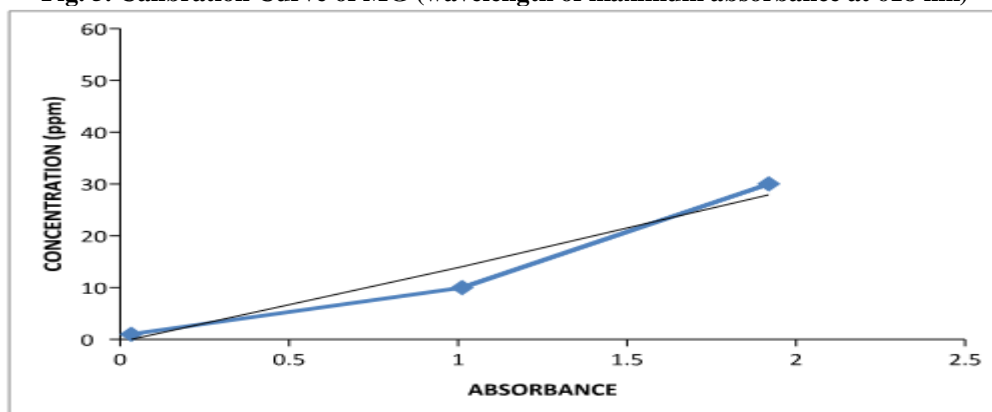
50 ml each of the MG solutions was mixed with 0.2 g of TiO₂ in 100 ml beaker. The suspension was continuously stirred with a magnetic stirrer while being irradiated by a 15 W UV lamp under ambient temperature in the photoreactor. Aliquots of the mixture were centrifuged and analyzed periodically at 0, 30, 60 and 100 mins respectively. The pH of the solutions was adjusted using 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) respectively. The degradation process for each of the dye solutions was monitored with a UV- Vis spectrophotometer at maximum absorbance wavelength corresponding to the various dyes (see table 5). The percentage degradation was calculated according to equation 9,

Where C_0 is the initial dye concentration, C_t is the final dye concentration at time, t .

Reaction parameters were varied to study the effects of pH, catalyst dose, reaction time and initial concentrations on the photodegradation of MG.

IV. RESULTS AND DISCUSSION

Fig. 5. Calibration Curve of MG (wavelength of maximum absorbance at 618 nm)



The results of photolysis and adsorption test

Both tests were carried out using 30 ppm MG, at pH 7, 30 minutes reaction time and a catalyst dose of 4g/l. Results showed 29.5 ppm of MG after photolysis and 28.9 ppm after adsorption test. This indicates a mere 1.67% and 4% removal of dye through photolysis and adsorption process respectively. Therefore, both processes played minor roles during photodegradation process and their influence on the photodegradation of the dye is insignificant.

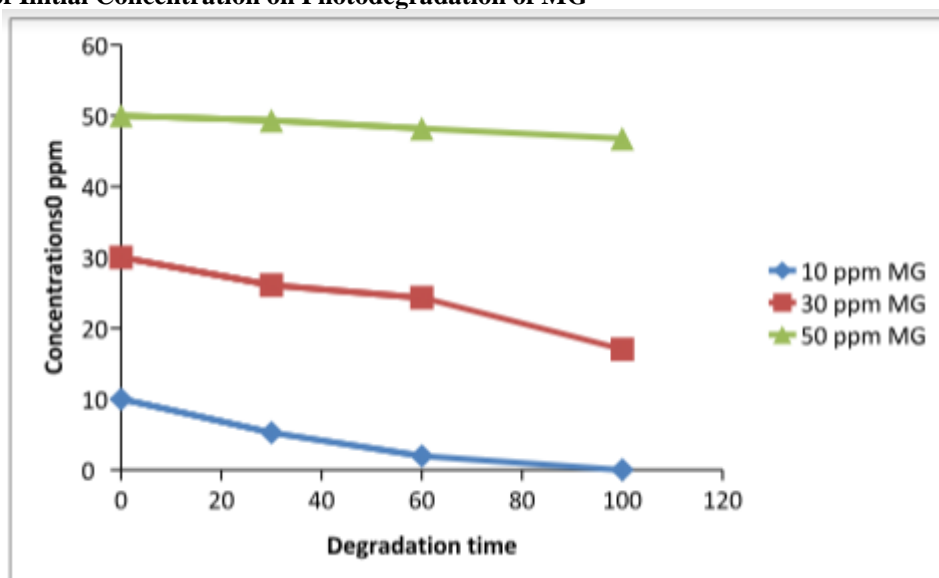
Influence of Initial Concentration on Photodegradation of MG

