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Rate of Photocatalytic Degradation of Acid Orange 7 Azo Dye on TiO₂ Coated Layers: Role of pH and Initial Dye Concentration

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Abstract:

This paper examined the role of pH and initial dye concentration on the rate of Acid Orange 7 photocatalytic degradation. A batch mode plate photocatalytic reactor fitted with a TiO₂ coated layer of dimensions (10cm×15cm) immobilized on microscopic glass was used. The coated layer was prepared by sedimentation from an aqueous suspension of 5 g.L⁻¹ phase and annealed at 300°C. Polychromatic sun beds lamps were used as a source of Ultra Violet (UV) light with maximum intensity at wavelength $\lambda = 365$ nm. An appropriate dye solution flow rate of 50 lit/hr was used. A UV-Vis spectrophotometer monitored changes in dye concentrations at $\lambda_{max} = 485$ nm. From changes in dye concentration during irradiation the rate of photocatalytic degradation was determined. The findings reveal that pH range 5 to 9 the degradation rate is almost constant, for pH values lower than 5 it marginally increases while for pH values above 9 it significantly decreases. Additionally the degradation rate increased significantly with increasing initial dye concentration in the range from (1×10⁻⁵ mol.L⁻¹ to 8×10⁻⁵ mol. L⁻¹). The amount of adsorbed Acid Orange 7 increases with increased dye concentration, however for concentrations greater than 1×10⁻⁴ mol. L⁻¹ it was observed that the increase was marginal. The findings confirm a direct correlation between the amount of dye adsorbed and resultant degradation rate. The optimum pH and initial dye concentration were determined ;[(pH= 3, $r = 1.6 \times 10^{-7}$ mol.m-2.s-1); (initial concentration = 8×10⁻⁵ mol.L⁻¹ to 1×10⁻⁴ mol.L⁻¹, $r = 3 \times 10^{-7}$ mol.m-2.s-1)]. A shift in dye solution pH from acidic to basic in the range 3 to 11.5 reduced photocatalytic degradation rates by 56.3%.

Keywords: Photocatalytic degradation rate, Acid Orange 7, initial concentration, pH, TiO₂ coated layer

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; Ajmal *et al.*, 2014; Al Rasheed and Cardin, 2003). Advanced Oxidation Processes (AOPs) have been used to remove organic contaminants in wastewater (Bergamini *et 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 (Chen *et al.*, 2011). The subsequent generation of hydroxyl radicals (\bullet OH), which are powerful oxidation species leads to non-selective reaction with the majority of electron-rich sites of organic pollutants. With UV light irradiation and selected 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 start 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 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; Bizani *et al.*, 2006) readily eliminating from wastewater all organic contaminants. Practical applications in slurry type suspensions is limited due to the challenges 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 possess 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' where they explained the photochemical splitting of H₂O into H₂ and O₂ using titanium dioxide semi-conductor photocatalyst. Photocatalysis was described as a cost effective and simple method to effective mineralization of organic molecules in waste water into CO₂ and H₂O. 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:-

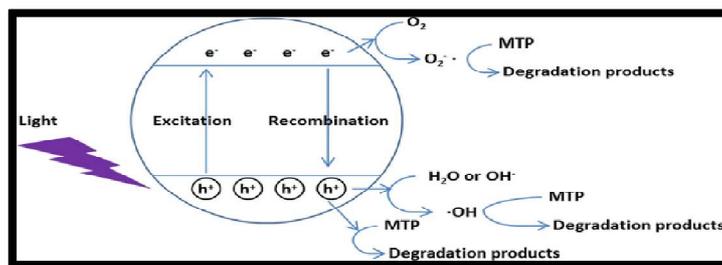


Figure 1: Photocatalytic Degradation Mechanism in Solutions with Oxidative and Reductive Species (Cernigoj, 2007)

