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PHOTOCATALYTIC DEGRADATION OF FAST GREEN DYE IN AQUEOUS SOLUTION USING TITANIUM DIOXIDE AS PHOTOCATALYST

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ABSTRACT:

Research on the photocatalytic degradation of dyes and other organic pollutants become an interesting topic in the last two decades. Under UV irradiation, investigation and optimization of various experimental parameters were done for the photocatalytic degradation of fast green dye (FG) in the presence of titanium dioxide (TiO_2) suspension. Initial dye concentration, photocatalyst dosage, and solution pH were the study parameters. Results showed that the rate at which FG dye degraded was accelerated by increasing the TiO_2 dose. However, the degradation rate was adversely impacted by the rise in FG dye content from 3 to 9 mg/L. It was found that the highest percentage of color removal occurred when the pH of the medium was 6.5. FG was found to be degraded process reached equilibrium in 50 minutes using TiO_2 photocatalyst, proving that it is an effective catalyst for the process. Additionally, the kinetics of FG dye degradation was studied, and it was followed by the pseudo first-order kinetics.

KEYWORDS: Photodegradation, Photocatalyst, TiO_2, Fast Green, Kinetic

1. INTRODUCTION

Research on the photocatalytic degradation of dyes and other organic pollutants become an interesting topic since the latter part of the 20th century. Dye contaminants have been identified in wastewater emanating from diverse chemical industries, encompassing sectors such as paints, paper, dyes, textiles, and others. This revelation poses a significant threat to environmental cleanliness, as these pollutants have the potential to inflict harm upon ecosystems and disrupt aquatic life. Numerous studies have indicated that approximately 1–20% of global dye production stands inadvertently lost throughout the synthesis process, ultimately finding its way into wastewater (Zollinger, 2003; Haji & Mohammed, 2019). The presence of these dye contaminants in wastewater raises serious concerns due to their adverse effects on the environment. The discharge of wastewater containing dyes such as undiluted fast green emerges as a critical environmental concern due to both its dark color and inherent toxicity, thereby posing substantial risks to environmental well-being (Idrees *et al*., 2023; SALIH *et al*., 2023). Consequently, over the past two decades, extensive research has been conducted to devise strategies for the removal, degradation, or recovery of dyes present in water systems (Petkowicz *et al*., 2010).

The objective is the diversion of *hazardous* wastewater into nontoxic drinkable water. The advanced oxidation method (AOM) is one of the most appropriate for wastewater treatment of the various methods developed. Photograph Fenton gives environment-friendly processes for the degradation of numerous organic pollutants. This method is considered a helpful technology for wastewater treatment (Idrees *et al*., 2018).

In the fields of histology and cytology, the commonly employed fast green dye has been identified as a catalyst for tumor development in experimental animals and exhibited mutagenic effects in both animal and human subjects. Additionally, in its undiluted state, this dye has the potential to induce irritation in the eyes, skin, digestive tract, and respiratory system. Fast green, a heterocyclic dye, finds application in various industrial processes such as dyeing, printing, leather processing, and the production of fluorescent pigments. It is extensively utilized in the cosmetics and pharmaceutical industries as a colorant. The discharge of wastewater containing undiluted fast green emerges as a critical environmental concern due to both its dark color and inherent toxicity, thereby posing substantial risks to environmental well-being (Kumar *et al*., 2008; Salih & Naman, 2019).

Currently, synthetic dyes are widely used in industrial products such as plastic products, furniture, leather accessories, and clothing. However, around 12% of these colors are discarded during the dyeing process as waste, and about 20% of this waste is discarded in the environment (Rauf *et al*., 2011). A significant number of dyes were found in the wastewater that the industry released. Large molecules oxidize to produce smaller molecules like carbon dioxide, water, and other mineral byproducts during the dye degradation process (Kumar *et al*., 2017)The aim of the current research is to study the effects of various parameters on the photocatalytic degradation of fast green (FG) dye using TiO_2 as a photocatalyst in aqueous solution.

