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Spectral and Sorption Characteristics of Acid Orange II and Methylene Blue Dyes on TiO₂ Photocatalyst

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Abstract:

In this work, the characteristic spectral and sorption characteristics of Acid Orange II and Methylene Blue (MB) dyes was investigated. TiO₂ (P25) commercial catalyst was used as a semi-conductor photocatalyst. The work investigated the following; (i) amount of Acid Orange II dye adsorbed on TiO₂, (ii) the wavelength at which TiO₂ catalyst, Acid Orange II and Methylene Blue exhibit maximum absorbance (iii) determine the absorbance of Acid Orange II & Methylene Blue dyes to calibrate the spectrophotometer and compute the molar extinction coefficient for each dye. Several concentrations of the individual dyes were used for the experiments. Adsorption experiments were done in a UV panel, consisting of a rectangular frame, covered with a suitable cloth to shield natural light from the frame and a magnetic shaker. UV lamps emitting light at $\lambda = 365 \text{ nm}$ were used as a source of irradiation. To measure the spectral and sorption characteristics of the dyes, a UV/Vis spectrophotometer was used. From the absorbance measured, equilibrium concentrations and the amount of dye adsorbed on to n-TiO₂ (mol.g^{-1}) established. Adsorption significantly influences the degradation of dyes under UV light irradiation. The amount of dye adsorbed on the surface of TiO₂ catalyst was experimentally measured. This work concluded that the amount of Acid Orange II adsorbed on TiO₂ catalyst increased with higher initial dye concentrations. However, at initial dye concentration greater than $1 \times 10^{-4} \text{ mol.L}^{-1}$ the adsorption decreases significantly.

Keywords: Acid Orange II, Methylene Blue, adsorption, TiO₂, calibration curve, molar extinction coefficient

1. Introduction

1.1. Background

More than 15% of the total world production of dyes is lost during the dyeing process and is therefore released and consequently becoming a source of textile mill pollution (Aleboyeh *et al.*, 2003; Galindo *et al.*, 2001). Textile wastewater is known to contain considerable amounts of non-biodegradable dyes, especially azo dyes. Dyes are an abundant class of coloured organic compounds that represent an increasing environmental danger (Morrison *et al.*, 1996; Mohey *et al.*, 2003; Kurbus *et al.*, 2002). During dye production and textile manufacturing processes a large amount of wastewater containing dyestuffs with intensive colour and toxicity can be introduced into aquatic systems. During dye production and textile manufacturing processes a large amount of wastewater containing dyestuffs with intensive colour and toxicity can therefore be introduced into aquatic systems (Georgiou *et al.*, 2002; Neamtu *et al.*, 2001).

1.2. Categorization of Dyes

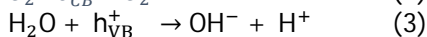
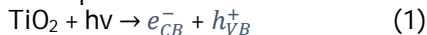
Dyes can be grouped according to their properties e.g. whether cationic or anionic, examples include, Cationic: Methylene blue (MB), Cationic blue: Anionic: AO II, Procion Red (PR), and Eosin. Dyes may be also classified according to their chemical structures for example, - Azoic. Congo red (CR), Methyl Orange (MO), Ponceau G (PG), Acid Orange II, and Ferrochrome Blue Black B (EB)), -Anthraquinonic (Alizarin S (AS)), -Heteropolyaromatic (Methylene Blue (MB)), - Fluorescent (Neutral Red (NR), Rhodamine B (RB)), -Sulfonic (Fuchsin Acid (FA)) (Konstantinou and Albanis, 2004; Namboodri *et al.*, 1996). Azo dyes can be divided into mono, diazo, triazo classes according to the presence of one or more azo bonds (-N=N-) and are found in various categories, i.e. acid, basic, direct, disperse, azoic and pigments. (Konstantinou and Albanis, 2004).

