# Photocatalytic Degradation of Acid Orange 7 Dye on $TiO_2$ -Coated Layers Produced by Anatase Paste Calcination in A Batch-Mode Photoreactor: Role of Calcination Temperature

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## Abstract

*Dyes are extensively used in the textile industry, and a considerable amount of water is consumed during the dyeing and finishing operations. These wastewaters are discharged in rivers or public sewage treatment plants and are highly coloured and contaminated. This creates a major environmental problem primarily due to substantial amounts of unfixed dyes released in wastewater. The dyes are characterized by low biodegradability, which makes them a source of pollution. The study sought to evaluate the effect of calcination temperature of $TiO_2$ anatase catalyst on the rate of Acid Orange 7 dye photocatalytic degradation, and determine the maximum absorption wavelength. ($\lambda_{max}$ ) for dye Acid Orange 7 and quantify the absorbance of five dye Acid Orange 7 solutions while calibrating the UV-Vis spectrophotometer and determining dye molar extinction coefficient (ε). The photocatalytic degradation of Acid Orange 7 azo dye c = ($1\times10^{-4}$ mol.$L^{-1}$) was used to investigate the efficiency of using $TiO_2$ anatase paste photocatalyst. Whereby, the $TiO_2$ anatase paste was immobilised on degreased microscopic glass (75mm×25mm), from an aqueous phase c = (10 g.$L^{-1}$) to cover a geometrical area of (8.75 $cm^2$). The coated layers were calcined at temperature values of 300°C, 400°C, 600°C, 700°C, 800°C, and 900°C in a muffle furnace and used in a four-hole photocatalytic reactor under UV light irradiation. As a source of UV light, two Osram Eversun fluorescent tubes emitting light of wavelength between 320 nm and 400 nm ( maximum λ= 355 nm) were used. A UV-Vis spectrophotometer CECIL 2021 was used to monitor changes in dye concentrations and determine the rate of photocatalytic degradation. The effect of calcination temperature on the efficiency of $TiO_2$ anatase paste catalyst for the removal of dyes was also studied. The results showed that Acid Orange 7 dye was effectively photodegraded using $TiO_2$ anatase paste under UV light irradiation. Calcination temperature influenced the resulting $TiO_2$ anatase paste photocatalytic activity, an increase in calcination temperature in the range 300°C-600°C resulted to a decrease of the dye i.e. 43.5%, in the rate of photocatalytic degradation. At higher calcination temperatures, i.e., 700-900°C, there is a significant*

*increase, i.e., 51.4%, in the rate of photocatalytic degradation. The results show the optimum calcination temperature for $TiO_2$ anatase paste to be used for Acid Orange 7-dye degradation is 900°C and 30 minutes calcination time. The current study concludes effective removal of dye Acid Orange 7 from aqueous systems using $TiO_2$ anatase paste under UV light irradiation in a batch mode photocatalytic reactor.*

**Keywords:** Dye Acid Orange 7, Photocatalytic Degradation, $TiO_2$ Anatase Paste, Calcination Temperature, Photocatalytic Reactor

## Introduction

### Advanced Oxidation Processes (AOPs)

The photocatalytic degradation mechanism is dependent on ultraviolet light (UV), in the form of a photon (hv), with energy equal to or higher than the band gap energy (E ), falling on the surface of a powder semiconductor catalyst exciting electrons from the valence band to the conduction band[1&2]. This leads to the generation of electron/hole (e /h ) pairs with free electrons in the empty conduction band, leaving an electron vacancy/hole in the valence band [3&4]. Under UV light illumination and an ideal semiconductor photocatalyst, electron/hole pairs with free electrons are generated in the unfilled conduction band, leaving positively charged holes (h+) in the valence band [4]. The formation of these holes in the valence allows adsorbed water to be oxidised to strong (OH) radicals, whose strong oxidative species (2.8 V vs. SHE) oxidise a majority of organic compounds [5]. The organic intermediates formed are oxidized by O2 or (OH) radicals and mineralized to CO2 and H2O as the final products [6]. Hydroxyl radicals (OH) are strong oxidizing species that react rapidly with most electron-rich sites of organic contaminants [7]. These electron-hole pairs initiate a series of chain reactions that mineralize organic pollutants to carbon dioxide and water [8]. The reactions involve cleaving of the conjugated carbon–carbon double bonds found in polyphenols by (•OH) radicals, causing decolourization of coloured dye wastewater [9&10]. This technique prevents the formation of sludge, avoiding secondary pollution [11 &12]. Photocatalytic degradation reactions eliminate from wastewater all categories of organic contaminants [13 & 9]. Its applications in slurry-type suspensions are limited due to limitations caused by difficult catalyst separation after photocatalytic degradation reactions [14 &15]. The development of knowledge in semiconductor electrochemistry has led to rapid growth in the field of photocatalysis [16].