1.2.1. Dye Photocatalytic Degradation and pH

The effect of pH is related to the ionization state of dye molecules onto the TiO₂ surfaces. The TiO₂ surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8) (Kansal *et al.*, 2007). The efficiency of photocatalytic processes strongly depends upon the pH of the reaction solution. This is due to the amphoteric nature of semi-conductors e.g. TiO₂ (Chong *et al.*, 2010). The surface-charge property of TiO₂ changes with solution pH. The point of zero charge (pzc) for TiO₂ at pH 6.8 (Al-Rasheed and Cardin, 2003; Wojnarovits and Takacs, 2008). The pH of dye solutions has been determined to affect its adsorption on the surface of the powder photocatalyst. The pH influences the loading characteristics of textile wastewater and in the reaction mechanisms contribute to dye degradation namely through hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron species in the conduction band (Cernigoj, 2007). Changes in the specification of the dye, protonation or deprotonation can change its adsorption characteristics and redox activity as shown in figure 1. The positive holes are considered as the major oxidation species as low pH whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels. In alkaline solutions hydroxyl radicals are generated by oxidizing more hydroxide ions available on TiO₂ surfaces enhancing efficiency of the process (Akpan and Hameed, 2009). At low pH, reduction by electrons in the conduction band contribute towards degradation of dyes due to the reductive cleavage of azo bonds. Subsequently the photocatalytic activity of anionic dyes (mainly sulphonated dyes) e.g. Acid Orange 7 maximizes in acidic environments (Kansal *et al.*, 2007). An additional explanation for the pH effects can be related to changes in dye specification i.e. protonation or deprotonation of the dye changes its adsorption characteristics and redox activity (Konstantinou and Albanis, 2004).

1.2.2. Dye Photocatalytic Degradation and Initial Concentration

The effect of substrate concentration on the rate of dye degradation is significant from a theoretical perspective and application. Generally dye degradation rates rise with increase in initial dye concentration (Konstantinou and Albanis, 2004; Akpan and Hameed, 2009). However the degradation efficiency of the dye decreases as the dye concentration further increases. At higher dye initial concentrations, the generation of hydroxyl radicals on the surface of catalyst is reduced as the dye ions permanently occupy active sites on the surface of the catalyst in addition to the 'UV screening effect' of the dye that effectively lowers the rate of dye degradation (Malato *et al.*, 2003). At high initial dye concentrations, a significant amount of UV light may be absorbed by dye molecules rather than by TiO₂ catalyst particles and thus reducing the efficiency of the catalytic reactions (Chong *et al.*, 2010; Malato *et al.*, 2003).

2. Experimental

2.1. Dye Studied, Formula and Physical Properties

Acid Orange 7 azo dye used in this study was supplied by SIGMA-ALDRICH. 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 HOC₁₀H₆N=NC₆H₄SO₃Na and molecular weight 350.32 g.mol⁻¹. Its physical and chemical properties include stability at normal temperature and pressure, melting point of 164°C and solubility in water 116 g/L⁻¹.

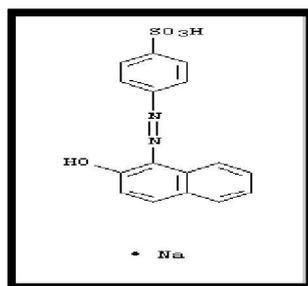


Figure 2: Structural Formula Acid Orange 7

2.2. Preparation of TiO₂ Coated Layer and Determination of Acid Orange 7 Photocatalytic Degradation Rates

The TiO₂ 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 TiO₂ which was adjusted with nitric acid to a pH value of 3 and concentration of 5 g.L⁻¹. The layer was then allowed to dry at room temperature and calcined in a furnace at 300°C for 3 hours. As a control the evaluation of the photocatalytic potential of the TiO₂ coated layer in a UV-TiO₂ and a UV only set-up 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 an initially optimised flow rate of 50 lit/hr. Subsequent experiments were done to determine the effect of pH and initial dye concentration on the rate of dye Acid Orange 7 degradation. The degradation rate of dye Acid Orange 7 was calculated using the formula shown below:-

$$r = \frac{V}{A} \frac{dc}{dt} \quad (1)$$

Where :-

| | |
|-------|------------------------------------------------------------|
| r | degradation rate [mol.m ⁻² /sec ⁻¹] |
| V | volume of dye [mL] |
| A | surface area of coated layer [m ²] |
| dc/dt | slope of the concentration versus time curve |

The emission spectra of the UV lamps used and the absorption spectra of TiO₂ are shown in Figure 3 below:

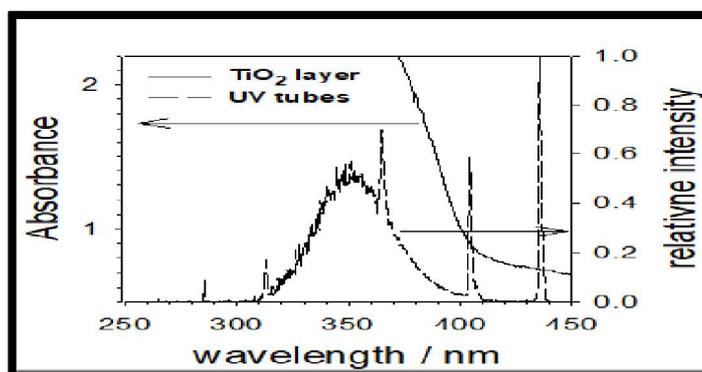


Figure 3: Emission Spectra of UV Lamps (Sylvania, Lynx CFS 11W BL350) and Absorption Spectra of TiO₂ Coated Layer

The spectra shown in figure 3 reveals that the UV lamps used for the study radiated maximum intensity at $\lambda=365$ nm and TiO₂ coated layer maximum absorption at $\lambda=380$ nm within the UV region of the electromagnetic spectrum (EM).

2.3. Batch Mode Photocatalytic Reactor

A perfectly mixed ideal batch mode flow-through reactor was fitted with a TiO₂ coated layer. The Acid Orange 7 dye solution run down over the surface TiO₂ catalyst (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 $\lambda=365$ nm) at a distance of 70 mm. The temperature inside the reactor was regulated by an adjacent thermostat at around 23°C. The flow rate of the dye solution in the photoreactor was maintained at 50 lit/hr and the volume was measured at 800 mL. A scheme of the photoreactor is shown in figure 4 below:-

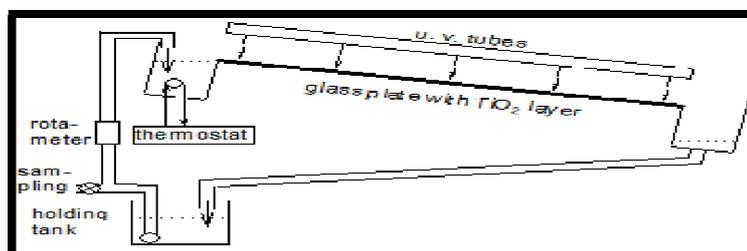


Figure 4: Schematic Representation of A Batch Mode Plate Reactor with Flowing Film of Dye Acid Orange 7 Solution, Glass Plate with TiO₂ Layer – Width, $W=0.1$ M, Length 0.15 M, Inclination Angle = 10°, Distance Between UV Light Lamps and TiO₂ Coated Layer = 0.7 M

3. Results and Discussion

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

The maximum absorption wavelength at (λ_{max}) for Acid Orange 7 was determined by measuring absorbance between the wavelength $\lambda=$ (200-800 nm). The results obtained is illustrated in figure 5 below.

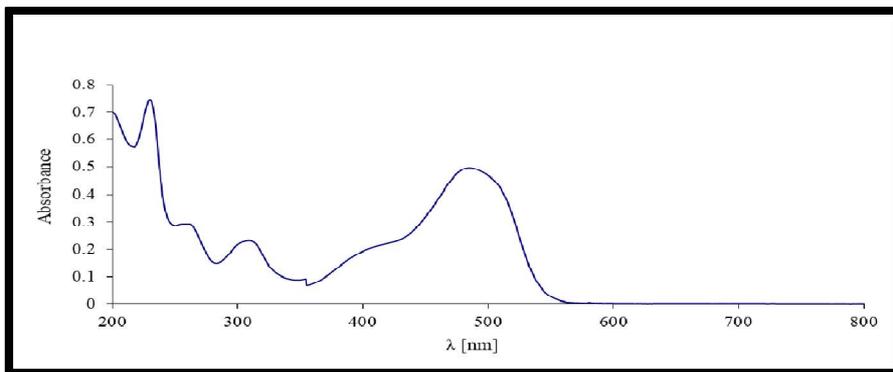


Figure 5: UV-Vis Spectra for dye Acid Orange 7 ($c=2.5 \times 10^{-5} \text{ mol.L}^{-1}$).