1.3. Titanium Dioxide as a Semi-Conductor Photocatalyst

Titanium dioxide as a semi-conductor has been successfully used as a photo catalyst for the oxidative degradation of organic compounds including dyes. It is biologically and chemically inert, stable with respect to photo-corrosion and chemical corrosion and is also inexpensive (Perez *et al.*, 2001). However, it has the disadvantage that its band gap energy (about 3.2 e.V) is too high. This means that titanium dioxide can absorb only UV light with wavelength lower than $\lambda=388 \text{ nm}$ and thus reducing the solar harvesting efficiency down to 5%. (Alfano *et al.*, 2000) Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for their decolorization and degradation (Souther and Alspaugh, 1957); (Hamza and Hamoda, 1980); (Sheng and Chi, 1993).

This has led to the study of other methods. Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds using semiconductors such as the anatase form of titanium dioxide and UV light irradiation (AL-Ekabi *et al.*, 1991; Blake, 1994; Hoffmann *et al.*, 1995). Lately, the combination of photocatalysis and solar technologies has attracted increasing attention. This process can be usefully developed for the treatment of wastewater pollution caused by dyeing compounds. This is because of the mild conditions required for the process and the high efficiency achieved (Minero *et al.*, 1993; Daoxin *et al.*, 1994; Linder *et al.*, 1995; Li and Zhang, 1996). Anatase-type TiO₂ has attracted great attention of scientists and engineers because of its practical applications. The pH of the medium is one of the important factors affecting the degradation process because of the amphoteric nature of most semiconductors.

The equations below indicate the reactions that take place when TiO₂ acts as a semi-conductor.



(Minero *et al.*, 1993)

TiO₂ is a superior photocatalyst compared to other semi-conductor photocatalysts e.g. WO₃, α-Fe₂O₃, SnO₂ and ZrO₂ under similar experimentation conditions (Ameta and Ameta, 2016)

1.4. Adsorption of Dyes on TiO₂ catalyst

Adsorption of molecules that react, on a surface, is important for heterogenous catalysis. The rate of a redox process for example may be dependent on the properties of the catalyst surface because the adsorption may be the rate-limiting step of the whole process (Linder *et al.*, 1995). Adsorption influences the distribution of substances between the aqueous phase and the solid particles affecting their transport through the different phases hence accelerating or delaying the rate of surface reactions (Linder *et al.*, 1995).

1.5. Dyes Studied, Formulas and Properties

Dye Acid Orange II is orange in colour and is commonly used for the high temperature dyeing of wool in strong acid bath among other industrial uses (Blake, 1994). It has molecular formula HOC₁₀H₆N=NC₆H₄SO₃Na and molecular weight 350.32 g/mol. It has the following properties, it is stable at normal temperature and pressure, has a melting point of 164°C and its solubility water is 116 g/l (Kaewprasit *et al.*, 1998). Dye Methylene Blue is green bronze in colour and is a well-known industrial dye. Its molecular weight is 319.85 g/mol. Molecular formula is C₁₆H₁₈N₃SCL.3H₂O. It has the following properties, its odourless, may decompose explosively when heated above 125°C and explodes (Bergmann and O'konski, 2002). Contact with the skin causes irritation in the short term. Ingestion causes blood disorders (Xu *et al.*, 1999). Solubility in water is 40g/l. Methylene Blue is also soluble in alcohol and chloroform but insoluble in ether (Xu *et al.*, 1999).

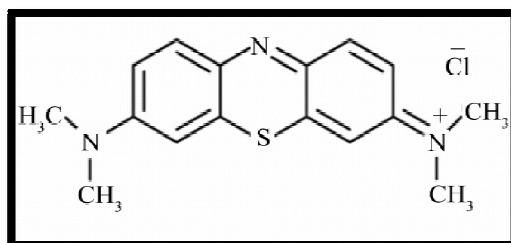


Figure 1: Methylene Blue

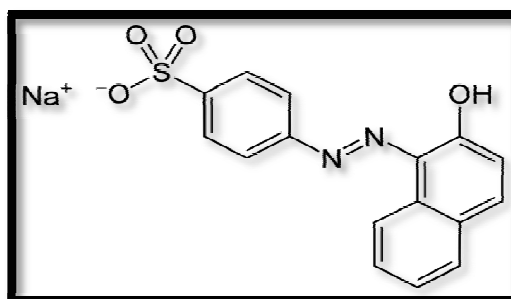


Figure 2: Acid Orange II

1.6. Objectives

The main objective of this study was to investigate the spectral and sorption characteristics of Acid Orange II and Methylene Blue dyes by TiO₂ catalyst. Experiments were performed under different dye compositions with the following specific objectives: (i) Determine the amount of Acid Orange II dye adsorbed on TiO₂, (ii) Determine the wavelength at which TiO₂ catalyst, Acid Orange II and Methylene Blue exhibit maximum absorbance (iii) Determine the absorbance of Acid Orange II & Methylene Blue dyes with a view to calibrating the spectrophotometer and hence computing the extinction coefficient for each dye.