2. MATERIALS AND METHODS

Materials:

Fast green dye was obtained by purchase from Lab-pak Ltd, UK, and used as received without further treatment used to prepare solutions. Table 1, illustrates the characteristics of the FG dye. FG stock solution (1000 µg/ml) was prepared using deionized water, and it was protected and stored in a dark place

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for further use. Then, different working solutions were prepared with (3, 5, 7, and 9 µg/ml) by diluting the stock solution of the FG. Titanium dioxide (TiO_2) was purchased from ROTH, Germany, and used as a photocatalyst. Various molarities of acid (HCl) and alkali (NaOH) solution (they were purchased from Sigma-Aldrich, Germany) were used to adjust the pH value of solutions during the degradation process between 3 and 12. Water used in this research was distilled and deionized before use. An ultraviolet (UV) water sterilization lamp 220-240 v 50 / 6 Hz (UVC-215 TS 8W) was used as the light source.

Table 1: Characteristics of Fast Green dye

Chemial Name	disodium; 2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino] phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl]azaniumylidene] cyclohexa-2,5-dien-1-ylidene]methyl]-5hydroxybenzenesulfonate.
Chemicl Formula	$C_{37}H_{34}N_2Na_2O_{10}S_3$
Moleculr Mass	808.9 g/mol
Colour	Dark green powder or granules with a metallic luster
Λmax	628 nm
Melting point	290 ºC
log Kow	-3.22 (estimated)

3. EXPERIMENTAL PROCEDURES:

Different concentrations of fast green dye were prepared from the stock solution of (1000 µg/ml) and for each concentration, 500 mL was put in a reactor (600 mL volume of the reactor) inside of the dark box and exposed to the UV lamp as light sources, as illustrated in Figure 1. It is worth to mention that different weight of (TiO_2) has been used in this study, were (30, 50, and 70 mg) added to fast green dye as a photocatalyst. A syringe of 5 mL was used to collect samples over a period of time and transfer them to the visible spectrophotometer (Jenway, 6700), which was used to analyze the collected samples.

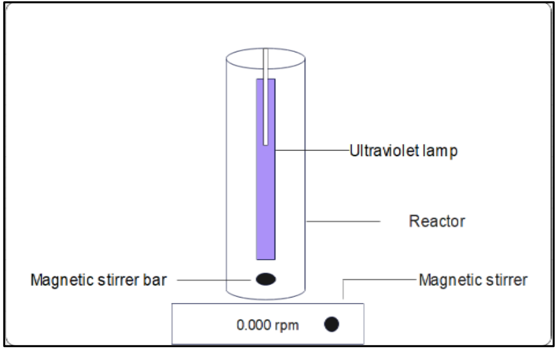

Figure 1: Photocatalytic system used in this study

4. RESULTS AND DISCUSSION

Effect of Photocatalyst Dose:

In a slurry photocatalytic process, the mass of the catalyst can significantly influence the degradation rate. This is because as much as the catalyst mass, results a higher in the number of active sites on the surface of photocatalyst, leading to the production of more $OH^{\bullet}$ and $O_2^{\bullet -}$ radicals. The investigation into the degradation of FG occurred in a semi-batch reactor situated within a chamber illuminated by a set of UV lamps. A volume of 500 mL of FG solution with constant concentration (4 mg/L) and pH (6.5) was loaded into a glass reactor with varying amounts of TiO_2 from 10 to 70 mg.

As shown in Figure 2, the rate constant increase proportionally to the catalyst concentration increase, the removal efficiency besides the concentration of FG is reduced with time. The optimum FG degradation was achieved, when 70 mg TiO_2 was used for 45 min of the reaction time. The removal efficiency of FG dye is unaffected by increasing the catalyst dosage. This is due to the increased photocatalyst quantity preventing light penetration (Aguedach *et al*., 2005; Idrees *et al*., 2021).

Effect of Initial Concentration and Kinetic Study:

The most significant factor liable for the photocatalytic process is the quantity of dye adsorbed on the photocatalyst surface (Rauf *et al*., 2011). A decrease in dye degradation is commonly observed with a fixed catalyst quantity and an increasing dye concentration. Figure 3, shows the data indicating the effect of the initial concentration of FG on the rate of photocatalytic degradation (3, 5, 7 and 9 mg/L of FG) using 30 mg of TiO_2. It is obvious that additional the concentration of FG dye decreased the rate of degradation, this phenomenon maybe accredited to secondary photo-chemical processes occurring throughout photocatalytic degradation. Additionally, the alteration is induced by the quenching process stemming from excimer formation, wherein certain inter-mediates absorb light and subsequently re-emit it as heat, thus failing to trigger semiconductor photocatalysts. Consequently, this leads to photons being unable to reach the surface of the photocatalys (Kumar *et al*., 2008; Idrees *et al*., 2023).

