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UV-Induced Photocatalytic Degradation of Organic Pollutants Using TiO_2 Nanoparticles

Dipak K. Chandre[1*], **Ganesh B. Shinde**[2], **Sushant S. Kurhe**[3].
[1,3]Assistant Professor, Department of Chemical Engineering, Sir Visvesvaraya Institute of Technology, Nashik, Maharashtra, India.
[2]Associate Professor, Department of Chemical Engineering, Sir Visvesvaraya Institute of Technology, Nashik, Maharashtra, India.
***Corresponding author:** Dr. Dipak K. Chandre; Email: dipakchandre@gmail.com

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Abstract
The present study investigates the photocatalytic degradation of metamitron, a commonly used herbicide, under UV irradiation using titanium dioxide (TiO_2) as the photocatalyst. TiO_2 nanoparticles were synthesized via the hydrolysis method employing dilute sulfuric acid as an oxidizing agent and ammonia solution for precipitation. The synthesized catalyst was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques to confirm its structural and morphological properties. Photocatalytic experiments were conducted under UV light to evaluate the degradation efficiency of metamitron. The degradation kinetics were found to follow first-order reaction behavior. The extent of degradation was quantitatively monitored using a UV-Visible spectrophotometer. Additionally, the influence of various operational parameters such as solution pH, initial metamitron concentration, and catalyst loading was systematically examined to determine the optimal conditions for maximum degradation efficiency.
***Key words**: Photocatalysis, Titanium Dioxide, UV Irradiation, Organic Pollutants, Wastewater Treatment*

INTRODUCTION

Over the past few decades, contamination of drinking water by organic compounds has become a growing environmental concern. These pollutants primarily originate from agricultural runoffs, industrial effluents, and accidental chemical spills. In recent years, increasing attention has been directed towards environmental protection, particularly with regard to the management of hazardous wastes and industrial discharges [1–3]. A significant proportion of these organic contaminants are non-biodegradable, allowing them to persist in aquatic environments for extended periods. As a result, they pose serious risks to both aquatic ecosystems and mammalian health [1, 4, 5]. Pesticides have become an integral component of modern agriculture and industrial practices. These chemical compounds are primarily used to inhibit, eliminate, or suppress the growth of various pests. Pesticides are broadly classified into categories such as insecticides, herbicides, fungicides, and bactericides. A significant proportion of industrial and agricultural wastewater originates from pesticide manufacturing and usage, often containing toxic and non-biodegradable substances that are resistant to conventional treatment methods. Inadequate waste management practices result in the discharge of such contaminated water into major water bodies, eventually allowing these pollutants to enter the human food chain. Consequently, human exposure to pesticides poses serious and long-term health risks [5–7]. Among various pesticide compounds, some are structurally based on 4-amino-1,2,4-triazin-5(4H)-one. Members of this chemical class, including widely used herbicides such as metribuzin and metamitron, are known for their chemical stability and persistence in the environment. These compounds can slowly migrate through the soil, leading to long-term contamination of underground drinking water sources [2].Given their environmental persistence and toxicity, there is an urgent need to develop effective treatment methods for the removal of such harmful pesticide residues from wastewater before it is discharged [6]. Numerous techniques have been employed for wastewater treatment, including coagulation, filtration, biological treatment, ozonation, and advanced oxidation processes (AOPs) [8]. In recent years, AOPs have gained significant attention as promising alternatives or complements to conventional treatment technologies for the degradation of toxic organic pollutants. AOPs involve the generation of highly reactive hydroxyl radicals (•OH) through the use of strong oxidants, ultraviolet (UV) irradiation, and various catalysts. These hydroxyl radicals possess a high oxidation potential (2.8 V) and are capable of breaking down complex organic molecules into simpler end-products such as carbon dioxide, inorganic ions, and water. Extensive research has demonstrated the effectiveness of AOPs in degrading a wide range of organic contaminants, including pesticides [6, 7, 9]. Common AOP techniques include hydrogen peroxide (H_2O_2) treatment, Fenton and photo-Fenton processes, and photocatalysis. In recent years, significant research has been devoted to the degradation of organic pollutants using advanced oxidation processes (AOPs). Among these, photocatalysis has emerged as an effective method for the removal of persistent organic compounds from aqueous systems. Malato et al. [7] investigated the photocatalytic degradation of water-soluble pesticides such as diuron, imidacloprid, formetanate, and methomyl using solar UV light via both the photo-Fenton process and TiO_2 catalysis. Their findings indicated that the photo-Fenton process was more efficient in achieving both degradation and mineralization of the target compounds compared to TiO_2. Konstantinou et al. [10] studied the light-induced degradation of herbicides molinate and propanil in aqueous suspensions of TiO_2 under simulated solar irradiation, reporting complete degradation of the herbicides in less than one hour. Similarly, Gora et al. [11] explored the degradation of herbicides such as simazine, propazine, and isoproturon over irradiated TiO_2 suspensions in both single and multicomponent systems. Their results demonstrated that the degradation followed a competitive Langmuir–Hinshelwood (L–H) mechanism, involving surface or near-surface reactions, as evidenced by differences in binding constants under dark adsorption versus photocatalytic conditions.

