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# Study the Activity of Titanium Dioxide Nanoparticle Using Crystal Violet Dye

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### ABSTRACT

In this study, titanium dioxide nanoparticles were used to photocatalyze the breakdown of the dye crystal violet. The factors tested included the quantity of photocatalyst, concentration of crystal violet dye, effect of light intensity, and influence of PH. At a titanium dioxide nanoparticle concentration of  $0.14 \text{ g} 100 \text{ cm}^{3-1}$  and a dye concentration of 15 ppm, the maximum photocatalytic degradation of crystal violet dye was noted. The pH 6.4 and 8.22 mW cm<sup>2-1</sup> light intensities were beneficial for the photocatalytic breakdown of crystal violet dye. The first order of reaction is followed by the photocatalytic breakdown of crystal violet dye. Different quantities of titanium dioxide nanoparticles suspended in an aqueous solution of crystal violet dye were exposed to 125 watts of UV radiation in a vessel reactor to study the photocatalytic degradation of crystal violet dye.

# **Graphical Abstract:**



Effect of crystal violet dyeconcentration on photocatalytic degradation under UV irradiation, initial condition: amount of titanium dioxide nanoparticles =  $0.14 \text{ gm}/100 \text{ cm}^3$  and pH = 6.4.

Keywords: Photo catalytic, semiconductor, TiO<sub>2</sub>, crystal violet dye.

#### **INTRODUCTION**

Focus has switched in recent years to the photocatalytic destruction of synthetic dyes and other organic contaminants. For the photocatalytic destruction of organic and inorganic contaminants, titanium dioxide is frequently used [1, 2]. For the treatment of multi-pollutant synthetic wastewaters that are laden with copper cations and two industrial colors, BemacidBlau and Bemacid Rot, prepared fly ash-Titanium dioxide nanocomposite has been used [3].

Using photo-Fenton systems, modified fly ash (FA) combined with TiO2 photocatalyst has been used to remove various pollutants, including dyes and heavy metals [4]. For the photocatalytic degradation of certain dyes as methylene blue and Congo red, nanocrystalline TiO<sub>2</sub> were created using the sol-gel approach [5]. By utilizing  $TiO_2$  and ultraviolet radiation, Fujishima and Honda (1972) demonstrated that water may be split into hydrogen and oxygen [6]. Titanium dioxide and other semiconductors, such as ZnO, CdS, and others, have been extensively used in recent years for the photocatalytic destruction of a variety of contaminants, including organic dyes, insecticides, and water purification [7]. Basically the environmental pollution has been treated using conventional method include chemical, physical and biological processes, this processes are not always succeeded for treating pollutants, recently the advanced oxidation process (AOP) has been applied for dye removal and many other organics treated [8, 9], in which method the hydroxyl radical firstly generated to mineralized organic materials. When the titanium dioxide nanoparticle has been bombarded with energy equal or greater than the band gap of semiconductor the electrons shifted into the conduction band of semiconductor leaving a positive hole in the valence band [10-12]. Titanium dioxide nanoparticles' surface-adsorbed particles are reduced by the electrons in the conduction band, while an adsorbate-adsorbed pollutant is reacted with by the positive hole in the valance band [13].

$TiO_2 + hv \rightarrow$	$TiO_2(e_{CB} + h_{VB})^+$	(1)
$TiO_{2}(h_{VB})^{+} + H_{2}$	$O \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^+$	(2)
$TiO_{2}(h_{VB}^{+}) + O\overline{H}$	$\rightarrow$ TiO <sub>2 +</sub> OH'	(3)
$TiO_2(e_{CB}) + O_2$	$\rightarrow$ TiO <sub>2</sub> +O <sub>2</sub> <sup>-</sup>	(4)
$O_2^{-\cdot} + H^+ \rightarrow$	HO <sub>2</sub> •	(5)
Dye + OH $\rightarrow$	Degradation products	(6)
$Dye + h_{VB}^{+} \rightarrow$	Oxidation products	(7)
$Dye + e_{C\overline{B}} \rightarrow$	Reduction products	(8)

Crystal violet is a triarylmethane dye used in Gram's method of categorizing bacteria and as a histology stain (also known as methyl violet 10B or hexamethylpararosaniline chloride). Crystal violet was once used as a topical antiseptic and contains antibacterial, antifungal, and anthelmintic effects. Despite still being on the World Health Organization's list, the dye's medical applications have been mostly replaced by more advanced medications.



Structure of Crystal violet dye. www.joac.info

The term "gentian violet," which was once applied to a combination of methyl pararosaniline dyes (crystal violet), is now frequently used interchangeably with crystal violet. The name alludes to its color, which resembles the petals of a gentian flower; gentians or violets were not used in its creation[14].

# **MATERIALS AND METHODS**

The chemicals used in this work are listed below and all chemicals are standard without further purification.

- 1. Titanium dioxide nanoparticle (TiO<sub>2</sub>): Supplied by Fluka AG.
- 2. Crystal violet dye:supplied by sigma Aldrich.
- 3. Sodium hydroxide (NaOH): Supplied by Fluka AG.
- 4. Hydrochloric acid (HCl): Supplied by Fluka AG.

Research was conducted in a glass photochemical reactor. The cylindrical annular reactor has two components. The reaction solution was cooled using running water that was passed through the first component, an outside thimble. The reaction solution's temperature was kept at ambient temperature as a result of the ongoing cooling. The reaction solution  $(100 \text{ cm}^3)$  was placed in the reaction chamber along with the second component, an interior thimble.



Figure 1. Main parts of the photocatalytic cell used in Photocatalytic degradation of crystal violet dye.