Fig. 6. Plot of MG concentration against reaction time (Reaction conditions: Cat. dose 4 g/l, pH 7, 15 W UV light, nano TiO₂ photocatalyst)

Effect of initial concentration on the photodegradation efficiency of MG was investigated. The initial dye concentrations evaluated were 10, 30 and 50 ppm respectively. Results obtained showed that the degradation efficiency of dyes in a TiO₂ – UV system was as follows: 20 mins (10 ppm – 47.3%, 30 ppm – 13.03%, 50 ppm – 1.36%); 30 mins (10 ppm – 80.34%, 30 ppm - 18.93%, 50 ppm – 6.46%); 60 mins (10 ppm – 100%, 30 ppm – 43.23% and 50 ppm – 3.67%). These results indicate that increasing initial organic compound concentration leads to a reduction in the photocatalyst degradation efficiency. It was observed that higher degradation efficiencies were generally obtained at lower initial dye concentrations, with 10 ppm MG recording a 100% degradation after 60 minutes of photodegradation. Photodegradation was found to be inhibited in 50 ppm MG. According to Mai, et al., 2008, this might be due to a corresponding surge in the amount of organic molecules adsorbed on the photocatalyst surface, thereby making the catalyst surface unavailable for the generation of hydroxyl radicals; this phenomenon reduces the photocatalytic activity of the catalyst. Also, Sobana et al. 2008, reported that, an increase in the initial concentration of organic compound leads to a decrease in the number of photons (or path length of photons) on the surface of photocatalyst (the Beer-Lambert law). This will in turn reduce the promotion of electrons from valance band to conduction band, subsequently resulting in a decrease in the photocatalytic activity of the nanocatalyst.

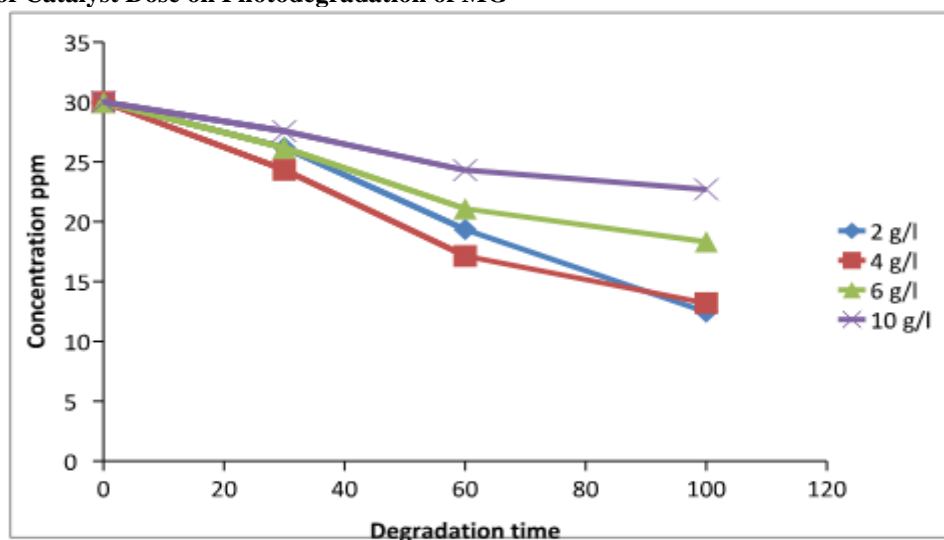
Influence of Catalyst Dose on Photodegradation of MG