2. Materials and Methods

2.1. Chemicals

The following materials were used as purchased without further purification: Acid Orange II is supplied by Acros Chemicals. Methylene Blue dye was supplied by Gurr limited London. The purity of both dyes used is about 95%, with 5% comprising mainly moisture. Nitric acid (purity 99%) and other chemicals in the study were obtained from Sigma – Aldrich Distilled water (H₂O) was used throughout this study. Membrane filters (MF™, filter type 0.45 μm with cellulose nitrate were required for the sorption experiments.

2.2. Immobilized TiO₂ Photocatalyst

Titanium dioxide layer was prepared on a degreased and clean glass plate by sedimentation of a liquid suspension of TiO₂ P 25 (Degussa) which was adjusted with nitric acid to a pH value of 3 and concentration of 5 g.L⁻¹. After the layer had dried at room temperature, it was heated at 300°C for a duration of 3 hours.

2.3. Equipment – UV panel photo reactor

Two UV lamps purchased from local suppliers were used to as a source of UV light emitting light mainly at λ=355 nm. A UV panel photoreactor consisting of a rectangular frame, covered with a suitable cloth to shield natural light from the frame and a magnetic shaker. The magnetic shaker, ensured that the dye solutions were well mixed during the adsorption reactions. A UV/Vis spectrophotometer, pH meter, glassware (borosilicate), all the other materials including aluminum foil, stainless steel and plastics parts required to fabricate the photoreactor were purchased locally.

2.4. Methods

2.4.1. Spectral Analyses

2.4.1.1. Absorption Spectrum (TiO₂) - Emission Spectrum (UV Lamps)

The emission spectrum (UV lamps) and absorption spectrum (TiO₂) were determined using a UV/Vis spectrophotometer (USB2E2201). TiO₂ absorbance and UV lamps relative intensity were measured at wavelengths between λ = 300-600nm. The following technical conditions were maintained during the measurement.

Software:	001Base32 version 1.0.3.0
Integration time (msec):	27
Spectra averaged:	1
Boxcar smoothing:	0
Dual beam reference:	disabled
Correct for electrical dark:	disabled
Reference channel:	master

2.4.1.2. UV/Vis Spectrum Acid Orange II – Wavelength of Maximum Absorbance (λ_{max})

After the preparation of a stock solution c (1×10⁻⁴ mol.L⁻¹) in a 500 ml round bottomed flask. The absorbance of the sample was measured using UV/Vis spectrophotometer. One quartz cuvette was cleaned and dried using distilled water and linen tissue to ensure the transparent side remained clear. A volume of 5 ml of Acid Orange II sample was put into the cuvette. The UV-Vis spectrophotometer was switched on. A cuvette (optical length 1 cm) containing distilled water (blank) was placed in the sample compartment with the transparent sides facing the light source and the sample compartment lid was closed. The auto zero button was pressed to set zero absorbance. A full UV-Vis scan of Acid Orange II sample was done at wavelengths between 200 nm-800 nm as shown in figure 6.

2.4.1.3. UV/VIS Spectrum Methylene Blue – Wavelength Of Maximum Absorbance (λ_{max})

The procedure followed to determine (λ_{max}) for methylene blue dye, similar to the procedure described in section (2.4.1.2) for Acid Orange II. After the preparation of a stock solution c (1×10⁻⁵ mol.L⁻¹) in a 500 ml round bottomed flask. A full UV-Vis scan of Methylene Blue was done at wavelengths between 200 nm-800 nm as shown in figure 5.