In another comparative study, Abramović et al. [1] evaluated the photocatalytic degradation of picloram using two types of TiO_2—Wackherr and Degussa P25. The results revealed that Wackherr TiO_2 exhibited superior degradation performance at higher catalyst loadings and substrate concentrations compared to P25 TiO_2.Various semiconductors have been extensively studied as photocatalysts for the oxidative degradation of organic pollutants. Among them, titanium dioxide (TiO_2) has emerged as the most widely used photocatalyst due to its numerous advantages, including non-toxicity, low cost, chemical stability, and resistance to photo corrosion [7, 12]. The photocatalytic activity of TiO_2, particularly at its surface, has attracted significant interest because of its promising applications in environmental remediation. In addition to its photocatalytic properties, TiO_2 exhibits superhydrophilicity and strong oxidative potential, making it suitable for use as an antibacterial agent as well [6, 12, 13]. TiO_2 displays high reactivity and stability under ultraviolet (UV) light with wavelengths shorter than 387 nm, corresponding to the band gap energy of approximately 3.3 eV in its anatase crystalline phase. Upon UV illumination, electron–hole pairs are generated as electrons are excited to the conduction band, leaving behind holes in the valence band. A portion of these charge carriers can migrate to the catalyst surface before recombination, where they participate in redox reactions. Photogenerated holes can oxidize adsorbed organic molecules if their oxidation potentials are less positive than the valence band edge. Numerous studies have shown that oxidation typically proceeds through the formation of hydroxyl and other oxygen-containing radicals, which result from the interaction of holes with water or hydroxyl groups adsorbed on the TiO_2 surface. These radicals are highly reactive and capable of decomposing a broad spectrum of organic contaminants [9]. Titanium dioxide (TiO_2) can be synthesized using a variety of techniques, including sol–gel, chemical vapor deposition, hydrothermal, and hydrolysis methods [14]. TiO_2 exists in three primary crystalline forms: rutile, anatase, and brookite [15]. Among these, the anatase phase has demonstrated superior photocatalytic activity due to its favorable electronic and structural properties [16]. Several studies have focused on the synthesis of anatase TiO_2 nanoparticles with enhanced photocatalytic performance. For instance, Kinga et al. [17] successfully synthesized crystalline TiO_2 nanoparticles via a continuous hydrothermal method, achieving particle sizes in the range of 7–13 nm. In another study, Chi-Hwan Han et al. [18] developed nanocrystalline TiO_2 using a sol–gel combustion hybrid method, employing acetylene black as a fuel. In the present work, TiO_2 photocatalyst was synthesized via the precipitation method. The prepared catalyst was characterized, and its photocatalytic performance was evaluated in comparison with commercial TiO_2 (Degussa P25) for the degradation of the herbicide metamitron under UV irradiation. Additionally, the influence of various process parameters was investigated to determine the optimal conditions for achieving maximum degradation efficiency.

