

THE INTERNATIONAL JOURNAL OF HUMANITIES & SOCIAL STUDIES

Nano-photocatalytic Mineralization and Degradation of Dye Acid Orange 7 on Titanium Dioxide Coated Layers in a Batch Mode Plate Photo Reactor: Role of Flow Rate and Inorganic Salts

Patrick Kimutai Tum

Lecturer, Department of Chemistry, University of Nairobi, Kenya

Abstract:

Recently, the environmental impact of discharged untreated dye wastewater has received extensive attention. Herein, the paper investigated the photocatalytic degradation of dye Acid Orange 7 in a batch mode photoreactor fitted with a TiO₂ coated layer of dimensions (10cm×15cm). The coated layer was prepared by sedimentation from an aqueous suspension of $c=5 \text{ g.L}^{-1}$ and annealed at 300°C. Polychromatic sun beds lamps were used as a source of Ultra Violet (UV) light with maximum intensity at $\lambda=365 \text{ nm}$. A UV-Vis spectrophotometer monitored changes in dye concentrations at $\lambda_{\text{max}}=485 \text{ nm}$. Photocatalytic degradation of dye Acid Orange 7; $c=(2.5 \times 10^{-5} \text{ mol. L}^{-1})$ was determined by changes in dye concentration under UV light irradiation. The results show that dyes can be effectively degraded by TiO₂ photocatalyst and UV light of wavelength 300-400 nm. The effect of flow rate and inorganic salts (sodium carbonate, sodium sulfate) on dye Acid Orange 7 degradation was examined. The maximum absorption wavelength λ_{max} and maximum coefficient of molar absorptivity (ϵ) was determined at 485 nm and $20647 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The presence of CO₃²⁻ ions in the dye solution accelerated photocatalytic degradation by 35.8% and 39.3% after 30 minutes and 60 minutes of photocatalytic degradation. Dye photodegradation was reduced by 76.4% after 2.5 hours of photocatalytic treatment with SO₄²⁻ ions dissolved in dye solution. Presence of SO₄²⁻ ions showed no effect. Additionally, a flow rate of 50 lit/hr. was effective by 85.1% compared to 100 lit/hr. after 4 hours of photocatalytic degradation.

Keywords: Photocatalytic mineralization, Acid Orange 7, photoreactor, flow rate, inorganic salts

1. Introduction

1.1. Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) techniques are dependent on production of powerful oxidizing species that effectively treat wastewater (Fujishima and Rao, 1997; Ajmalet *al.*, 2014; Al Rasheed and Cardin, 2003). Advanced Oxidation Processes (AOPs) as a novel technique has been used to eliminate organic contaminants in wastewater (Bergaminiet *al.*, 2009). Photocatalysis as a novel wastewater treatment technique involves a light induced process that results in the oxidation of organic compounds by oxidation-reduction reactions activated by electron-hole pairs that form on the surface of powder catalysts i.e. semi-conductors (Chen *et al.*, 2011). The subsequent generation of hydroxyl radicals ($\bullet\text{OH}$), which are powerful oxidation species (2.8V vs. SHE) leads to non-selective reaction with the majority of electron-rich sites of organic pollutants. With Ultra Violet (UV) light irradiation and appropriate photocatalyst, electron/hole pairs with free electrons are produced in the unfilled conduction band, leaving positively charged holes in the valence band (Wojnarovits and Takacs, 2008). These electron/hole pairs initiate a chain of chemical reactions that mineralize organic contaminants into CO₂ and H₂O. This process involves the cleavage of the conjugated carbon-carbon double bonds found in polyphenols by ($\bullet\text{OH}$) radicals that causes decolourization of coloured wastewater and mineralization to CO₂ and H₂O (Chong *et al.*, 2010; Gogate and Pandit, 2004). The process gradually degrades organic contaminants and prevents formation of sludge and secondary pollution. Suitable powder photocatalyst including TiO₂ act as semi-conductor photocatalysts to degrade organic and inorganic pollutants into CO₂ and H₂O (Cernigoj, 2007; Bizaniet *al.*, 2006) readily eliminating from wastewater all organic contaminants. Practical applications in slurry type suspensions are limited due to draw-backs caused by catalyst separation after photocatalytic treatment (Cernigoj, 2007).