2.4.1.4. Determination of Molar Extinction Coefficient (ε) - Acid Orange II

The coefficient (ε) mol⁻¹.dm³.cm⁻¹ is calculated from the Beer Lamberts law shown in below;

$$A = \epsilon Lc$$

Where:

- A is the amount of light absorbed by samples at specific wavelengths (λ)
- ε is the molar extinction coefficient
- L is the length of cuvette used to measure absorbance
- c is the concentration of the absorbing sample

To determine the extinction coefficient of Acid Orange II (ε), at 485 nm the following concentrations of solutions were prepared; 1×10⁻⁵ mol. L⁻¹, 2.5×10⁻⁵ mol. L⁻¹, 5×10⁻⁵, 7.5×10⁻⁵ mol. L⁻¹ and 1×10⁻⁴ mol. L⁻¹. Using a cuvette of optic length 1 cm and a UV-Vis spectrophotometer, absorbance was measured at wavelength 485 nm. A calibration curve using different

solution concentrations is shown in figure 6. Using the linear extrapolation of the data obtained an experimental the molar extinction coefficient was calculated.

2.4.1.5. Determination of Molar Extinction Coefficient (ϵ) – Methylene Blue (MB)

In determining the extinction coefficient of Methylene Blue (MB), the procedure described in section (2.4.1.4) was followed. The following concentrations of dye solutions were prepared; (1×10^{-5} mol.L⁻¹, 2×10^{-5} mol. L⁻¹, 5×10^{-5} mol. L⁻¹, 2×10^{-6} mol.L⁻¹). Using a cuvette of 1 cm and a UV/Vis spectrophotometer. The wavelength of maximum absorbance (λ_{max}) was 660 nm. A calibration curve was plotted. A calibration curve using different solution concentrations is shown in figure 7.

2.4.2. Sorption Analyses

2.4.2.1. Adsorption of Acid Orange II – UV panel

Adsorption experiments were done in a several dye solutions of Acid Orange II of various concentrations were used in the adsorption experiments. Bottles were filled each with 20 ml of various dye concentrations and 0.1 g TiO₂ P25 powder was added into the bottles making direct contact with the Acid Orange II dye solution. Three bottles of the same initial concentrations were used in each batch. The slurry was then shaken in a vibrator for two hours after which centrifugation was done for at least 10 minutes. The suspension was filtered with a membrane filter (MF™ filter type 0.45 μ m HA, which contains cellulose nitrate). The filtrate was then stored in mini - glass bottles. The absorbance of the dye solutions was measured using a UV-Vis spectrophotometer. The absorbance values were then used to calculate the equilibrium concentrations and the amount of dye adsorbed in (mol.g⁻¹) was computed. The results obtained (average of three values) are shown in figure 8 and table 1.

3. Results and Discussions

3.1. Spectral Analyses

3.1.1. Emission Spectrum (UV Lamps) - Absorption Spectrum (TiO₂)

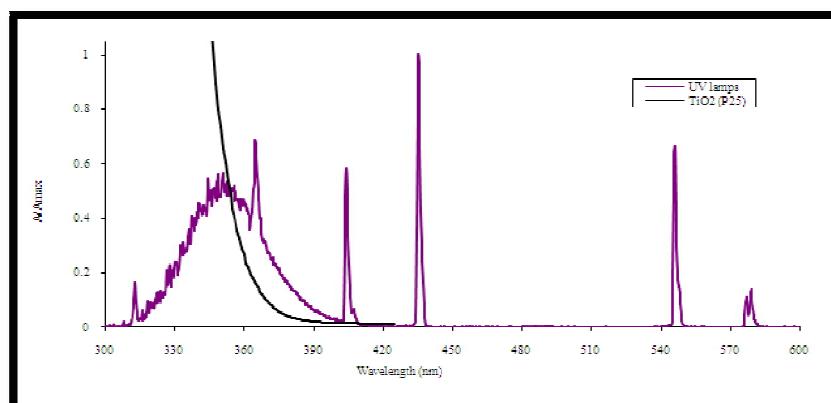


Figure 3: Emission Spectrum of UV Tubes and Absorption Spectrum of TiO₂ Layer

Figure 3 shows that the UV lamps used in the study emitted maximum light at a wavelength of $\lambda=365$ nm. The TiO₂ used in the study absorbed maximum light at a wavelength of $\lambda=355$ nm. The above observed wavelengths were in the UV region of electromagnetic spectrum.