Another reason adverse effect of initial concertation may attribute to the fact that, photocatalyst surface is covered and blocked from radiation with some organic molecules. However, because fewer photons and hence fewer active species are available to reach the catalyst surface, the degradation rate is slowed. As a result, the light absorbed is ineffective in carrying out the degradation (Yang *et al*., 2008).

As FG concentration increased from 3 to 9 mg/L Figure 3, the removal percentage of FG at 50 min of reaction time declined from 98.15 % to 96.74 %, respectively. The results of this work accord with those of prior studies using ZnO as a photocatalyst for various dyes such as reactive orange 5, toluidine blue Dye (Benjelloun *et al*., 2021).

In order study the kinetics parameters of photo-catalytic degradation, different rate laws, has been employed. The accuracy of the kinetic order then can be evaluated through the correlation coefficient derived from curve fitting, particularly as R^2 closely approaches unity (Idrees *et al*., 2018; Molla-Babaker & Idreesb, 2020). The rate constant, k', was found to grow linearly when the starting FG concentration rose. The photodegradation of FG dye on the active sides of TiO_2 catalyst follows a pseudo first order kinetic equation, which is written as

$$Ln\left({}^{C}/_{C_o}\right) = -k't \qquad \text{eq (1)}$$

Where k' is the rate constant and Co and C are the dye concentrations at t = 0 as well as t = t. Figure 4 reveals typical first order kinetics plot of FG dye discoloration reaction, a plot ln (Co/C) versus time that gives a straight line slope, which is equal to the first-order rate constant and regression coefficient R^2

shown in table 2 the kinetic parameters of photocatalytic FG degradation by TiO_2 in an aqueous solution at varied initial FG concentrations.

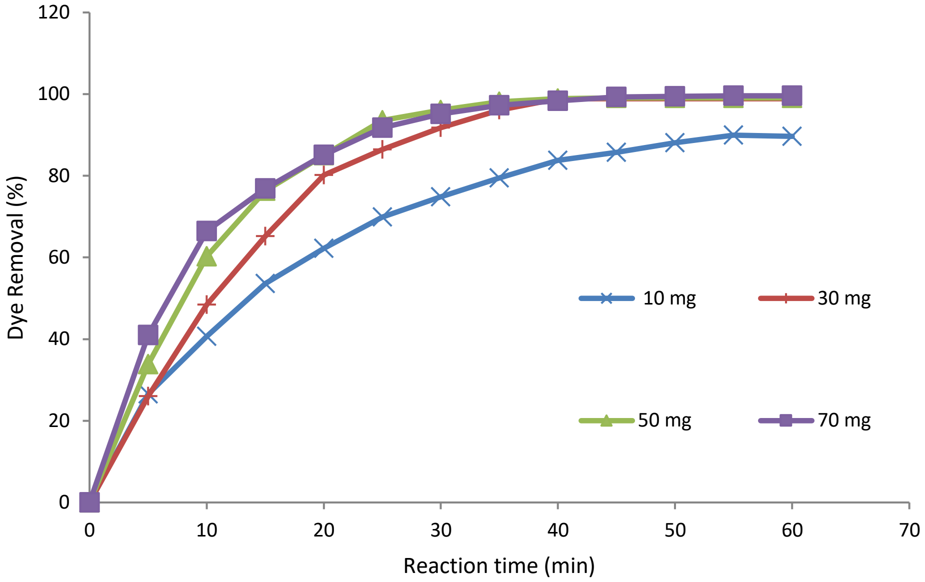

Figure 2: Effect of Photocatalyst Dose 10 mg,30mg,50 mg and 70 mg ([FG]o= 7 mg/L, Volume = 500 mL, pH = 6.5)