### Application of $Tio_2$ as a Semiconductor Photocatalyst

Titanium dioxide as a semiconductor has been successfully used as a photo catalyst for the oxidative degradation of organic compounds, including dyes [17]. The anatase modification is the most practical for photo-catalytic environmental applications such as water purification, wastewater treatment, and water disinfections [9&18]. It is biologically and chemically inert, stable with respect to photo-corrosion, chemical corrosion, and affordable. Its disadvantage is, however, a too-high band gap energy (about 3.2 eV) that allows titanium dioxide to absorb only UV light with a wavelength lower than $\lambda<388$ nm. This reduces the amount of solar energy absorbed by the catalyst down to 5% [9 & 14]. The photogenerated holes ($h^+$) formed after the excitation of electrons (e-) from the valence band to the conduction band exhibit a strong oxidizing potential [19]. The excited electrons are scavenged by oxygen and reduced to form superoxide from Dioxygen. Fujishima demonstrated the “Honda-Fujishima effect” that involved the photochemical splitting of $H_2O$ into $H_2$ and $O_2$ using $TiO_2$ semiconductor photocatalyst [20 & 21]. The photocatalytic degradation mechanism and photochemical reactions are illustrated in Figure 1.

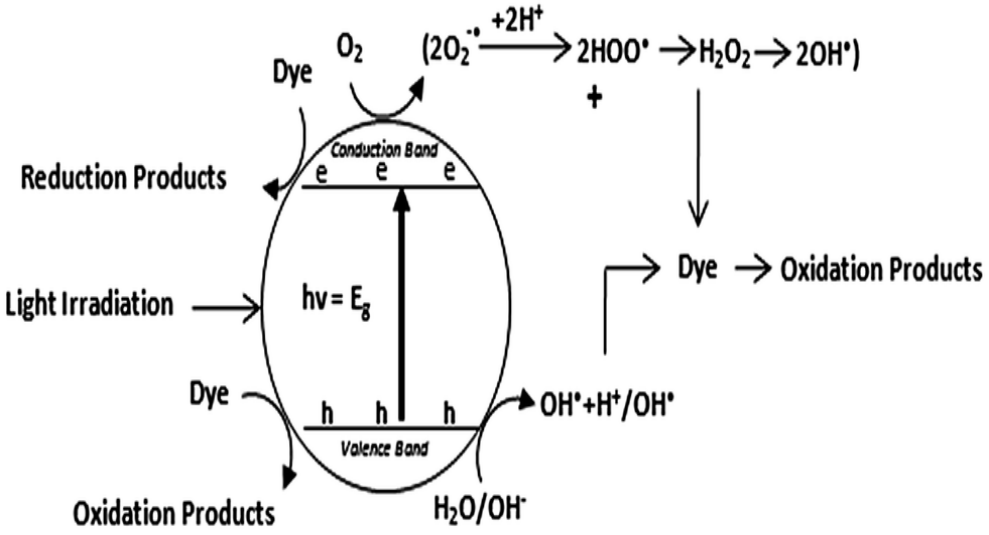


*Figure 1: Photocatalytic degradation mechanism in solutions with oxidative and reductive species [8]*

$$Dye + h\nu \rightarrow Dye^* \quad (1)$$

When the dye molecule absorbs a photon of light (hv), it becomes excited to a higher energy state (Dye*). This is the initial activation step where solar or UV energy is harnessed.

$$Dye^* + TiO_2 \rightarrow Dye^{\bullet+} + TiO_2\,(e) \quad (2)$$

The excited dye transfers an electron to the conduction band of $TiO_2$. As a result, the dye becomes oxidized ($Dye^{\bullet+}$), while $TiO_2$ gains a free electron ($e^-$).

$$TiO_2\,(e) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (3)$$

The electron in $TiO_2$ reduces molecular oxygen, forming a superoxide radical ($O_2^{\bullet-}$). This is a reactive oxygen species (ROS) crucial for pollutant breakdown.

$$O_2^{\bullet-} + TiO_2\,(e) + 2H^+ \rightarrow H_2O_2 \quad (4)$$

Superoxide radicals combine with additional electrons and protons to form hydrogen peroxide ($H_2O_2$), another intermediate oxidant.

$$H_2O_2 + TiO_2\,(e) \rightarrow {}^{\bullet}OH + OH^- \quad (5)$$

Hydrogen peroxide reacts with $TiO_2$ electrons to generate hydroxyl radicals (•OH). These radicals are highly reactive and attack dye molecules, breaking them down into smaller, less harmful compounds.