Experimental Procedure for TiO_2 synthesis:

Materials:

Titanium tetrachloride ($TiCl_4$), sulfuric acid (H_2SO_4, 98%), and ammonium hydroxide (NH_4OH) were procured from Thomas Baker, Mumbai, India. Distilled water was used throughout the synthesis process. All reactions were carried out using a magnetic stirrer equipped with a heating plate. An ice bath was employed to maintain low reaction temperatures during the initial stages of synthesis.

Synthesis of TiO_2 Nanoparticles:

TiO_2 nanoparticles were synthesized via a hydrolysis-precipitation method. Initially, 15 mL of 10% dilute sulfuric acid solution was prepared using distilled water and cooled in an ice bath to maintain a temperature of 0 °C under continuous magnetic stirring. Once the temperature was stabilized, 1 mL of $TiCl_4$ was added dropwise to the acid solution. The addition was performed cautiously due to the evolution of fumes, primarily hydrogen chloride (HCl). Following the complete addition of $TiCl_4$, the mixture was stirred continuously for one hour. Subsequently, the temperature of the solution gradually raised to 65 °C and maintained for a short duration before allowing it to cool to room temperature naturally. Once cooled, an ammonium hydroxide solution was added dropwise until the pH of the solution reached 7, leading to the formation of a white precipitate. The precipitate was allowed to settle overnight. The resulting TiO_2 nanocrystals were then washed repeatedly with distilled water and acetone to remove residual impurities. The washed product was dried in an oven at 60 °C for 12 hours. Finally, the dried catalyst was calcined in a muffle furnace at 400 °C for 2 hours to enhance crystallinity.

Characterization of TiO_2 Catalyst

The synthesized TiO_2 nanoparticles were characterized to determine their structural and morphological properties. X-ray diffraction (XRD) analysis was carried out to identify the crystalline phase and estimate the crystallite size of the catalyst. Scanning electron microscopy (SEM) was employed to observe the surface morphology and particle size distribution. These analyses confirmed the formation of TiO_2 in the desired anatase phase with nano-scale dimensions.

Photocatalytic Degradation Experiments

Materials

Metamitron, the target herbicidal compound, was obtained as a free sample from Gharda Chemicals, Mumbai, India. The pH of the reaction medium was adjusted using dilute sulfuric acid (H_2SO_4) for acidic conditions and sodium hydroxide (NaOH) for basic conditions. All solutions were prepared using distilled water.

Photocatalytic Experiment Setup

Photocatalytic degradation experiments were conducted in a cylindrical quartz glass reactor with dimensions of 27 cm height × 7 cm internal diameter and a total volume capacity of 250 mL. The reactor was equipped with a water-cooling jacket to maintain a consistent reaction temperature between 20–25 °C during irradiation. UV light served as the irradiation source, and continuous stirring was provided by a magnetic stirrer located at the base of the reactor to ensure uniform suspension of the photocatalyst. A 250 mL aliquot of metamitron solution was used for each experiment. The solution pH was adjusted to the desired value using H_2SO_4 or NaOH and was monitored using a calibrated digital pH meter. The catalyst (synthesized TiO_2 or commercial Degussa P25) was added to the solution, and the mixture was stirred in the dark for 30 minutes prior to irradiation to establish adsorption–desorption equilibrium.

Analytical Method

At specified time intervals during UV irradiation, 5 mL samples were withdrawn from the reactor. These samples were centrifuged at 4000 rpm for 5 minutes using a Remi RC 800 centrifuge to separate the TiO_2 catalyst. The clear supernatant was collected and analyzed using a PerkinElmer UV–Visible spectrophotometer. The degradation of metamitron was monitored by measuring the absorbance at the maximum absorption wavelength (λ_{max} = 301 nm).

Characterization of TiO_2 Photocatalyst:

The phase composition and crystalline structure of the synthesized TiO_2 were determined using X-ray diffraction (XRD) analysis. The XRD pattern of the prepared TiO_2 catalyst is presented in Figure 1. Characteristic diffraction peaks corresponding to the anatase phase of TiO_2 were clearly observed at 2θ

values of approximately 25.38° (101), 37.82° (004), 48.18° (200), 54.4° (211), 62.92° (204), 69.92° (220), and 74.9° (215). These peak positions are in good agreement with standard JCPDS data for anatase TiO_2, confirming the successful synthesis of the desired crystalline phase. The surface morphology and particle distribution of the synthesized catalyst were examined using scanning electron microscopy (SEM). The SEM micrograph, shown in Figure 2, reveals the cross-sectional morphology of the TiO_2 nanoparticles, indicating relatively uniform particle size and porous surface features. These structural characteristics are favorable for enhanced photocatalytic activity due to increased surface area and active sites.