Fig. 7. Plot of MG conc. against degradation time (Reaction conditions: initial conc. 30 ppm, pH 7, 15 W UV light, nano TiO₂ photocatalyst)

Photocatalyst dose or load plays an important role in the photodegradation process as stated by San et al., 2001, Saquib and Muneer, 2002, & Kavitha and Palanisany, 2010. In this study, it was observed that the amount of catalyst used was directly proportional to the photodegradation of the dye up to an optimum dose; however, addition of more photocatalyst beyond the optimum dose hindered photodegradation. The effect of TiO₂ loading on the percentage degradation of the dye under UV irradiation was examined by varying the amount of catalyst from 2 g/l to 10 g/l at 30 ppm dye concentration.

Figure 7 shows that after 30 minutes photodegradation of 30 ppm MG, 2 g/l, 4g/l, 6 g/l and 10 g/l catalyst dose gave the following results; 26.2 ppm, 24.31, 26.17, and 27.56 respectively. The degradation time was further increased to 60 minutes and then to 100 minutes as in fig. 7, with results indicating a similar trend with that of the 30 minutes degradation time. This trend can be summarized as follows; the optimum catalyst dose for MG is 4 g/l; further increase of TiO₂ led to a reduction in photodegradation. This implies that addition of more TiO₂ beyond the 4 g/l optimum dose, decreased photodegradation gradually. This concept of optimum catalyst dose can be attributed to the fact that the presence of photocatalyst can enhance photodegradation only at a particular concentration. Increased photocatalyst amount will lead to increased active sites for photodegradation to occur; however, this will enhance photodegradation up to a saturation point. Addition of more photocatalyst beyond this saturation point, will lead to a cloudy suspension which will obstruct photons from penetrating the bulk of the solution. Since the photons are necessary for the activation of the photocatalyst, photodegradation of the dye will be hindered.

Influence of pH on Photodegradation of MG

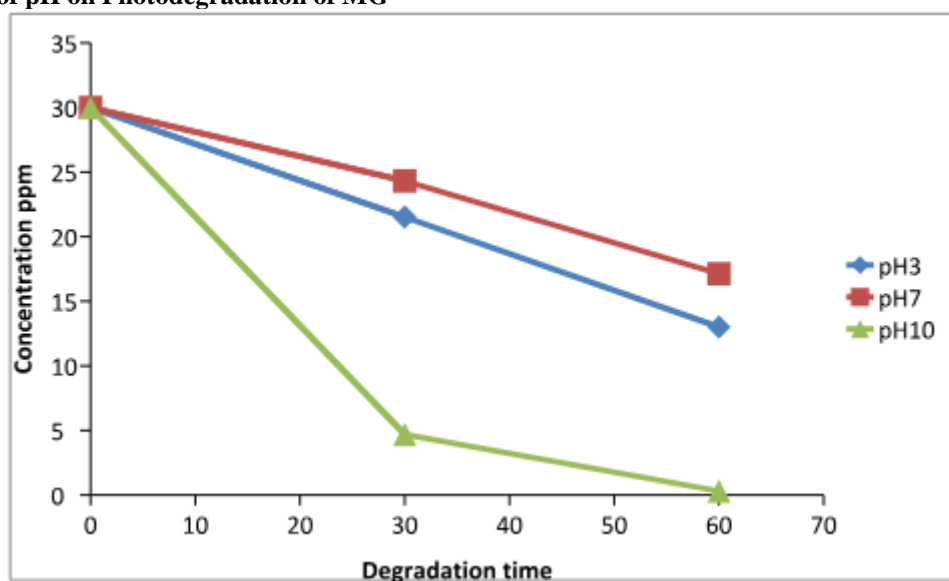


Fig. 8. Plot of MG conc. against time at different pH mediums (Reaction conditions: initial conc. 30 ppm, cat. dose 4 g/l, 15 W UV light, nano TiO₂ photocatalyst)