3.1.2. UV/VIS spectrum Acid Orange II – wavelength of maximum absorbance (λ_{max})

To determine $\lambda_{(max)}$ for Acid Orange II, a full UV/Vis scan was done between $\lambda=$ (200 nm – 800 nm). A solution of c (2.5×10^{-5} mol. L⁻¹) was used. The obtained spectra are shown in figure 4 below.

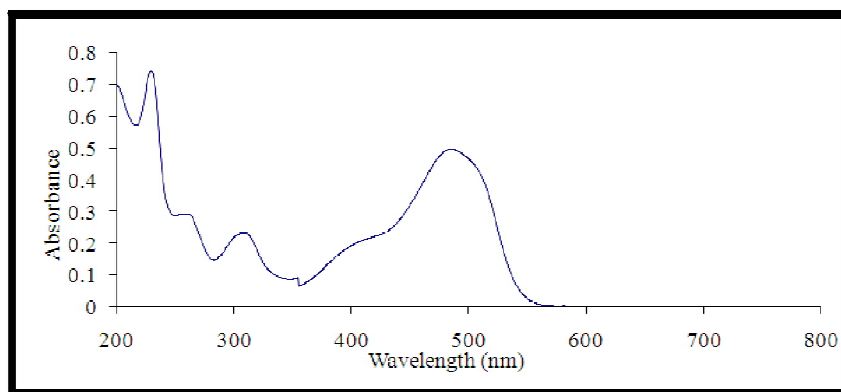


Figure 4: UV-Vis Spectra Acid Orange II

Figure 4 above, shows that Acid Orange II has absorption peaks at the following wavelengths; (232 nm, 310 nm and 485 nm). The spectra determine the wavelength of maximum absorbance (λ_{max}) which corresponds to the maximum absorption peak $\lambda= 485$ nm.

3.1.3. UV/VIS spectrum Methylene Blue – Wavelength of Maximum Absorbance (λ_{max})

To determine $\lambda_{(max)}$ for Methylene Blue, a full UV/Vis scan was done between $\lambda= (200$ nm – 800 nm). A solution of $c (1.5 \times 10^{-5}M)$ was used. The obtained spectra are shown in figure 5 below.

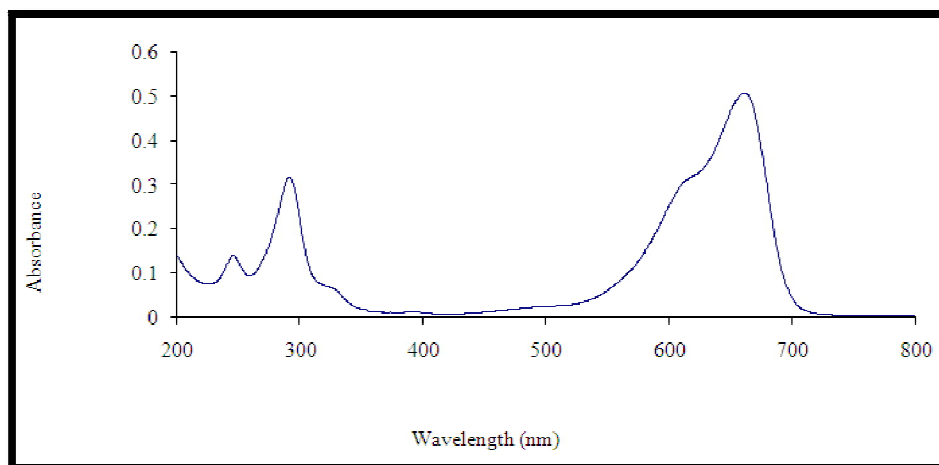


Figure 5: UV-Vis Spectra Methylene Blue

Figure 5 above shows that Methylene Blue dye has absorption peaks at the following wavelengths; (249 nm, 293 nm and 660 nm). The wavelength of maximum absorbance (λ_{max}) which corresponds to the maximum absorption peak was $\lambda=660$ nm.