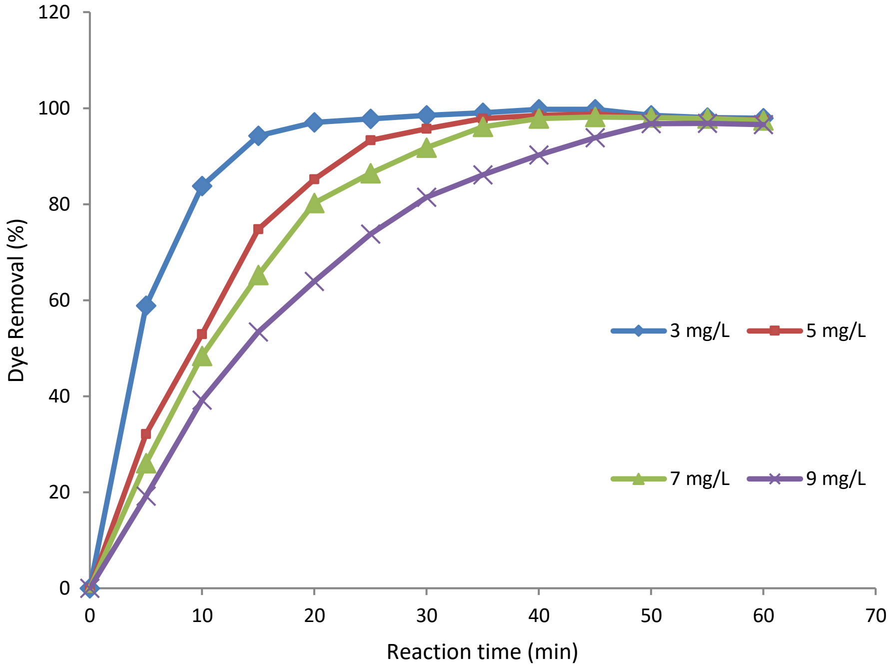

Figure 3: Effect of Dye concentration responding to removal % (TiO_2= 30 mg/L, Volume = 500 mL, pH = 6.5)

Table 2: Kinetic parameters of photocatalytic degradation of FG dye as a function of initial FG dye concentration

FG concentration (mg/L)	k’	R^2	Dye Removal %
3	0.0839	0.941	99.98
5	0.1409	0.953	99.82
7	0.2141	0.945	97.24

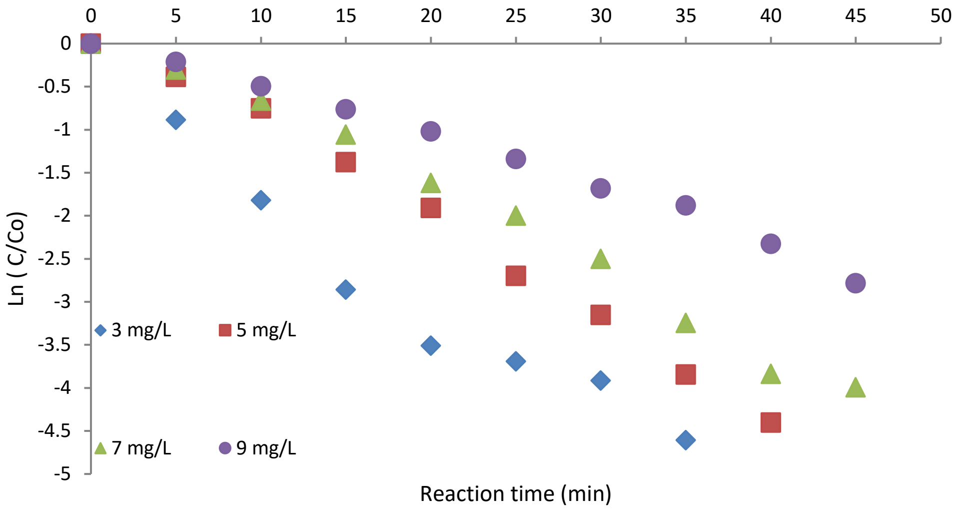

Figure 4: Pseudo first-order kinetics (1^{st}) of FG dye photocatalytic degradation as a function of initial FG concentration (TiO_2= 30 mg, Volume = 500 mL, pH = 6.5)

Effect of Ph:

The pH at which a surface exhibits zero net charge (pH ZPC) serves as a convenient indicator of its propensity to acquire either a positive or negative charge in relation to pH levels. The pHZPC is essential for identifying the both the sign and magnitude of the net charge by the photocatalyst surface, in processes like adsorption and photocatalytic degradation. Many semiconductor oxides, being amphoteric, can either associate with protons (as in Equation 2) or dissociate them (as in Equation 3) (Idrees *et al.*, 2023; Idrees *et al.*, 2018).