## Experimental

### Dye Studied, Formula, and Physical Properties

Dye Acid Orange 7, an azo dye, is an orange-red powder that exhibits high solubility in water (40 $g.L^{-1}$). The dye was purchased from Saffron Exim and used in the chemical industry for the following operations: liquid dye for paper, wool, silk, jute, and leather dying. The dye can also be used as an indicator and

biological shading. The dye is stable at room temperature and pressure with a melting point of 164°C. The molecular formula of the dye is $C_{16}H_{11}N_2NaO_4S$, and the molecular weight is 350.32 g/mol. The structural formula of the dye is shown in Figure 2.

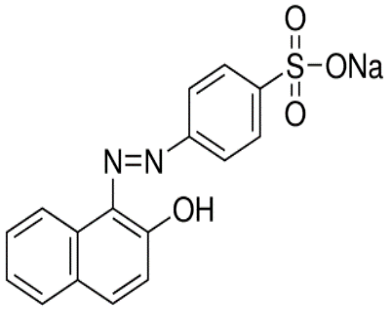


*Figure 2: Chemical structure Acid Orange 7 [9]*

*Figure 3: Acid Orange 7 dye powder [8] (Saffron Exim)*

**Preparation Of $Tio_2$ Photocatalyst from Anatase Paste**

The sulphate process that involves three main stages was followed in the production of anatase $TiO_2$ photocatalysts. As a substrate, Ilmenite ore ($FeTiO_3$) is reacted with sulphuric acid to form a mixture of sulphates. Traces of residual iron are eliminated from the resulting solution as hydrated iron (II) sulphate paste is dried in an oven at 40°C to maintain a distinct white colour. The Titanyl sulphate ($TiOSO_4$) inorganic salt was subsequently hydrolysed in solution to give insoluble, hydrated Titanium dioxide $TiO_2.nH_2O$. This material was dried. The sulphate process is summarised in equation (6): -

$$FeTiO_3 + 2\ H_2SO_4 = TiOSO_4 + FeSO_4 + 2H_2O \quad (6)$$

The final stage involves calcination at temperatures ranging from 300-950°C for a duration of 30 minutes each. Thereafter the materials were calcined at temperatures 700°C, 800°C and 900°C for different durations of time. The calcination is done to evaporate the water, decompose the sulphuric acid in the solid mixture, and transform amorphous $TiO_2$ into the anatase crystalline form.

**Preparation of $Tio_2$ Anatase Paste-Coated Layers**

The $TiO_2$ particulate layers were prepared from an anatase paste at a concentration of 10 $g.L^{-1}$. Anatase paste was immobilised onto microscopic glass slides of dimensions (75mm×25mm) using a 10 mL syringe and subsequently dried in an oven at 60°C. This resulted in a $TiO_2$ thin film dosage rate of 0.5 $mg.cm^{-2}$ on each glass slide. The resulting $TiO_2$ particulate films were then calcined at temperatures between 300°C and 950°C. The final geometrical area covered by the anatase paste $TiO_2$ photocatalyst was trimmed down using a scalpel to at least (25mm×35mm) with a geometrical area of 8.75 $cm^2$ for use in photocatalytic degradation experiments. Images of the coated layers are shown in Figures 4 &5 below: -