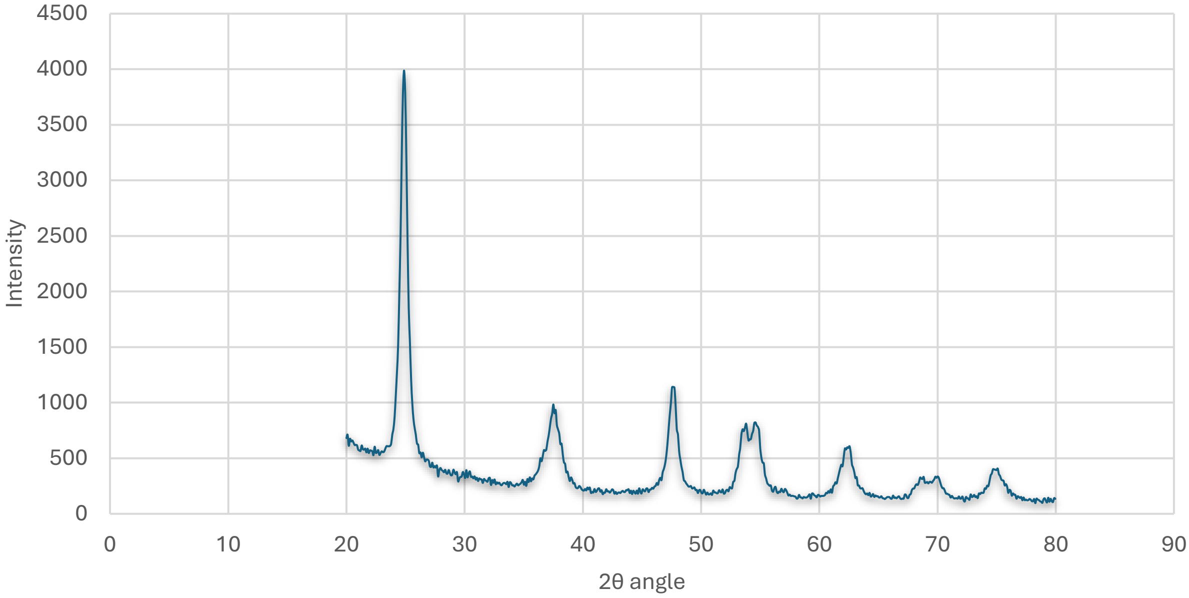

Figure-1: XRD pattern of anatase TiO_2 calcined at 400^0C.