1.2. Photocatalytic Degradation Mechanism

The photogenerated holes formed after the excitation of electrons from the valence band to conduction band exhibit strong oxidizing potential. The excited electrons are scavenged by oxygen and reduced to form superoxides from Dioxygen (Fujishima *et al.*, 2000; Fujishima and Rao, 1997). Fujishima *et al.*, (2000) described the 'Honda-Fujishima effect' that involved the photochemical splitting of H₂O into H₂ and O₂ using titanium dioxide semi-conductor photocatalyst.

Photocatalysis was described as a novel cost effective and simple method to effectively mineralize organic contaminants in waste water into CO_2 and H_2O . This novel technique of wastewater treatment was referred to as the Advanced Oxidation Process (AOPs) (Demkov and Posadas, 2014; Hussein and Abass, 2010; Gaya and Abdulla, 2008). The photocatalytic degradation mechanism is illustrated in figure 1 below:-

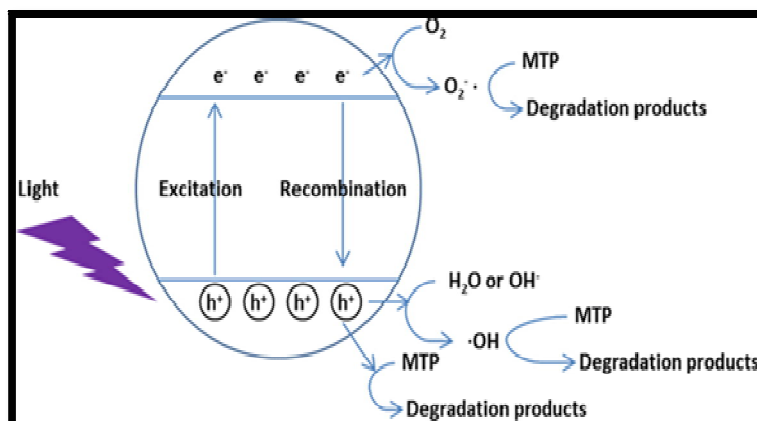


Figure 1: Photocatalytic Degradation Mechanism in Solutions with Oxidative and Reductive Species (Cernigoj, 2007)

1.3. Photocatalytic Oxidation and Photosensitized Oxidation

The first step in photocatalytic degradation process is absorption of UV light ($\lambda < 390$ nm) in TiO_2 and the production of electrons and holes in conduction band and valence band. The photogenerated holes that escape direct recombination reach the surface of TiO_2 and react with surface adsorbed hydroxyl groups or water to form trapped holes (Akpan and Hameed, 2009). The trapped hole is usually described as a surface-bound or adsorbed hydroxyl radical ($\bullet\text{OH}$). If electron donors are present at the TiO_2 surface, electron transfer may take place (Mahmoodiet al., 2006). In aerated systems, oxidative species, such as H_2O_2 generate from the reduction site. The excited electrons in the conduction band (CB), is scavenged by O_2 to form superoxide radicals ($\text{O}_2^{\bullet-}$) as illustrated in figure 1. Photosensitized oxidation, a photodegradation mechanism in the presence of visible light ($\lambda > 390$ nm) is different (Konstantinou and Albanis, 2004). In this oxidation process, dye absorbs visible light ($\lambda > 390$ nm) and injects an electron (e^-) on to the conduction band of TiO_2 (Guillardet al., 2003 ; Guillardet al., 2002). Excited dye converts to cationic dye radicals ($\text{Dye}^{\bullet+}$) and electron (e^-) in TiO_2 leads to the formation of several oxidation species ($\text{O}_2^{\bullet-}$, HO_2^{\bullet} or HO^{\bullet}).