3.1.4. Determination of Molar Extinction Coefficient (ϵ) - Acid Orange (AO II)

The Molar Extinction Coefficient was determined through a standard calibration curve plotted as shown in Figure 6 below.

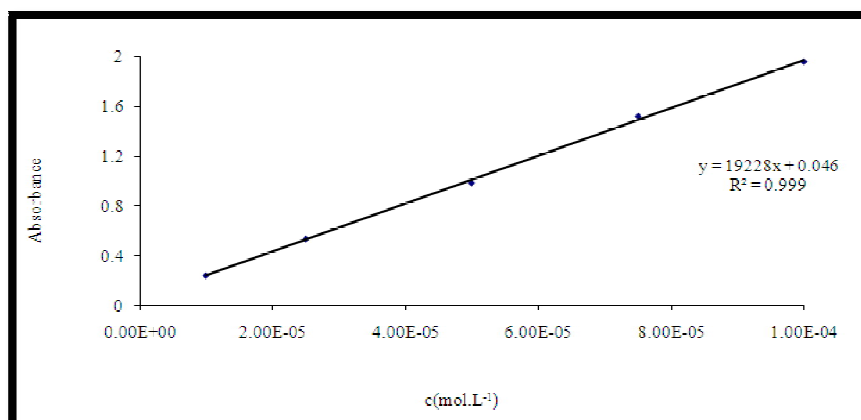


Figure 6: Calibration Curve for Acid Orange II

To determine the extinction coefficient (ϵ) of Acid Orange II, the following concentrations 4 solutions of various concentrations were prepared from a stock solution of 1×10^{-4} mol. L $^{-1}$. These were, (1×10^{-5} mol.L $^{-1}$, 2.5×10^{-5} mol.L $^{-1}$, 5×10^{-5} mol.L $^{-1}$, 7.5×10^{-5} mol.L $^{-1}$, 1×10^{-4} mol.L $^{-1}$). A cuvette of 1 cm unit length and a UV/Vis spectrophotometer, absorbance for these solutions was measured at $\lambda_{\max} = 485$ nm. By plotting absorbance against concentration, a calibration curve was generated and using the line equation, the molar extinction coefficient (ϵ) was determined at $19228 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ which is quite close to the literature value of $21000 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (Ferguson and Mau, 1972).

3.1.5. Determination of Molar Extinction Coefficient (ϵ) – Methylene Blue (MB)

The Molar Extinction Coefficient was determined through a standard calibration curve plotted as shown in Figure 7 below.

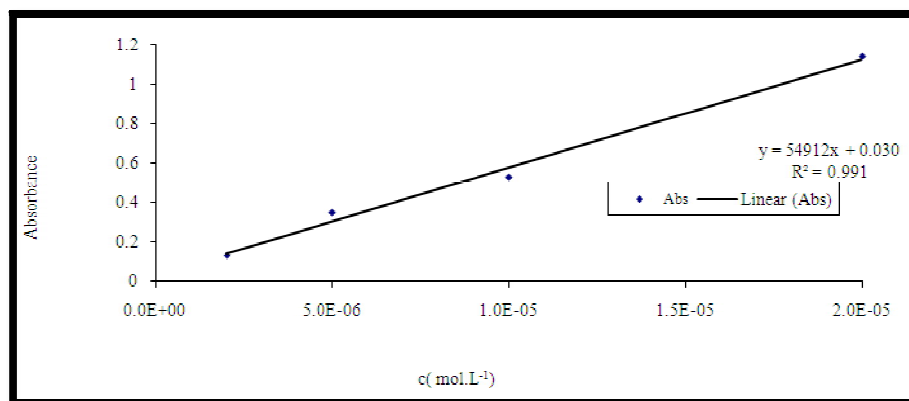


Figure 7: Calibration Curve for MB

To determine the extinction coefficient (ϵ) of Methylene Blue, the following concentrations of dye solutions were prepared; these were, (1×10^{-5} mol.L $^{-1}$, 2.5×10^{-5} mol.L $^{-1}$, 5×10^{-5} mol.L $^{-1}$, 7.5×10^{-5} mol.L $^{-1}$, 1×10^{-4} mol.L $^{-1}$). A cuvette of 1 cm unit length and a UV/Vis spectrophotometer, absorbance for these solutions was measured at $\lambda_{\max} = 660$ nm. By plotting absorbance against concentration, a calibration curve was generated and using the line equation, the molar extinction coefficient (ϵ) was determined at $54912 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ which is quite close to the literature value of $21000 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (Ferguson and Mau, 1972). This value can be compared with the value reported in literature of $79510 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (Houas *et al.*, 2002) and $46000 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (Kaewprasit, *et al* 1998).