$$\text{photocatalyst} - \text{OH} + \text{H}^{+} \rightarrow \text{photocatalyst} + \text{OH}_2^{+} \quad \text{pH} < \text{pH}_{\text{ZPC}} \qquad \text{eq (2)}$$

$$\text{photocatalyst} - \text{OH} + \text{OH}^{-} \rightarrow \text{photocatalystO}^{-} + \text{H}_2\text{O} \quad \text{pH} > \text{pH}_{\text{ZPC}} \qquad \text{eq (3)}$$

The pH of the solution also influences the process of photodegradation efficiency. As the pH of a medium changes, it leads to a change in the charge on the surface of TiO2 particles. Consequently, the dye adsorption on the catalyst surface changes, causing the degradation rate to shift. To examine the influence of pH on photocatalytic degradation of FG dye, a number of experiments were achieved at various pH levels within the range of 3-11, as demonstrated in the Figure 5, pH of the medium has a significant role in determining the removal of FG dye in the presence of TiO_2. The results showed an initial increase in the degradation values from an acidic medium up to approximately neutral medium, followed by a decrease in the degradation rate. It was found that at pH 6.5 the colored dyes almost removed while increasing the acidity of the medium the percentage of removal decreased at pH 3 with almost 80.2 %.

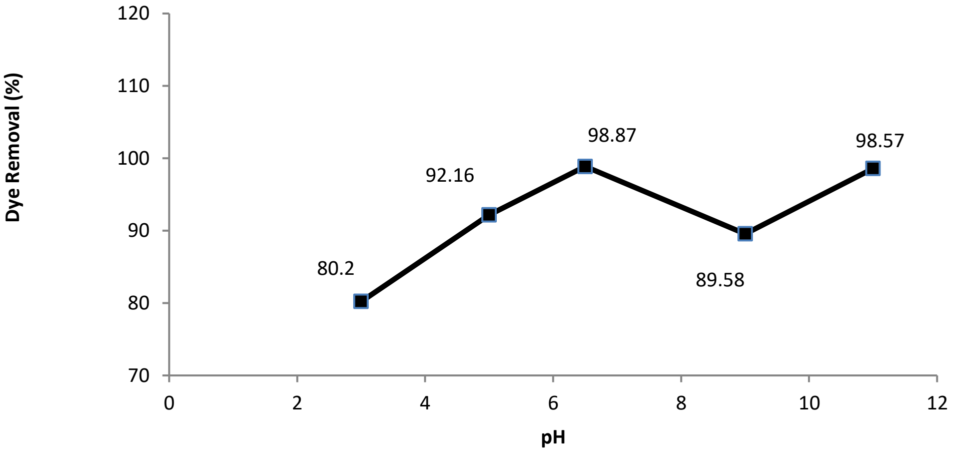

Figure 5: Effect of pH on the degradation process ([FG]o= 7 mg/L, TiO_2= 30 mg/L, Volume = 500 mL)

CONCLUSIONS

Photocatalytic degradation of FG dye in the presence of TiO_2 as a photocatalyst was destroyed in an aqueous solution using UV/TiO_2 light. The degradation of FG was studied using a variety of operating conditions, including FG concentration, TiO_2 dosage, and solution pH. With a starting FG concentration of 3 mg/L, the most effective improvements in FG degradation were observed. It was also found that increasing the amount of TiO_2 improved the FG removal reaction rate. In the lowest acidic medium, the removal efficiency of FG was favorable and reached its maximum value. The degradation of FG at different initial dye concentrations follows the pseudo first-order kinetics.

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Ethical Statment

Ethical approval was not required for this research.

Author Contributions:

Conceptualization, A.A.H. and R.A.R.; methodology, A.A.H. and I.S.K.; software, A.A.H.; validation, A.A.H. and I.S.K.; formal analysis, A.A.H. and R.A.R.; investigation, A.A.H.; resources, R.A.R.; data curation, I.S.K.; writing—original draft preparation, R.A.R.; writing—review and editing, A.A.H. and R.A.R.; visualization, A.A.H.; supervision, A.A.H.; All authors have read and agreed to the published version of the manuscript.

Declaration:

We confirm that all authors of the manuscript have no conflict of interest to declare.

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