1.4. Effect of Ions on Photocatalytic Degradation of Dye Solutions

Some inorganic anions such as SO_4^{2-} , ClO_4^- , H_2PO_4^- , may be adsorbed on the surface of TiO_2 in acidic environments by electrostatic attraction (Malatoet al., 2003). In alkaline solutions, such adsorption would be unlikely because of repulsive electrostatic forces. The addition of sulphate ions changes the surface charge of TiO_2 . Excess sulphate ions reduces the photocatalytic decolourization of selected dyes. The degradation of anionic Acid Orange 7 declines significantly with dissolved SO_4^{2-} ions (Thiruvengkatachariet al., 2008). Dissolved SO_4^{2-} ions in the dye solution trap hydroxyl ions (OH^-); this decreases the decolourization rate of dyes. Generally sulphate ions, especially at concentrations greater than 1×10^{-3} mol. L^{-1} , can lower photocatalytic degradation by 20-70% due to the competitive adsorption at the photoactivated reaction sites (Pelaezet al., 2012). The sulphate ions in the solution trap hydroxyl ions; this decreases the decolourization rate of dyes. Some inorganic anions such as SO_4^{2-} ions, are adsorbed on the surface of TiO_2 in acidic environments by electrostatic attraction. In alkaline solutions, such adsorption would be unlikely because of repulsive electrostatic forces. According to Pelaezet al., (2012) addition of sulphate ions changes the surface charge of TiO_2 affecting the Photocatalytic oxidation process (PCO). Excess sulphate ions block the photocatalytic decolourization of selected dyes. Fluoride ions affect the photodegradation of cationic and anionic dyes. An increase in fluoride ions concentration decreases the photodegradation of cationic and anionic dyes at strongly basic environments (Kubackaet al., 2011; Muruganadhamet al., 2014). When dye molecules are not adsorbed on the surface of TiO_2 , photodegradation is due to hydroxyl radicals ($\bullet\text{OH}$) and the addition of $\text{CH}_3\text{CH}_2\text{OH}$ or CH_3OH inhibits the photocatalytic degradation of dyes (e.g. Acid Red 14) but due to the fact that dyes are mostly strongly adsorbed (Daneshvaret al., 2003).

2. Experimental

2.1. Dye Studied, Formula and Physical Properties

Acid Orange 7 azo dye used in this study was supplied by Acros London. The purity of Acid Orange 7 used in the experiments is about 95%, with the remaining 5% comprising mainly of moisture. Dye Acid Orange 7 is orange in colour and commonly used for high temperature dyeing of wool in strong acid bath among other industrial uses. It has molecular formula $\text{HOC}_{10}\text{H}_6\text{N}=\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$ and molecular weight $350.32 \text{ g}\cdot\text{mol}^{-1}$. The physical and chemical Properties include stability at normal temperature and pressure, melting point of 164°C and its solubility in water $116 \text{ g}\cdot\text{L}^{-1}$.

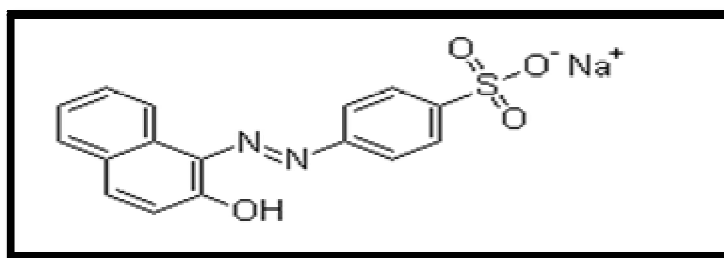


Figure 2: Structural Formula Acid Orange 7
(Guillard et al., 2002)