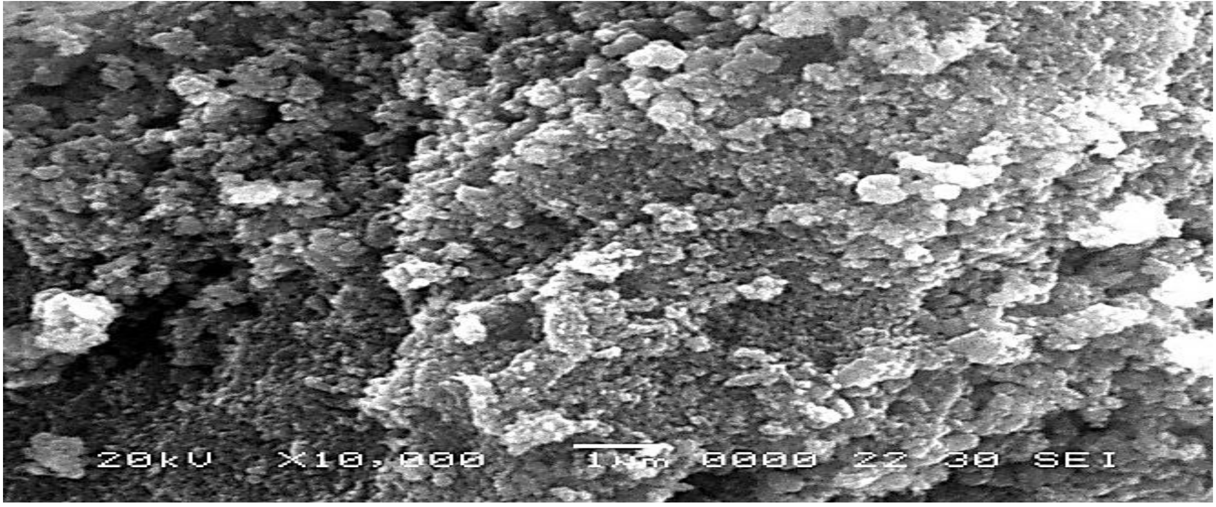

Figure-2: SEM image of TiO_2 calcined at 400^0C

RESULTS AND DISCUSSIONS

The photocatalytic activity of TiO_2 in studied in the degradation of herbicide compound Metamitron in UV light.

1. Effects of TiO_2 and comparison with other processes

The photocatalytic activity of prepared catalyst is compared to the commercial catalyst Degussa P25 under UV light and various other conditions as shown in Figure-3. It was observed that there was practically no degradation in the absence of UV light either with or without TiO_2. The degradation rate of our synthesized TiO_2 is same as the commercial catalyst Degussa P25. The Table-1 summarizes the values of k (rate constant) and R^2 (linear coefficient value) for the various processes and the percentage of degradation in each process.

It is seen from Table-1 that the degradation is very less in the absence of UV light with or without TiO_2. In contrast, significant degradation of metamitron is observed in the presence of UV light and it was even more enhanced when carried out with the addition of catalyst. The degradation rate was more or less similar with our synthesized catalyst and commercial catalyst Degussa P25. The initial degradation, higher in synthesized catalyst than Degussa P25 is noteworthy as its surface area is larger than the commercial catalyst.

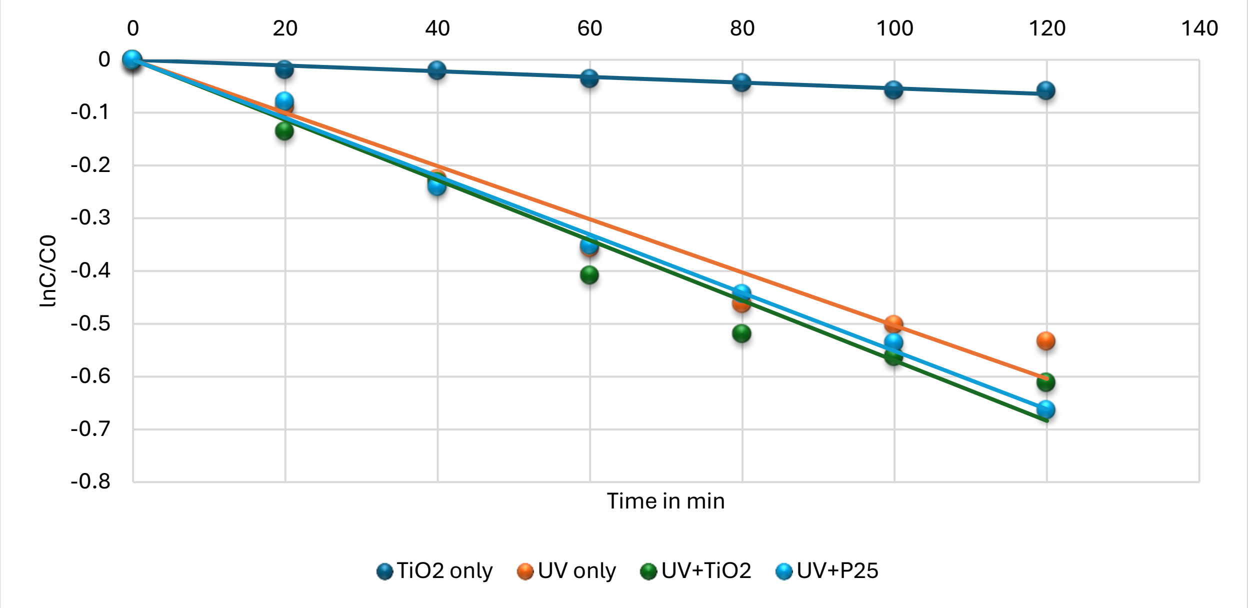

Figure-3: Rate of degradation of metamitron for various processes.