Malachite green is a positively charged triaryl methane dye, with an ammonium cationic group. Consequently, this implies that degradation of malachite green will be enhanced in basic medium, when compared with an acidic medium. The results obtained in this study support the aforementioned assertion as shown in fig. 8. After 30 mins of photodegradation, the degradation efficiency of MG in pH 3, 7 and 10 was given as 28.27%, 18.93% and 84.3% respectively. Since the surface of TiO₂ photocatalyst becomes negatively charged at basic medium, more MG molecules are adsorbed on its surface at pH 10 enhancing their photodegradation, thus giving the highest degradation efficiency of 84.3% compared to acidic and neutral mediums. This outcome may be attributed to the point of zero net charge (PZC) of TiO₂, which is pH 6.8 (Mai, et. al., 2008). In an alkaline solution (pH > 6.8), TiO₂ surface becomes negatively charged, whereas Malachite green molecule is positively charged due to the presence of ammonium cationic group. This situation favors the adsorption of the cationic dye onto the TiO₂ catalyst surface at the alkaline pH. As more dye molecules are absorbed on the active sites of TiO₂ photocatalyst, the degradation efficiency is enhanced. On the other hand, at pH < 6.8 value, the surface of the TiO₂ photocatalyst becomes positively charged, and lower amounts of the dye molecules are attracted to it. This is confirmed by the relatively lower degradation efficiency of MG at lower pH values.

Photodegradation Kinetics Of MG

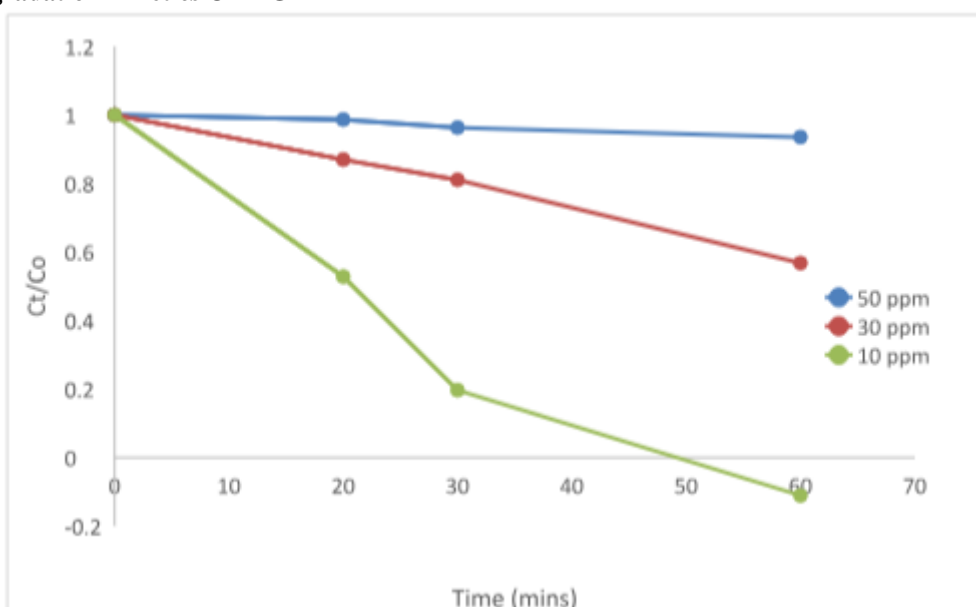


Fig. 9. Photodegradation kinetics of MG (Reaction conditions: catalyst dose 4g/l, pH 7, 15 W UV light, nano TiO₂ photocatalyst)