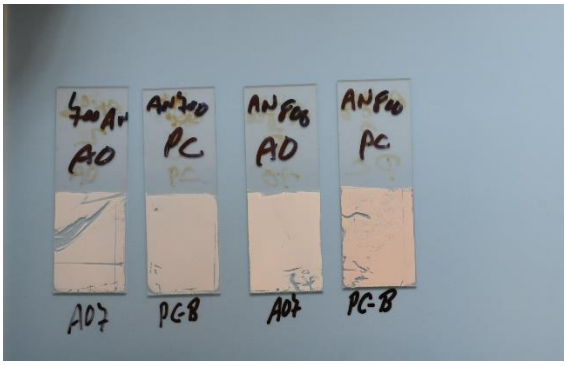


*Figure 4: TiO2 anatase-coated layers*

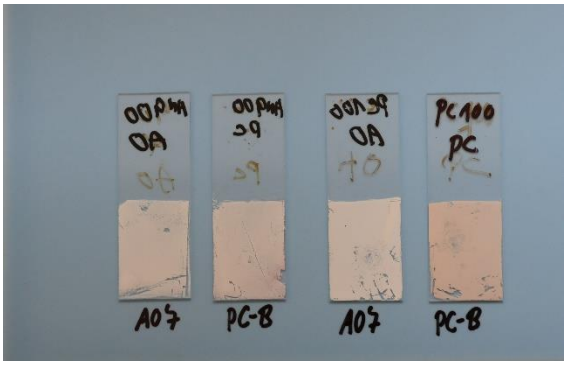


*Figure 5: TiO2 anatase on macroscopic glass*

**Determination of Acid Orange 7 Dye Photocatalytic Degradation Rates**

To determine the rates of dye photocatalytic degradation, the model dye Acid Orange 7 was used. The experimental procedure involved irradiation by UV light of 25 mL of the dye solution c = ($1\times10^{-4}$ moL.$L^{-1}$) in four customized high-volume glass cuvettes. The cuvettes were placed on the four holes in the photocatalytic reactor where UV light irradiated the dyes, Acid Orange 7 solution directly, and the TiO2-coated layers were immersed in the solution while suspended using clips. The dye solution was mixed using a stirrer at about 400 revolutions per minute (rpm). The dye solutions of volume 5mL were sampled after 30 minutes, and the absorbance was measured using a UV-Vis spectrophotometer. To determine changes in dye concentration, mixing and irradiation of the dye solution was interrupted after an interval of 30 minutes, after which 5 mL of the dye solution was, withdrawn from the high volume cuvette using a 10 mL pipette and put into a smaller cuvette of optical length 1 cm. The change in dye concentration was determined by measuring absorbance at wavelength λ=485 nm. The measured dye solution was returned into the high-volume cuvette, and irradiation continued for a further 30 mins for a duration of 120 minutes.

**Measurements of Light Irradiation Intensity**

UV light irradiated by the four-hole apparatus was measured by a light- intensity meter (UVA-365) at about 0 cm away from the (4) hole protrusions. The intensity values were measured at the end of each experiment and included in the final value of the rate of photocatalytic degradation. The average light irradiation intensity measured from the two Osram Eversun fluorescent tubes, through the (4) holes in the photocatalytic reactor, was determined at 3 mW/$cm^2$.

**Rate Of Acid Orange 7 Dye Photodegradation**

The rates of photocatalytic degradation were determined from changes in Acid Orange 7 dye concentration during irradiation with UV light. The photocatalytic degradation rate is considered to cover a geometrical area of 8.75 $cm^2$ that is coated with $TiO_2$ anatase paste.

Rate of dye photocatalytic degradation was calculated as shown in equation (7): -

$$r_A = \frac{(c_0 - c_{60})V}{t_{60} - t_0} \cdot \frac{1}{A} \qquad (7$$

Where $r_A$ is the rate of dye photodegradation [$mol.m^{-2}.h^{-1}$]

$c^o$ …initial dye concentration [$mol.dm^{-3}$]
$c_{60}$ …dye concentration per hour [$mol.dm^{-3}hr^{-1}$]
t ….time at which irradiation started [0 hrs]
$t_{30}$ ….time of irradiation [30 min]
V….volume of dye in cuvette reactor (25 mL)
A….irradiated geometric surface area of particulate film in $m^2$ (0.000875 $m^2$)
The rate of dye photodegradation related to incident light intensity is calculated by equation (8):

$$r_I = \frac{r_A}{I} \tag{8}$$

Where $r_I$ is the rate of dye photocatalytic degradation expressed as [$r = mol.h^{-1}.W^{-1}$] and $I$ is the Intensity of UV light [$W/m^2$] emitted by two Osram Eversun fluorescent tubes fitted into the reactor, determined in section (2.5).

***Photocatalytic Degradation Experiments***

A stock solution of Acid Orange 7 dye c=$1.0\times10^{-4}$ $mol.L^{-1}$ was prepared by dissolving 0.037g dye powder in 1000 mL of distilled water in a round-bottomed flask. Prepared stock solution was serially diluted to obtain dye solutions of the following concentrations: (i)$1\times10^{-5}$ $mol.L^{-1,}$ (ii) $2.5\times10^{-5}$ $mol.L^{-1,}$ (iii) $5\times10^{-5}$ $mol.L^{-1,}$ (iv) $7.5\times10^{-5}$ $mol.L^{-1}$. For the photocatalytic degradation, dye c=$1\times10^{-4}$ $mol.L^{-1}$ was used after a full UV-Vis scan 200-800 nm, to evaluate maximum absorption wavelength ($\lambda_{max}$). Dye solutions of v=25 mL were filled into four high-volume cuvettes (v=30 mL) and placed onto the four-hole photocatalytic reactor set-up shown in figures 6 & 7 in section (2.1.2). To achieve uniform dye mixture concentration, a magnetic stirrer rotating at 400 rpm was inserted into each of the (4) cuvettes. The dye solutions were irradiated with UV light of λ= 355 nm for a duration of 120 minutes using two Osram Eversun fluorescent tubes that emitted UV light of wavelength between 320 and 400 nm. To determine the change in dye absorbance, after an interval of 30 minutes, 5 mL was drawn from each cuvette, absorbance was measured using a UV-Vis spectrophotometer at $\lambda_{max}$= 485 nm, and thereafter the dye solution was poured back into the 25 cuvettes.