2.2. Preparation of TiO_2 Coated Layer and Acid Orange 7 Photocatalytic Degradation

The TiO_2 coated layer used in this study was prepared on a degreased and clean glass plate of dimensions (10×15cm) by sedimentation of a liquid suspension TiO_2 which was adjusted with nitric acid to a pH value of 3 and concentration of $c=5\text{ g.L}^{-1}$. The layer was then allowed to dry at ambient room temperature followed by annealing in a furnace at 300°C for 3 hours as shown in figure 5. Photocatalytic degradation of Acid Orange 7 dye was determined by changes in dye concentration in the photoreactor was used to determine the extent of degradation of an aqueous solution of Acid Orange 7, $c= (2.5\times 10^{-5}\text{ mol. L}^{-1})$ at a dye flow rate (i) 50 lit/hr. (ii) 100 lit/hr. The concentration of inorganic salts (Na_2CO_3 & Na_2SO_4) used in the experiment was 0.1 mol.L^{-1} .

2.3. Emission Spectra of UV Lamps and Absorption Spectra of TiO_2

Figure 2 below, shows the emission spectra of UV lamps and absorption spectra of TiO_2 used in this study.

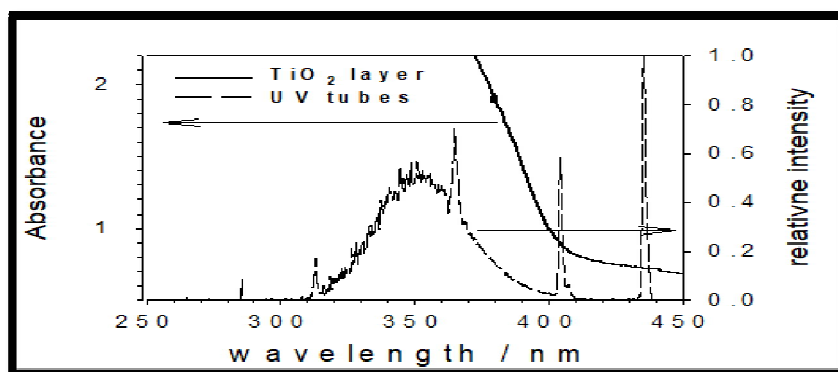


Figure 3: Emission Spectra of UV Lamps (Sylvania, Lynx CFS 11W BL350) and Absorption Spectra of TiO_2 Coated Layer

The spectra shown in figure 3 shows that UV lamps used radiated maximum intensity at $\lambda=365\text{ nm}$ and TiO_2 coated layer maximum absorption at $\lambda=380\text{ nm}$. These wavelengths (λ) lie within the UV region of the electromagnetic spectrum (EM).

2.4. Batch Mode Plate Photocatalytic Reactor

A perfectly mixed ideal batch mode flow-through reactor was fitted with a TiO_2 coated layer and a flowing film of Acid Orange 7 dye solution $c=2.5\times 10^{-5}\text{ mol.L}^{-1}$ flowed over the surface TiO_2 coated film (inclined at an angle of 10°) and irradiated by 3 fluorescent lamps (Lynx S, 11W, wavelengths ranging from 315 to 400 nm, maximum intensity at $\lambda=365\text{ nm}$ at a distance of 70 mm). The internal reactor temperature was regulated by an adjacent thermostat at around 23°C . The flow rate of the dye solution in the photoreactor was maintained throughout the experiments at (i) 50 lit/hr. (ii) 100 lit/hr. and dye volume at $v= 800\text{ mL}$. A scheme of the photoreactor and furnace are shown in figure 3 &4 below:-



Figure 4: Batch Mode Plate Photoreactor



Figure 5: Furnace Used for Annealing TiO_2 Coated Layers

2.5. Dye Acid Orange 7-Spectral Analysis

2.5.1. Maximum Absorption Wavelength (λ_{max})

Quartz cuvettes were used in the analysis. A cuvette was cleaned and dried using distilled water and linen tissue to ensure the transparent side remained clear. UV-Vis spectrophotometer (CECIL 2041) was switched on before the quartz cuvette (optical length 1 cm) containing distilled water (blank) was placed in the sample compartment with the transparent sides facing the UV light source and sample compartment lid closed. The auto zero button was pressed to set zero absorbance value. The maximum absorption wavelength (λ_{max}) value was then recorded for individual dye concentrations after a UV-Vis scan at $\lambda = 200-800$ nm.