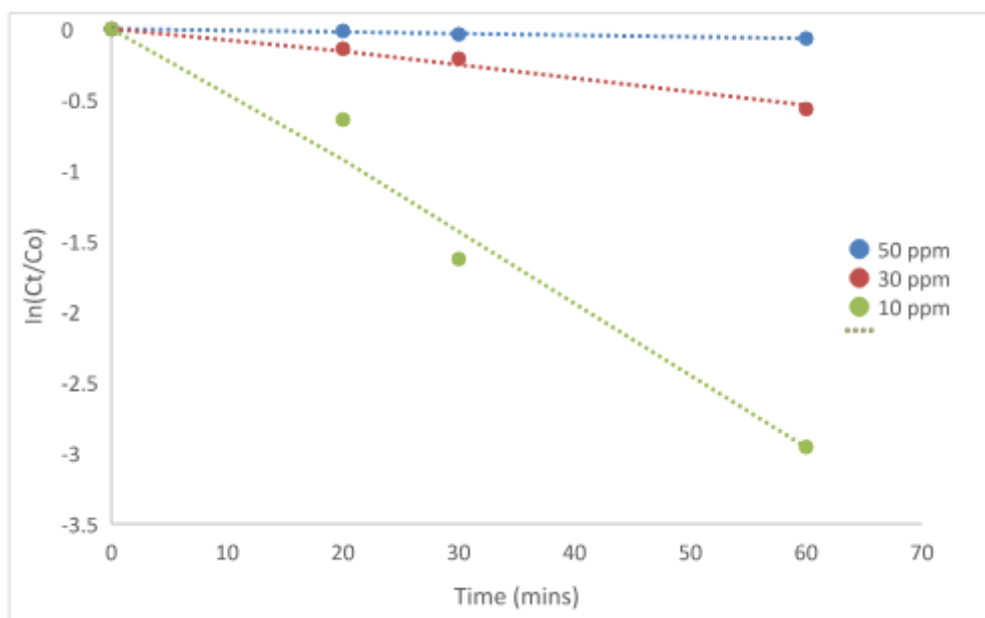


Fig. 10. Pseudo-first-order kinetics plot for MG (Reaction conditions: catalyst dose 4g/l, pH 7, 15 W UV light, nano TiO₂ photocatalyst)

Table 1. Pseudo-first-order parameters for the photodegradation of MG

MG conc. (ppm)	K ₁	R ²
10	0.05	0.974
30	0.0095	0.977
50	0.001	0.967

The degradation of dye molecules by the photocatalyst, TiO₂, as investigated was seen to largely follow the pseudo-first-order kinetics. This finding correlates with the findings of Neppolian et al. (2002) who stated that the photodegradation of most organic compounds is described by pseudo-first-order kinetics. Thus, the kinetics of the degradation of dye molecules can be represented as follows;

where k_1 is the first-order rate constant (min^{-1}), $[\text{MG}]_t$ and $[\text{MG}]_0$ are the concentrations of the dye molecules at time t and $t = 0$, respectively.

Table 1 shows the correlation values and rate constants obtained from the pseudo-first-order plot of the photodegradation of MG. It was observed that MG gave the highest correlation values in their pseudo-first-order plots, which agrees with the observation that the photodegradation of these dyes followed the pseudo-first-order kinetics. The pseudo-first-order rate constant, k' obtained was 0.05 for 10 ppm MG, 0.009 for 30 ppm MG and 0.001 for 50 ppm MG. This trend shows that the rate of degradation was highest for 10 ppm MG, followed by 30 ppm MG while 50 ppm MG gave the least photodegradation rate. This result corresponds with the degradation efficiency of the dyes as shown in fig. 7. R^2 values for dye degradation at different concentrations are given as, MG 10 ppm (0.974), 30 ppm (0.977) and 50 ppm (0.967). Since the photodegradation of these dye molecules follow the pseudo-first-order kinetics (as confirmed by their high R^2 values), it may be concluded that the rate of their degradation depends on only the concentration of the dye solution.