***Four-Hole Photocatalytic Reactor***

The photocatalytic reactor operated in batch mode, fitted with a thermostat to regulate the operating temperature at 25°C. Four 30 mL cuvettes were placed against four holes through which UV light λ =355 nm irradiated from two UV tubes of 11 W each. Exactly 25 mL of dye solution was filled into each cuvette, irradiated with UV light, and stirred with a magnetic stirrer at 400 rpm. The glass microscopic layers coated with $TiO_2$ anatase paste catalyst were suspended in the cuvettes using metal clips, making contact with the dye solution as shown in Figures 6 & 7.

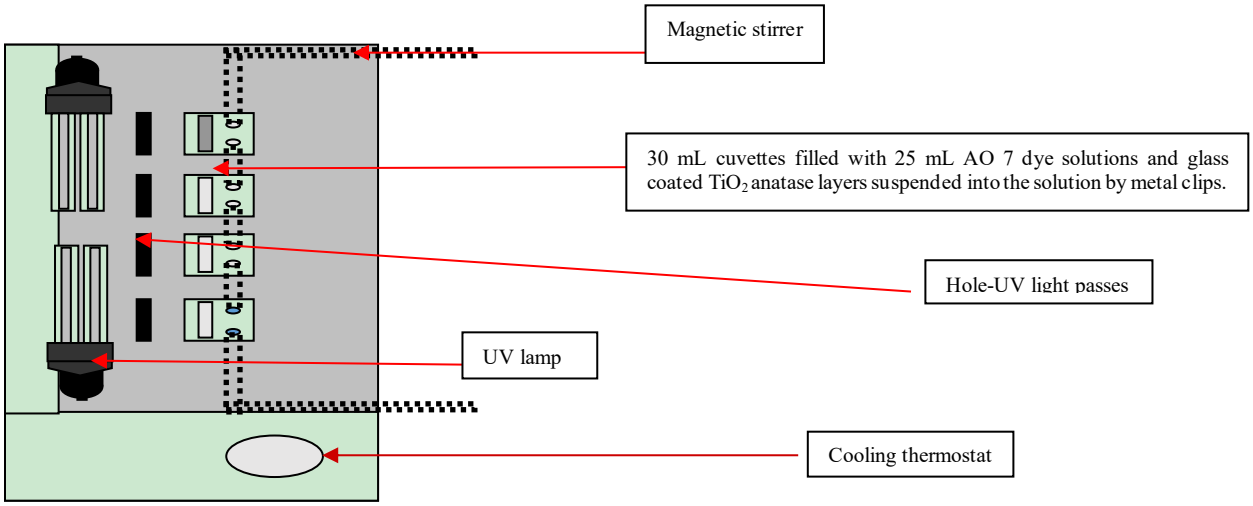


*Figure 6: Photocatalytic reactor*

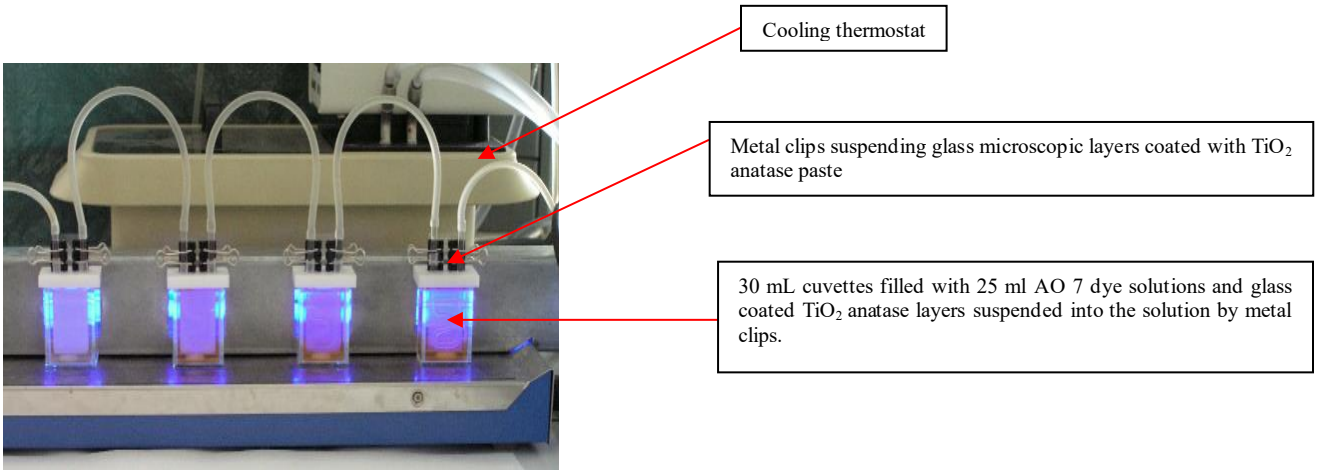


*Figure 7: Photocatalytic reactor with magnetic stirrer*

## Spectral Analysis

### *Maximum Absorption Wavelength ($\lambda_{max}$)*

To determine the maximum absorption wavelength ($\lambda_{max}$) of the dye solution c = ($1\times10^{-4}$ mol.$L^{-1}$), a UV-Vis spectrophotometer (CECIL 2041) was used. One quartz cuvette (optical length 1 cm) was prepared for use by cleaning and drying using distilled water and dry linen tissue. This ensured that the transparent side remained clear, thereby eliminating interference as the UV light passes through the dye solution in the cuvette. The UV-Vis spectrophotometer was switched on and calibrated using distilled water in a quartz cuvette as a blank in the sample compartment with the transparent sides facing the UV light source, and the sample compartment lid closed. After calibration, dye absorption was recorded for various dye solution concentrations for a full scan at λ= (200-800 nm).