2.5.2. Calibration Curve - Molar Extinction Coefficient (ϵ)

The extinction coefficient is derived from the Lambert-Beer law i.e. $A = \epsilon cl$ when the concentration of the dye solution and the length of the cuvette used are known:-

- A Absorbance
- ϵ molar absorption coefficient ($dm^{-3}.mol^{-1}.cm^{-1}$)
- c molar concentration ($mol.L^{-1}$)
- l Optical path length (cm)

To determine the molar extinction coefficient of Acid Orange 7 at $\lambda = 485$ nm the following concentrations of dye solutions were prepared from a stock solution of known concentration i.e. ($1 \times 10^{-5} mol.L^{-1}$, $2.5 \times 10^{-5} mol.L^{-1}$, $5 \times 10^{-5} mol.L^{-1}$, $7.5 \times 10^{-5} mol.L^{-1}$, $1 \times 10^{-4} mol.L^{-1}$). Using a cuvette of optic length 1 cm and a UV-Vis Spectrophotometer, absorbance values for each dye concentration was measured at wavelength $\lambda_{max} = 485$ nm determined in (section 2.5.1) Through a linear extrapolation of the data obtained a calibration curve was plotted to determine the molar extinction coefficient (ϵ).

2.6. Objectives

The objectives of the study was (i) determine the maximum absorption wavelength (λ_{max}) for dye Acid Orange 7 (ii) measure the absorbance of Acid Orange 7 for various solutions, calibrate the UV-Vis spectrophotometer and determine the molar extinction coefficient (ϵ) and (iii) determine the effect of flow rate and inorganic salts (Na_2CO_3 & Na_2SO_4) on photocatalytic degradation of dye Acid Orange 7.

3. Results and Discussion

3.1. Spectral Properties of Dye Acid Orange 7 (UV-Vis Spectroscopy)

The maximum absorption wavelength at (λ_{max}) for dye Acid Orange 7 ($c = 2.5 \times 10^{-5} mol.L^{-1}$) was determined by measuring dye absorbance between wavelength $\lambda = (200-800$ nm) as indicated in figure 6 below.

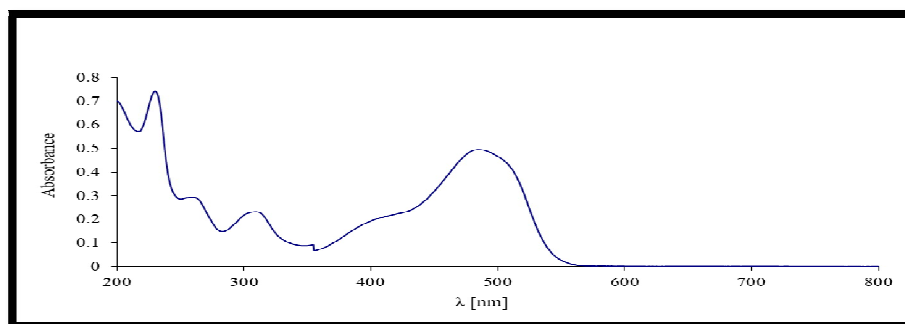


Figure 6: UV-Vis Spectra for Acid Orange 7

The results in figure 6 show the spectral properties of Acid Orange 7 i.e maximum absorption wavelength at $\lambda = 485$ nm which lies within the UV region of Electromagnetic Spectrum (EM). We observe minimal dye absorption of visible (Vis) in the range between $\lambda = (390-550$ nm) and near zero visible light (Vis) between $\lambda = 550-800$ nm. Dye Acid Orange 7 absorbs UV light effectively in the UV region.