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

3.2. Optimization of Photocatalytic Degradation Reaction Conditions

The experimental conditions for the photocatalytic degradation of dye Acid Orange 7 were optimized as shown in figure 5 below:-

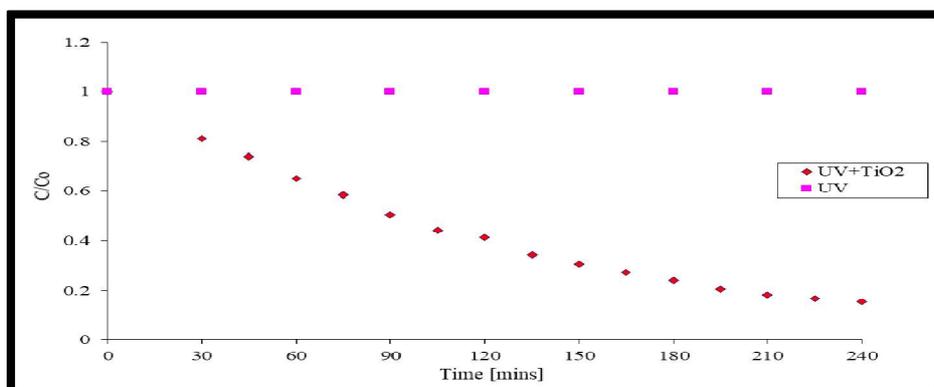


Figure 6: Photocatalytic Degradation of Acid Orange 7 $C= (2.5 \times 10^{-5} \text{ Mol. L}^{-1})$ with UV+TiO₂/UV System

The concentration of Acid Orange 7 declined consistently in a UV-TiO₂ photoreactor set-up over a period of 4 hours reflecting a significant photocatalytic activity of TiO₂ for Acid Orange 7 degradation. In the absence of TiO₂ catalyst i.e. coated layer but with UV light irradiation minimal dye degradation was observed as seen in figure 5 above. The application of a UV-TiO₂ system resulted in rapid photocatalytic degradation of the dye.

3.3. Effect of Initial Dye Concentration on the Rate of Dye Acid Orange 7 Photocatalytic Degradation

The role of initial dye concentration on the rate of photocatalytic degradation of dye Acid Orange 7 was determined and is shown in figure 7 below:-

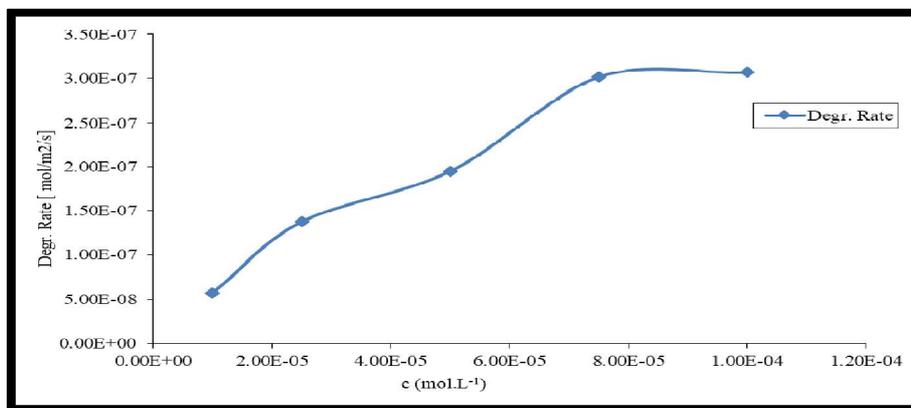


Figure 7: The Rate of Photocatalytic Degradation of Acid Orange 7 Dye for Various Initial Dye Concentrations

From the results in figure 7, the optimal initial dye concentration range to achieve maximum degradation rates was determined at ($c= 8 \times 10^{-5} \text{ mol. L}^{-1}$ to $1 \times 10^{-4} \text{ mol. L}^{-1}$). Additionally, increase in initial dye concentration in the range

(1×10^{-5} mol. L⁻¹ to 1×10^{-4} mol. L⁻¹) resulted in a corresponding increase in dye degradation rates by 83.3%. There is a direct correlation between the amount of dye adsorbed and resulting degradation rate.