Impact of the presence of Cu(ii) ions on the photodegradation of mg

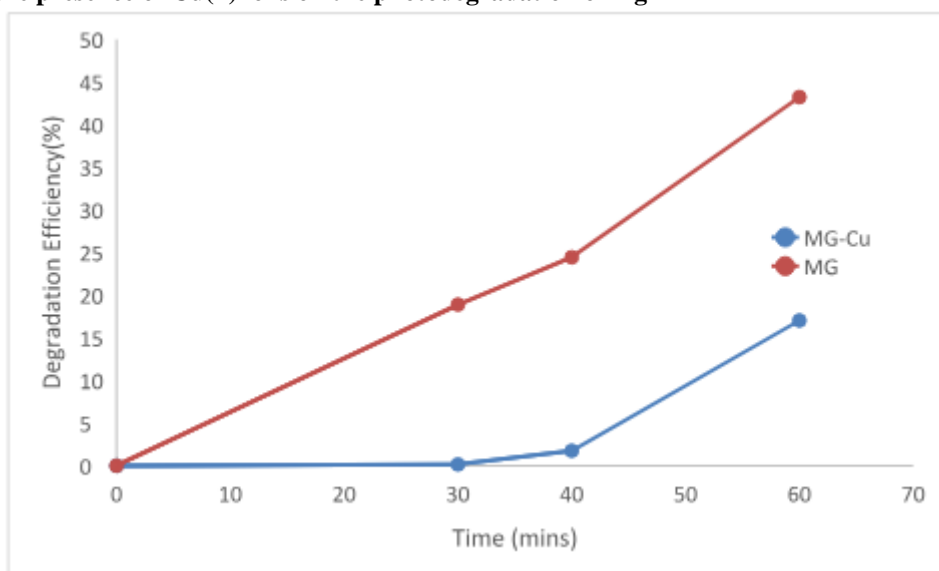


Fig. 11. Influence of the presence of Cu^{2+} ions on the Photodegradation Efficiency of MG (Reaction conditions: catalyst dose 4g/l, pH 7, 30 ppm MG, 200 ppm Cu^{2+} , 15W UV light, nano TiO_2 photocatalyst)

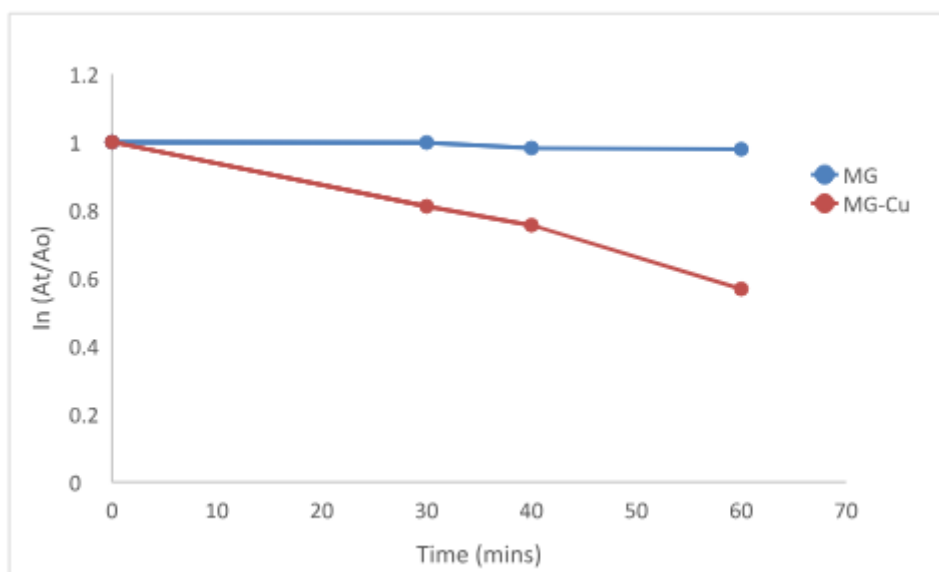


Fig. 12. Comparison of the Photodegradation kinetics of MG in the presence and absence of Cu^{2+} ions