### *Molar Extinction Coefficient (ε) – Calibration Curve*

The molar extinction coefficient of dye Acid Orange 7 was derived from the Lambert-Beer law shown in equation (9):-

$$A = \varepsilon c l \qquad \text{Equation 9}$$

Where:-

A - Absorbance
ε - molar absorption coefficient
c - dye molar concentration (mol. $L^{-1}$)
l - optical path length (cm)

The coefficient was determined using a calibration curve plotted from absorbance values of dye solutions of known concentrations. Serial solutions of dye Acid Orange were prepared as described in section (2.1.1) as follows: ($1\times10^{-5}$ mol.$L^{-1}$, $2.5\times10^{-5}$ mol.$L^{-1}$, $5\times10^{-5}$ mol.$L^{-1}$, $7.5\times10^{-5}$ mol.$L^{-1}$, $1\times10^{-4}$ mol.$L^{-1}$ ). The absorbance of these individual dye solutions was measured at λ=485 nm as determined in section (2.1.2) using a cuvette of optical path length 1 cm and a UV-Vis Spectrophotometer. The molar extinction coefficient (ε) was determined by using the absorbance values obtained to plot a calibration curve using a linear extrapolation.

## Results and Discussion

### Spectral Properties of Dye Acid Orange 7

### *Maximum Absorption Wavelength ($\lambda_{max}$)*

The maximum absorption wavelength at ($\lambda_{max}$) The dye Acid Orange 7 (c=$2.5\times10^{-5}$ mol.$L^{-1}$) was determined by measuring absorbance between the wavelength λ= (200-800 nm) as indicated in Figure 8.

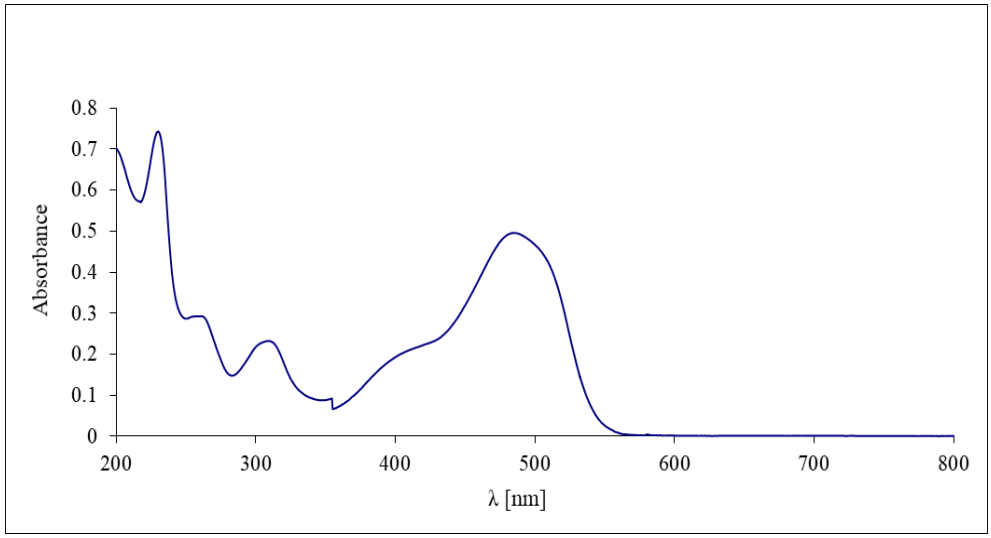


*Figure 8: UV-Vis spectra for Acid Orange 7*

The results in Figure 8 show the spectral properties of Acid Orange 7, i.e., maximum absorption wavelength at λ=485 nm. The wavelength lies within the UV region of the electromagnetic spectrum (EM). Minimal dye absorption in the visible range between λ= (390-550 nm) is observed. Near-zero dye absorption is observed in the range between λ=550-800 nm.

### *Molar Extinction Coefficient (ε)*

Figure 9 shows the calibration curve for dye Acid Orange 7, used to determine its molar extinction coefficient.