3.2. Sorption Analyses

3.2.1. Adsorption of Acid Orange II

The adsorption curve depicted in figure 8 below shows the correlation between the amount of Acid Orange II dye adsorbed and its initial concentration.

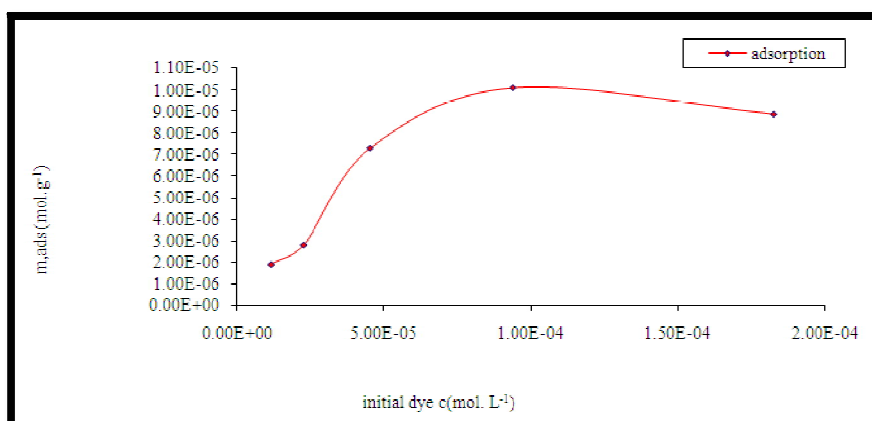


Figure 8: Correlation between the Amounts of Acid Orange II Dye Adsorbed and Its Initial Concentration

The findings in figure 8 show that the initial concentration of Acid Orange II dye directly affected the amount of dye adsorbed by TiO $_2$ catalyst. It shows that the amount of adsorbate increases with increase in dye concentration. At dye concentrations higher than c (1×10^{-4} mol. L $^{-1}$) the amount of dye adsorbed decreases significantly. The results shown in table 1 below correlates the findings shown in Figure 8

Conc. (mol/l)	Initial conc. (mol/l)	Equilibrium conc.(mol/l)	Delta conc. (mol/l)	n, ads (mols)	m,ads (g/mol)
2E-04M	1.83E-04	1.38E-04	4.45E-05	8.90E-07	8.90E-06
1E-04M	9.40E-05	4.32E-05	5.08E-05	1.02E-06	1.02E-05
5E-05M	4.55E-05	8.77E-06	3.67E-05	7.34E-07	7.34E-06
2.5E-05M	2.28E-05	8.67E-06	1.41E-05	2.82E-07	2.82E-06
1.25E-05M	1.19E-05	2.35E-06	9.50E-06	1.90E-07	1.90E-06

Table 1: Showing the Amount of Acid Orange II Dye of Various Concentrations Adsorbed

The findings in table 1. Indicate that the amount ($\text{g}\cdot\text{mol}^{-1}$) of Acid Orange II dye adsorbed on TiO_2 increases with a rise in initial dye concentration.

4. Conclusions

The amount of Acid Orange II dye adsorbed on TiO_2 is directly proportional to the initial concentrations of the dye. The optimum Acid Orange II dye concentration required to achieve maximum dye adsorption was determined at c (1×10^{-4} mol. L^{-1}). At higher concentrations the amounts of dye adsorbed declines significantly. The catalyst and UV lamps used in this study absorbs maximum light at $\lambda=355\text{nm}$ and $\lambda=365\text{ nm}$. This wavelength lies in the UV region of the electromagnetic spectrum. These conditions favour UV light mediated photocatalytic degradation experiments.

5. References

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