Table-1: Kinetics of degradation rate of metamitron for different conditions.

Sr. No.	**Process of degradation**	**Value of rate constant k min^{-1}**	**R^2**	**% Degradation**
1	TiO_2 only	0.0001	0.955	5.75
2	UV only	0.005	0.953	40.37
3	TiO_2 + UV	0.005	0.956	45.7
4	P25 + UV	0.005	0.994	47.0

Effect of operational parameters:

The photocatalytic process generally depends on the generation and reaction of highly reactive species i.e. the OH• radical. A lot of factors affect the efficiency of the process. We studied the effect of initial concentration of metamitron, catalyst loading and pH variation.

1. Effect of initial concentration of metamitron

The effect of initial concentration of metamitron was studied in the range from 10 ppm to 40 ppm on the rate of degradation. The rate of degradation is depicted in Figure-4 where the pH of the solution and the catalyst concentration were kept constant while the concentration of metamitron was changed. Table-2 shows the kinetic study for the degradation rate at different concentrations of metamitron. It was observed that the degradation was achieved maximum at 25 ppm. The parameters of pH and catalyst concentration were maintained at 3 and 100 mg/L respectively.Under the relevant experimental conditions, the reactions followed a first order kinetics (as the linear correlation coefficients were in the range 0.956- 0.989.

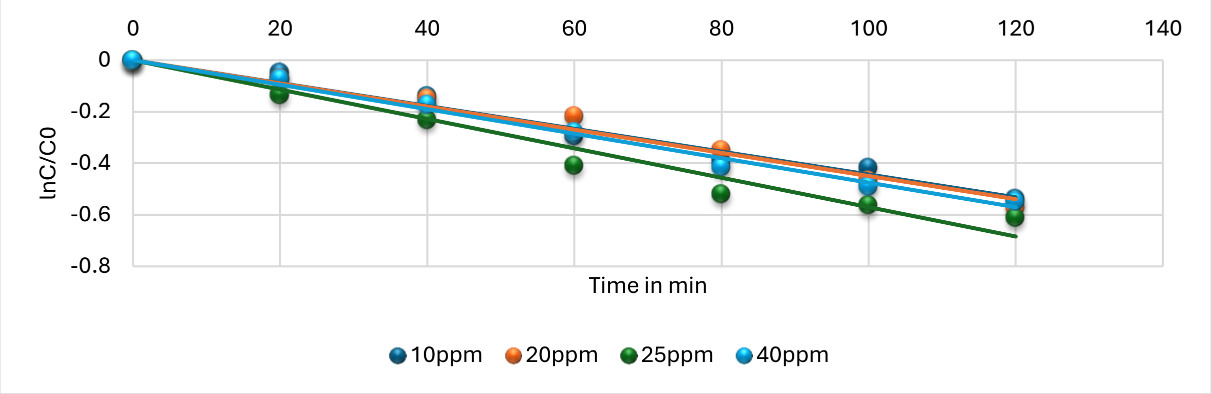

Figure-4: The effect of change in initial concentration of metamitron on its degradation. The pH is maintained at 3 and the catalyst concentration is 100mg/L.

Table-2: Kinetics study for the effect of change in initial concentration of metamitron with other parameters at optimal conditions.

Sr. No.	Initial concentration in ppm	Value of rate constant k (min^{-1})	R^2	% Degradation
1	10	0.004	0.975	41.48
2	20	0.004	0.979	43.51
3	25	0.005	0.956	45.70
4	40	0.004	0.989	42.23

2. Effect of catalyst concentration:

The loading range of catalyst was varied from 50mg/L to 300mg/L to examine the effect of change in concentration of catalyst on the degradation of metamitron as shown in Figure-5.