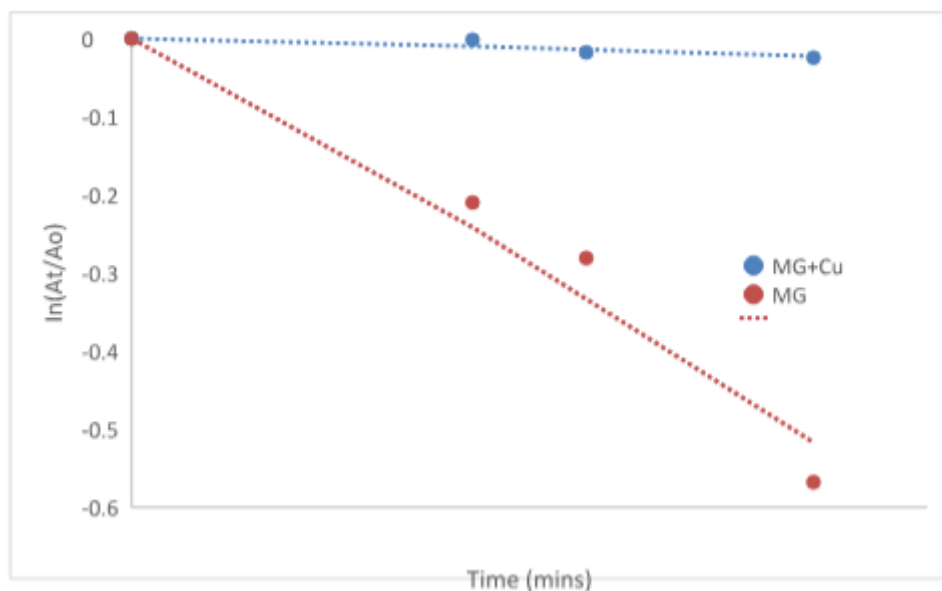


Fig. 13. Comparison of the pseudo-first-order kinetic of MG photodegradation in the presence and absence of Cu²⁺

The effect of Cu²⁺ ions on the photodegradation of MG is highlighted on fig. 11, 12 and 13. The aim of this investigation was to determine the effect of Cu²⁺ ions would on the photodegradation of MG. Longli, et al., 2013 had reported a synergistic effect between organic and inorganic contaminants during photodegradation while Chaudharya, et al., 2001 stated that in mixed wastewater streams, the presence of metal ions can retard the destruction of organic contaminants and also, the metal recovery efficiency is hindered by the presence of organic species. In this research, the presence of Cu²⁺ was found to inhibit the degradation of MG. After 60 minutes of photodegradation, the dye removal efficiency reduced from 43.23% (in the absence of Cu²⁺) to 2.408% in the presence of Cu²⁺ ions. Also, the photodegradation kinetics (fig. 12) and k₁ values (fig. 13) for MG degradation in the presence and absence of Cu²⁺ ions shows that the ions inhibited the rate of MG degradation. Chaudharya, et al., 2001 explained that the reduction in photodegradation of organic species in mixed wastewater was as a result of the formation of complexes between the organic species and metal ions in solution. Thus, the inhibitory effect of Cu²⁺ ions on the MG photodegradation may be due to the formation of an extensive Cu²⁺ - MG complex.

V. CONCLUSION

In conclusion, the photodegradation of the dye MG has been successfully achieved. It was found that initial concentration of dye, catalyst loading, pH and reaction time influenced the photodegradation process. Generally, it was observed that the photodegradation of MG followed the pseudo first-order-kinetics as confirmed by their high correlation, R² values. Also, low MG concentration gave a higher pseudo-first-order rate constant, k₁ than high MG concentration. This implies that degradation is improved in low MG concentration than in high MG concentration. This can be attributed to the low light penetration in concentrated MG solutions, thereby hindering photodegradation. Also, the presence of Cu²⁺ ions in the MG solution inhibited the degradation of MG.

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