3.2. Molar Extinction Coefficient (ϵ) - Calibration Curve

Figure 7 below shows a calibration curve for Acid Orange 7 using dye solutions of varying concentrations as described in (section 2.5.2).

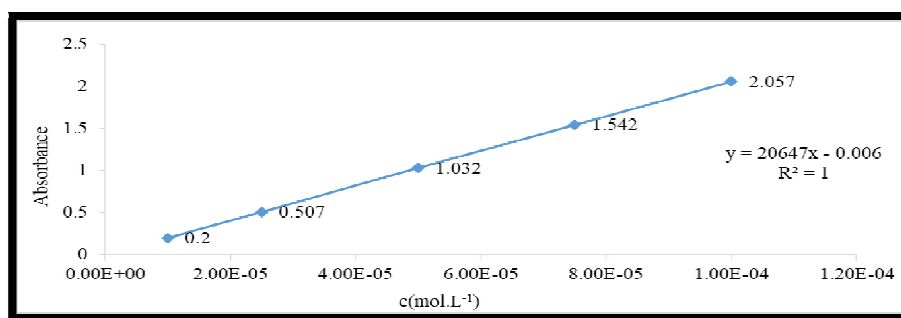


Figure 7: Calibration Curve - Dye Acid Orange 7

Maximum absorbance values were determined for individual dye solutions as described in (section 2.5.2) and a resulting calibration curve for Acid Orange 7 obtained. Using the data obtained a calibration curve was plotted as illustrated in figure 7. Using the linear extrapolation of the data obtained an experimental extinction coefficient value of $20647 \text{ dm}^{-3} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ was calculated. This value indicates that Acid Orange 7 dye absorbs light efficiently at $\lambda=485 \text{ nm}$, which lies in the UV region of the electromagnetic spectrum (EM).

3.3. Effect of Flow Rate

The effect of flow rate on dye Acid Orange 7 ($c=2.5 \times 10^{-5} \text{ mol.L}^{-1}$) photocatalytic degradation was determined and the findings are shown in figure 8 below:-

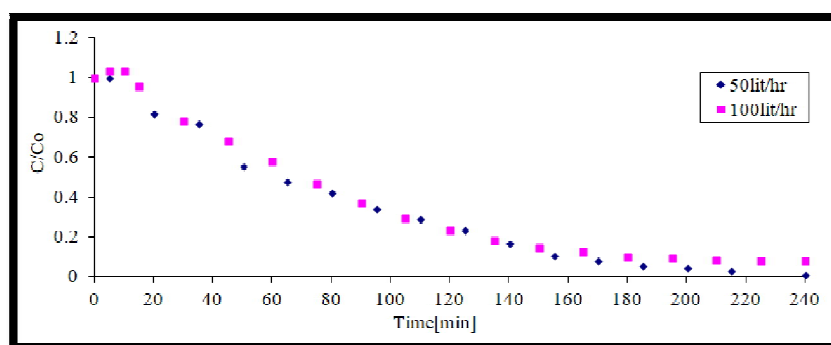


Figure 8: Photocatalytic Degradation of Acid Orange 7 at a Flow Rate (I) 50 Lit/Hr. (II) 100 Lit/Hr

The results show that after the initial 2 hours of photocatalytic degradation, dye flow rate indicated represented a minimal effect on dye Acid Orange 7 photodegradation. However, significant observations were observed after 4 hours of photocatalytic degradation. A slower flow rate i.e. 50 lit/hr. was seen to provide effective photodegradation by 85.1% compared to 100 lit/hr. We conclude from the observations in figure 8, that flow rate has a minimal effect in dye photodegradation up until 4 hours. For photodegradation after 4 hours a slower flow rate i.e. 50 lit /hr was proved more effective by 85.1% compared to 100 lit/hr.

3.4. Role of Inorganic Salts in Dye Solution (Na_2CO_3 , Na_2SO_4)

Figure 9 below shows the effect of inorganic salts dissolved in dye Acid Orange 7 ($c=2.5 \times 10^{-5} \text{ mol.L}^{-1}$) on photocatalytic degradation.