The information summarized in Table-3 implies that with increase in the concentration of catalyst the rate of degradation initially increased but after a critical point, the degradation began to decrease, which was the optimal concentration of TiO_2 that is needed for maximum efficiency. With initially increase in the amount of catalyst, the degradation increased due to the increase in available surface (active sites) for reaction. But with further increase in the catalyst amount the surface of the catalyst gets clogged due to agglomeration, hence causing a decrease in the number of active sites and consequently the rate of degradation. Dusan Mijin et al carried out the degradation of metamitron using suspensions of ZnO and observed that complete disappearance of metamitron was observed using high catalyst loading (about 2g/L) in about 4 hours. (2)

The experimental results showed that the procedure follows a first order kinetics as the linear correlation coefficient is in the range 0.943- 0.965.

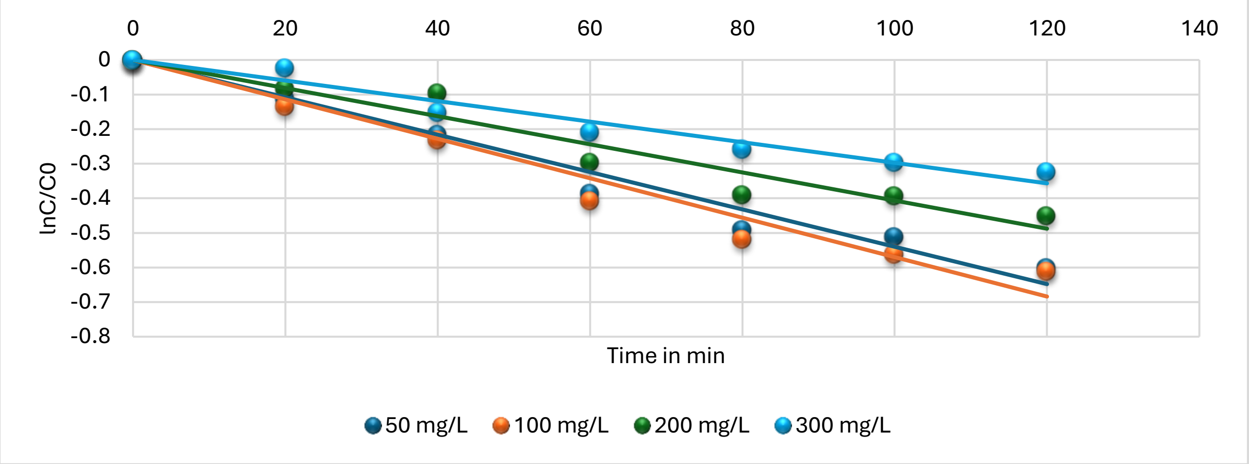

Figure-5: Effect of catalyst loading on the rate of degradation of metamitron at pH 3 maintained throughout with 25ppm initial concentration of metamitron solution.

Table 3: Effect of change in catalyst loading on the kinetics of rate of degradation of metamitron

Sr No.	Catalyst loading mg/L	Value of rate constant k min^{-1}	R^2	% Degradation
1	50	0.005	0.965	44.37
2	100	0.005	0.956	45.70
3	200	0.004	0.943	36.25
4	300	0.003	0.951	25.68

3. Effect of pH:

It has been observed that the pH has an influence on the photodegradation of certain organic compounds. As shown in Figure-6, the pH values 3, 4, 7 and natural were studied to find the optimum pH for the higher efficiency of degradation of metamitron with catalyst concentration of 100mg/L. The optimal value of pH is obtained at 3. Kinga A. Malinger et al synthesized anatase nanoparticle TiO_2 of controlled size in the range 7-13nm by precipitation of $TiCl_4$ using NaOH at pH 3 [17]. The pH was adjusted prior to the photocatalytic reaction by addition of H_2SO_4 and NaOH for acidic and basic pH respectively. It can be seen from Table-4 that the reactions followed first order kinetics where the linear coefficient value ranges from 0.930- 0.986. The pH of the solution when on acidic side showed higher degradation and the rate of degradation decreased with increase in pH and was negligible on the basic side. With direct photolysis the degradation was found higher on the basic side. In the neutral form the adsorption on the surface was not affected hence there was a slight increase in the rate of degradation at natural pH.