3.4. Effect of Ph on the Rate of Dye Acid Orange 7 Photocatalytic Degradation

The role of pH on the rate of dye Acid Orange 7 photocatalytic degradation was determined is illustrated in figure 7 below:-

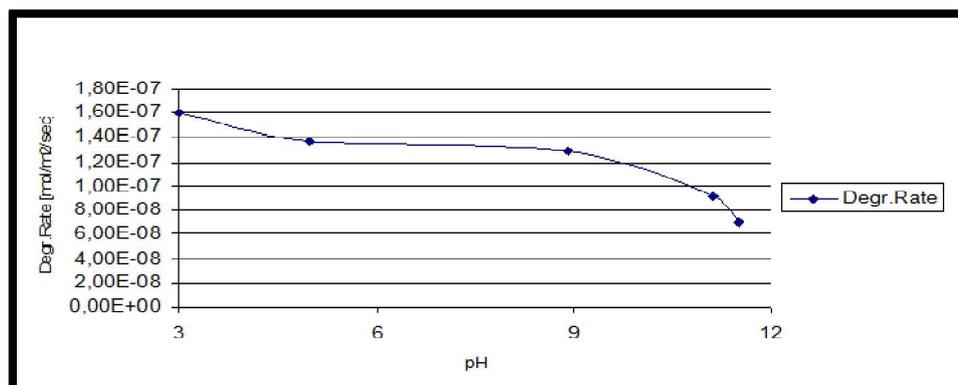


Figure 8: Effect of Dye Solution pH on the Degradation Rate, ($C=2.5 \times 10^{-5}$ Mol.L⁻¹)

From the results in figure 8, in the range of pH from 3 to 7, the degradation rate slightly decreases however for pH above 9, the decrease is pertinently significant. The optimal pH to achieve maximum dye degradation rates was determined; [(pH=3; $r=1.6 \times 10^{-7}$ mol.m⁻².s⁻¹)]. The results show that dye Acid Orange 7 dye is effectively degraded at in strongly acidic environments i.e pH=3. Overall, in the pH range from 4 to 9, dye degradation rate decreases by 18.8% and in the range 9 to 11.5, the degradation rates decline rapidly by 46.2%. Shift in dye pH from strongly acidic i.e. pH=3 to strongly basic i.e. pH=11.5 resulted in decreased degradation rates by 56.3%.

4. Conclusions

This study concludes that TiO₂ powder catalyst immobilized on microscopic glass showed great photocatalytic activity to degrade dye Acid Orange 7 under UV light irradiation. A direct correlation between amounts of dye adsorbed and resulting degradation rates was established. Variations in dye solution pH, significantly influenced the rate of dye Acid Orange 7 photocatalytic degradation. The results show that increased rates of dye degradation is achieved in strongly acidic environments. The role of pH and initial dye concentration is dependent on the dye type and TiO₂ catalyst particles properties. Studies on actual photocatalytic efficiency should be done prior to practical applications in large scale textile wastewater remediation.

5. References

- i. Ajmal, A., Majeed, I., Malik, R. N., Idriss, H., & Nadeem, M. A. (2014). Principles and mechanisms of photocatalytic dye degradation on TiO₂ 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 TiO₂-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 TiO₂, 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 TiO₂ suspensions: Decolorization kinetics. *Chemical Engineering Journal*, 149(1), 215-220.
- v. Bizani, E., Fytianos, K., Poullos, I., & Tsiroidis, 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.
- ix. 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.
- 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 TiO₂ 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. Hussein, F. H., & Abass, T. A. (2010). Photocatalytic treatment of textile industrial wastewater. *International Journal of Chemical Sciences*, 8(3).
- xvi. Kansal, S., Singh, M., & Sud, D. (2007). Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. *Journal of hazardous materials*, 141(3), 581-590.
- 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. 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.
- xix. Wojnarovits, L., & Takacs, E. (2008). Irradiation treatment of azo dye containing wastewater: An overview. *Radiation physics and chemistry*, 77(3), 225-244.