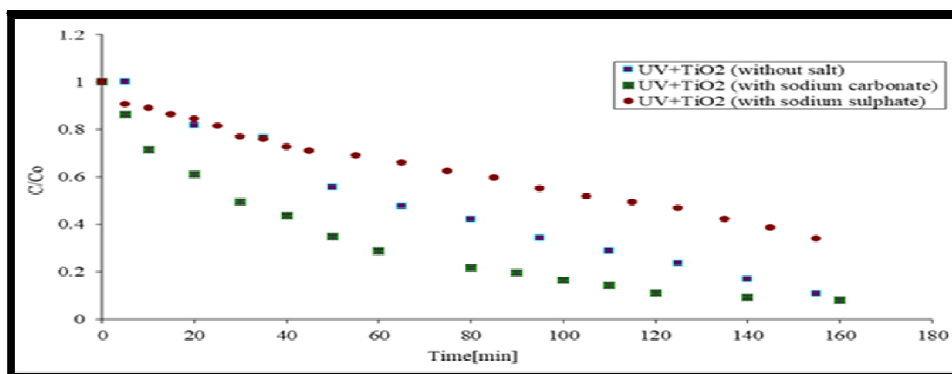


Figure 9: Effect of Inorganic Salts (Na_2CO_3 & Na_2SO_4 ; $c=0.1 \text{ mol.L}^{-1}$) on Dye Acid Orange 7 Photodegradation

From figure 9, we observe that the photocatalytic degradation of dye Acid Orange 7 greatly declined with SO_4^{2-} ions dissolved in the solution. Dissolved SO_4^{2-} ions significantly lowered dye photodegradation inactivating TiO_2 catalyst. From literature (Akpan and Hameed, 2009) dissolved sulphate ions in dye solutions at concentrations above 0.001 mol.L^{-1} decreases dye photocatalytic degradation by 20-70%. The possible explanation for the negative effect of SO_4^{2-} ions is their adsorption on the catalyst surface thus reducing the number of active sites in the catalyst i.e. the ions irreversibly deactivate the TiO_2 powder catalyst. We observe from the results in figure 9 that the presence of CO_3^{2-} ions in the dye solution accelerated photocatalytic degradation by 35.8% and 39.3% after 30 minutes and 60 minutes of degradation. Dye photocatalytic degradation was reduced by 76.4% after 2.5 hours of UV/ TiO_2 and SO_4^{2-} ions dissolved in the solution.

4. Conclusions

The present study found that Acid Orange 7 dye can be effectively degraded under UV light irradiation and TiO_2 coated layers. The presence of CO_3^{2-} ions in dye solution positively influenced photocatalytic degradation. However dissolved SO_4^{2-} ions in the dye negatively affected photodegradation making the TiO_2 coated layer less effective. The results confirm viability of microscopic glass as a suitable support for TiO_2 powder catalyst immobilization.