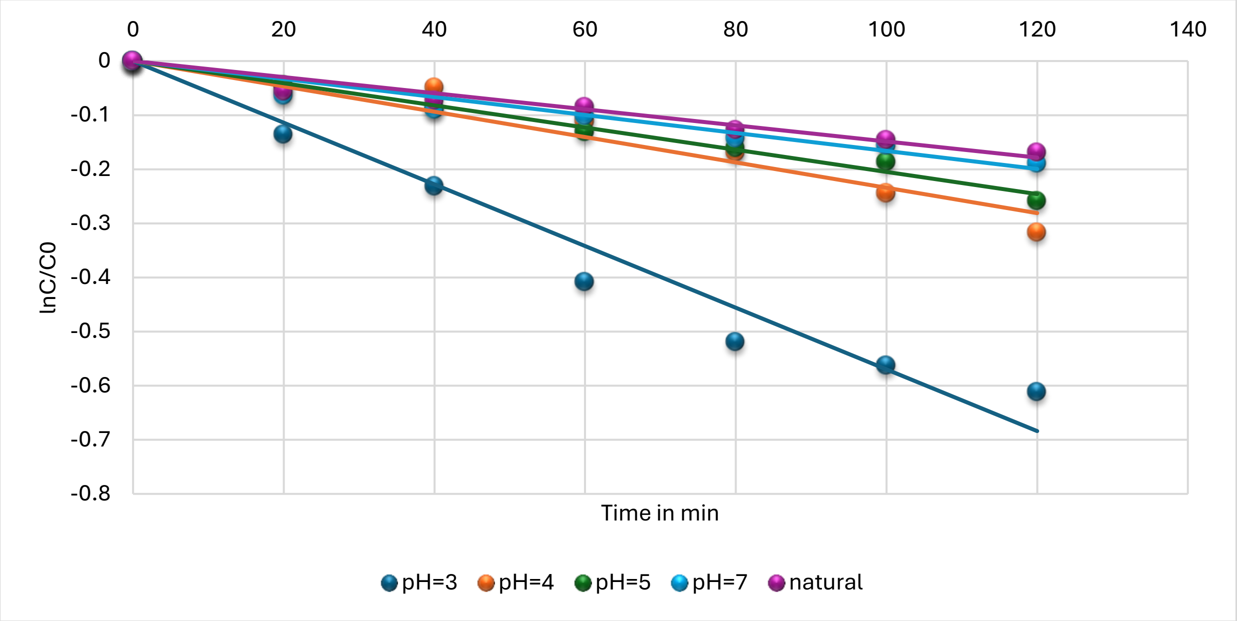

Figure 6: Effect of pH on the degradation of metamitron with catalyst loading of 100mg/L and initial concentration of metamitron of 25ppm.

Table 4: Kinetic study of the degradation of metamitron for the effect of change in pH (with initial concentration of metamitron 25ppm and the catalyst concentration at 100mg/L).

Sr. No.	pH	Value of rate constant k, min^{-1}	R^2	% Degradation
1	3	0.005	0.956	45.7
2	4	0.002	0.942	27.3
3	5	0.002	0.986	22.71

4	7	0.001	0.930	17.13
5	natural	0.001	0.949	25.56

CONCLUSION

The present study investigated the photocatalytic degradation of the herbicide metamitron using TiO_2 as a catalyst under UV irradiation. The performance of the synthesized TiO_2 catalyst was found to be comparable to that of the commercial Degussa P25 catalyst, demonstrating substantial degradation efficiency. Experimental results confirmed that photocatalysis is a viable technique for the removal of metamitron from aqueous solutions. Parametric studies revealed that the degradation rate is significantly influenced by operational conditions such as the initial concentration of metamitron, catalyst loading, and solution pH. The optimal conditions for maximum degradation were determined to be an initial metamitron concentration of approximately 25 ppm, a catalyst dosage of 100 mg/L, and an acidic pH of 3. These findings highlight the potential of TiO_2-based photocatalysis as an effective method for treating pesticide-contaminated water.

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