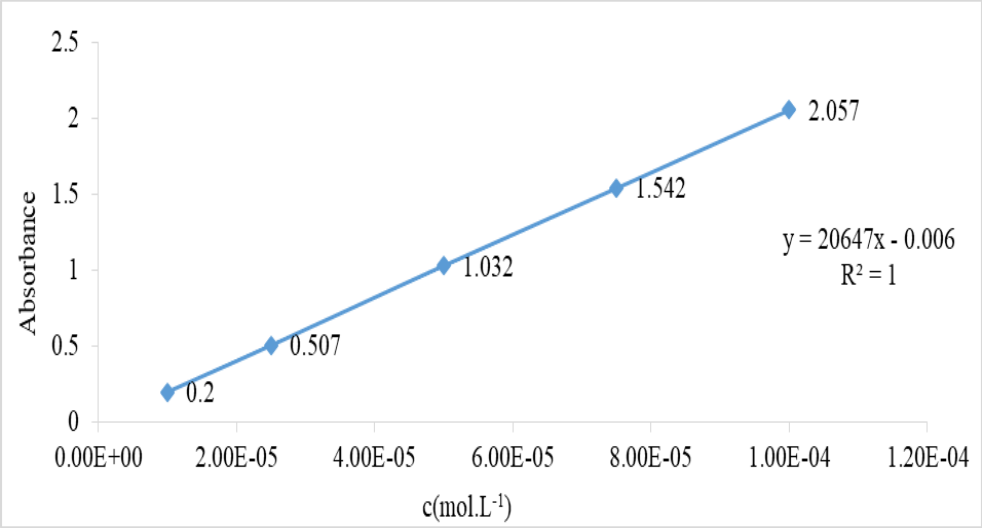


*Figure 9: Calibration curve - dye Acid Orange 7*

From Figure 9 above, the calibration curve for dye Acid Orange 7 was plotted by measuring the absorbance of (5) dye solutions as described in (section 2.2.2). Maximum absorbance values were determined for each dye solution. Using the absorbance values, a calibration curve was plotted as illustrated in Figure 9. Using linear regression of the absorbance vs. concentration data, an experimental extinction coefficient value of 20647 $dm^{-3}.mol.^{-1}.cm^{-1}$ was calculated. The value indicates that Acid Orange 7 dye absorbs light effectively at λ=485, i.e., the UV region of the electromagnetic spectrum (EM).

### Effect of Anatase Temperature on Photocatalytic Degradation of Acid Orange 7 Dye – UV/$Tio_2$ (Anatase Paste)

The effect of $TiO_2$ anatase paste calcination on Acid Orange 7 dye photocatalytic degradation is shown in Figure 10: -

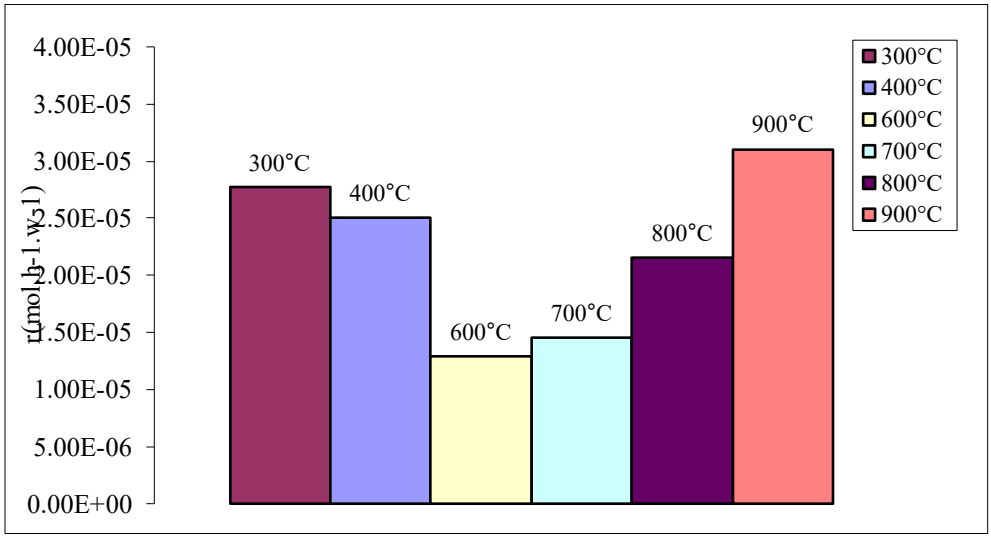


*Figure 10: Effect of calcination temperature on rate of photocatalytic degradation of Acid Orange 7 dye c = (1×10-4 moL.L-1) on TiO2 prepared from anatase paste (mTiO2 =0.5 mg/cm2).*

From Figure 10 and Table 1, we observe that with an increase in calcination temperature between 300°C-600°C, the rate of Acid Orange 7 dye photocatalytic degradation steadily decreases by 43.5%. At a calcination temperature of 700°C, there is a sudden increase in the rate of photocatalytic degradation. Between 700°C-900C, there is an increase in dye photocatalytic degradation by 51.4%. The results show the optimum calcination temperature for $TiO_2$ anatase paste to be used for Acid Orange 7 dye degradation is 900°C.