5. References

- i. Ajmal, A., Majeed, I., Malik, R. N., Idriss, H., & Nadeem, M. A. (2014). Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts: A comparative overview. *Rsc Advances*, 4(70), 37003-37026.
- ii. Akpan, U., & Hameed, B. (2009). Parameters affecting the photocatalytic degradation of dyes using TiO_2 -based photocatalysts: A review. *Journal of hazardous materials*, 170(2), 520-529.
- iii. Al-Rasheed, R., & Cardin, D. J. (2003). Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: Influence of TiO_2 , temperature, pH, and air-flow. *Chemosphere*, 51(9), 925-933.
- iv. Bergamini, R. B., Azevedo, E. B., & De Araújo, L. R. R. (2009). Heterogeneous photocatalytic degradation of reactive dyes in aqueous TiO_2 suspensions: Decolorization kinetics. *Chemical Engineering Journal*, 149(1), 215-220.
- v. Bizani, E., Fytianos, K., Poullos, I., & Tsiiridis, V. (2006). Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide. *Journal of hazardous materials*, 136(1), 85-94.
- vi. Cernigoj, U. (2007). Photodegradation of organic pollutants in aqueous solutions catalyzed by immobilized titanium dioxide: Novel towards higher efficiency, dissertation nova Gorica.
- vii. Chen, X., Liu, L., Peter, Y. Y., & Mao, S. S. (2011). Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science*, 331(6018), 746-750.
- viii. Chong, M. N., Jin, B., Chow, C. W., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: A review. *Water research*, 44(10), 2997-3027.
- ix. Daneshvar, N., Salari, D., & Khataee, A. (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2 . *Journal of Photochemistry and Photobiology A: Chemistry*, 162(2), 317-322.
- x. Demkov, A. A., & Posadas, A. B. (2014). *Integration of functional oxides with semiconductors*: Springer Science & Business Media.
- xi. Fujishima, A., & Rao, T. N. (1997). Recent advances in heterogeneous TiO_2 photocatalysis. *Journal of Chemical Sciences*, 109(6), 471-486.
- xii. Fujishima, A., Rao, T. N., & Tryk, D. A. (2000). Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 1(1), 1-21.
- xiii. Gaya, U. I., & Abdullah, A. H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 9(1), 1-12.
- xiv. Gogate, P. R., & Pandit, A. B. (2004). Sonophotocatalytic reactors for wastewater treatment: A critical review. *AIChE Journal*, 50 (5), 1051-1079.

- xv. Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., & Herrmann, J.-M. (2003). Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry*, 158(1), 27-36.
- xvi. Hussein, F. H., & Abass, T. A. (2010). Photocatalytic treatment of textile industrial wastewater. *International Journal of Chemical Sciences*, 8(3).
- xvii. Konstantinou, I. K., & Albanis, T. A. (2004). TiO₂ assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. *Applied Catalysis B: Environmental*, 49(1), 1-14.
- xviii. Kubacka, A., Ferrer, M., Fernández-García, M., Serrano, C., Cerrada, M. L., & Fernández-García, M. (2011). Tailoring polymer-TiO₂ film properties by presence of metal (Ag, Cu, Zn) species: Optimization of antimicrobial properties. *Applied Catalysis B: Environmental*, 104(3), 346-352.
- xix. Mahmoodi, N. M., Arami, M., Limaee, N. Y., Gharanjig, K., & Ardejani, F. D. (2006). Decolorization and mineralization of textile dyes at solution bulk by heterogeneous nanophotocatalysis using immobilized nanoparticles of titanium dioxide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 290(1), 125-131.
- xx. Malato, S., Blanco, J., Campos, A., Cáceres, J., Guillard, C., Herrmann, J., & Fernandez-Alba, A. (2003). Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale. *Applied Catalysis B: Environmental*, 42(4), 349-357.
- xxi. Muruganandham, M., Suri, R., Jafari, S., Sillanpää, M., Lee, G.-J., Wu, J., & Swaminathan, M. (2014). Recent developments in homogeneous advanced oxidation processes for water and wastewater treatment. *International Journal of Photoenergy*.
- xxii. Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., Dunlop, P. S., Hamilton, J. W., Byrne, J. A., & O'shea, K. (2012). A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Applied Catalysis B: Environmental*, 125, 331-349.
- xxiii. Thiruvengkatachari, R., Vigneswaran, S., & Moon, I. S. (2008). A review on UV/TiO₂ photocatalytic oxidation process (journal review). *Korean Journal of Chemical Engineering*, 25(1), 64-72.
- xxiv. Wojnarovits, L., & Takacs, E. (2008). Irradiation treatment of azo dye containing wastewater: An overview. *Radiation physics and chemistry*, 77(3), 225-244.
- xxv. Guillard, C., Beaugiraud, B., Dutriez, C., Herrmann, J.M., Jaffrezic, F., Renault, N.J., and Lacroix, M. (2002). *Applied Catalysis B: Environmental*, 39(4), pp.331-342.