*Table 1: Photocatalytic degradation AO 7 of concentration 1×10-4M on TiO2 prepared from 'anatase paste' against temperature (mTiO2 =0.5 mg/cm2)*

| Temperature [°C] | Acid Orange 7 r (mol.$h^{-1}$. $w^{-1}$) |
|---|---|
| 300°C | 3.08E-05 |
| 400°C | 2.80E-05 |
| 600°C | 1.74E-05 |
| 700°C | 1.80E-05 |
| 800°C | 2.65E-05 |
| 900°C | 3.70E-05 |

**Effect of Anatase Temperature on Photocatalytic Degradation of Acid Orange 7 Dye – UV/$Tio_2$ (Anatase Paste)**

The effect of $TiO_2$ anatase paste calcination at t=700-900°C, at various calcination times, on Acid Orange 7 dye photocatalytic degradation is shown in Figure 11: -

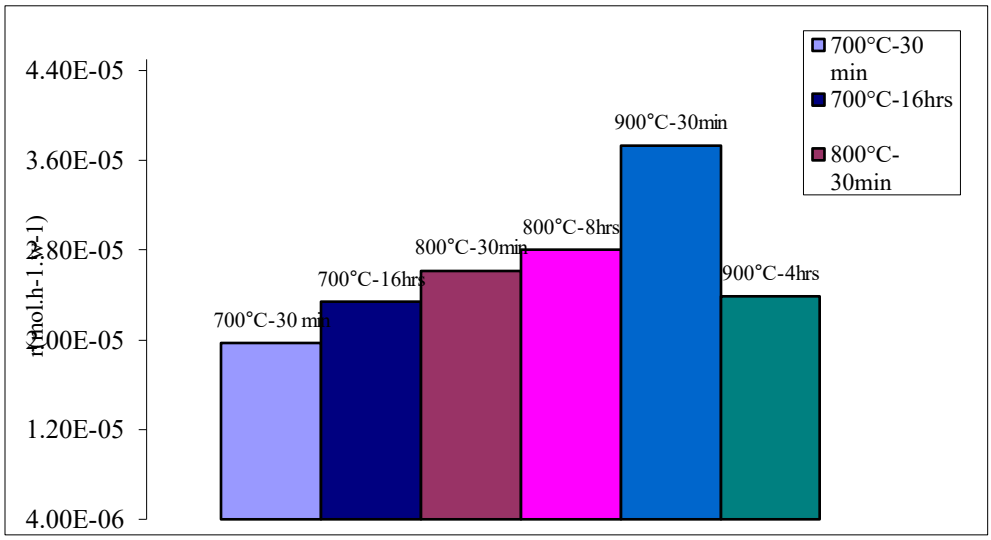


*Figure 11: Effect of calcination temperature (700-900°C) on rate of photocatalytic degradation of Acid Orange 7 dye c = (1×10-4 moL.L-1) on TiO2 prepared from anatase paste (mTiO2 =0.5 mg/cm2).*

From figure 11 and table 2, elevated calcination temperatures between 700-800°C display a favourable effect on the rate of Acid Orange 7 dye photocatalytic degradation. However, we observe that, at 900°C, the photodegradation rate reaches its maximum, with optimum calcination time at 30 minutes. Increased calcination time, i.e., 4 hrs, resulted in decreased $TiO_2$ anatase paste photocatalytic activity by 40%. This concludes the optimum calcination temperature at 900°C for 30 mins.

*Table 2: Effects of TiO2 anatase paste calcination temperature (700-900°C) and time on the rate of Acid Orange 7 dye photocatalytic degradation*

| Calcination Temperature [°C]/Time [Mins.] | Acid Orange 7 R($Mol.H^{-1}. W^{-1}$) |
|---|---|
| 700°C 30 min | 1.97E-05 |
| 700°C 16 hrs | 2.34E-05 |
| 800°C 30 min | 2.62E-05 |
| 800°C 8 hrs | 2.80E-05 |
| 900°C 30 min | 3.73E-05 |
| 900°C 4 hrs | 2.39E-05 |

## Conclusions

It was shown that dye Acid Orange 7 is effectively photodegraded using calcined $TiO_2$ anatase paste under UV light irradiation in a batch mode photocatalytic reactor. Longer calcination temperatures between 700-800°C have a positive effect on the rate of photocatalytic degradation of Acid Orange 7. At 700°C, there is a sudden increase in the rates of photocatalytic degradation of Acid Orange 7, with the optimum rate at 900°C. At higher calcination temperatures of 900°C, longer calcination duration has a negative effect on the rates of photocatalytic degradation.

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