### **RESULTS AND DISCUSSION**

**The Effect of dosage masses of Titanium dioxide nanoparticle on photocatalytic degradation of crystal violet dye:** To achieve the maximum crystal violet dye degradation efficiency, a series of studies were conducted with titanium dioxide nanoparticle dose masses ranging from 0.04 to 0.35 gm 100 cm<sup>3-1</sup>. The ideal circumstances under which all experiments were conducted were 15 ppm crystal violet dye, pH=6.4, 10 cm<sup>3</sup> min<sup>-1</sup> air bubble flow rate, and room temperature of 298 K. According to figure 2, the photocatalytic degradation of crystal violet dye increases as the quantity of titanium dioxide nanoparticles increases. The highest light-absorbing titanium dioxide nanoparticle concentration, 0.14 g 100 cm<sup>3-1</sup>, was used to achieve the highest percentage of photodegradation. Additionally, as titanium dioxide nanoparticle masses rise, an increase in the number of active sites and an improvement in the number. The proportion of degradation decreased as titanium dioxide nanoparticle loading mass was raised beyond 0.14g 100 cm<sup>3-1</sup>. This can be explained by the fact that

light will only be absorbed by the initial layers of crystal violet dye. In addition, the solution's turbidity has increased, which lessens the light's ability to pass through it, a phenomenon known as the "light screening effect." Moreover, titanium dioxide nanoparticles at large dosages scatter light As a result, the photocatalytic reaction is reduced [15, 16] because a portion of the titanium dioxide nanoparticle surface area is likely to diminish and become unavailable for photon absorption and crystal violet dye adsorption.



Figure 2. Effect of photocatalyst loading on photodegradation of o crystal violet dye using UV radiation, initial condition: 15 ppm crystal violet dye and pH = 6.4.

**2The Effect of initial concentration of crystal violet dye onphotocatalytic degradation processes:** Using 0.14g /100 cm<sup>3-1</sup> of titanium dioxide nanoparticle, PH=6.4, irradiated with 8.22 Mw cm<sup>2-1</sup> ultraviolet, flow rate of air bubble 10 cm<sup>3</sup> min<sup>-1</sup>, at room temperature, a series of experiments were conducted to investigate the effect of initial concentration range (15-40 ppm) on photocatalytic degradation process of crystal violet dye. Figure 3 displays a list of the outcomes. It has been found that as the initial concentration of crystal violet dye increases, the rate of photocatalytic degradation steadily decreases. This behavior may be explained by the fact that a concentration of 15 ppm was ideal for covering the most titanium dioxide nanoparticle particles. As a result, the titanium dioxide nanoparticle semiconductor was produced at a greater concentration by absorbing the most stimulating photons. Beyond 15 ppm of crystal violet dye, it is assumed that the active sites are covered by the dye, which may result in decreased formation of an electron-hole pair and thus decreased photodegradation efficiency. The extra crystal violet dye on the surface of the titanium dioxide nanoparticles stops light from passing through the successive layers of crystal violet dye, which is another factor that could be to blame for the decrease in photocatalytic degradation efficiency **[17, 18]**.



Figure 3. Effect of crystal violet dyeconcentration on photocatalytic degradation under UV irradiation, initial condition: amount of titanium dioxide nanoparticles =  $0.14 \text{ gm} / 100 \text{ cm}^3$  and pH = 6.4.



Figure 4. Kinetics studies of the photocatalytic degradation of crystal violet dyeunder UV irradiation, amount of titanium dioxide nanoparticles =  $0.14 \text{ gm}/100 \text{ cm}^3$  and pH = 6.4

The present experiment has been performed for investigated the order of reaction under optimized condition, 0.14 g 100 cm<sup>3-1</sup> of titanium dioxide nanoparticles, 8.22 mW cm<sup>2-1</sup>, pH=6.4.Plotting ln  $A_0/A_t$  versus Time give straight line as shown in figure 4, these resultsshow that the photocatalytic degradation of crystal violet dye follows the first order reaction [19].

**Effect of PH parameter on photocatalytic degradation of crystal violet dye:** Investigating the charge between the semiconductor surface and crystal violet dye at pH values between 2 and 10 was of interest for this parameter. The pH of the aqueous solution was altered using 0.01 N HCl and 0.01 N NaOH. Several tests have been carried out in the ideal conditions of 0.14 g100 cm<sup>3-1</sup> of titanium dioxide nanoparticles loaded mass, 15 ppm of crystal violet dye concentration, 10 cm min<sup>-1</sup> flow rate of air bubble, irradiated with 8.22 mW cm<sup>2-1</sup>, and room temperature. This process essentially consists of two phases, beginning with hydroxylated titanium dioxide nanoparticles (Ti-OH) in aqueous solution. In the second step, protons that have been absorbed by the hydroxide surface (Ti-OH) and an acidic medium (low pH) become positively charged and

 $Ti-OH + H^+ \rightarrow TiOH_2^+$  acidic medium ... (9)

 $Ti-OH + OH \rightarrow TiO + H_2Oalkaline medium \dots(10)$ 

Figure 5 shows that the photodegradation efficiency of crystal violet dye increased with increasing pH until it reached pH = 6.4 (the zero point charge of titanium dioxide =6.3), in which photocatalytic efficiency equals 93.71% because it produces the hydroxyl radical that is generated from oxidizing hydroxyl ions, while on the other hand increasing absorption of crystal violet dye on the surface of titanium dioxide nanoparticles. The photocatalytic breakdown of crystal violet dye above the titanium dioxide nanoparticles' zero point charge in alkaline medium has been steadily declining due to a reduction in the orange G dye absorbed on the titanium dioxide nanoparticles' negative charge surface.

The effect of light intensity on photo degradation of crystal violet dyeusing titanium dioxide nanoparticles: In the range of 2.15 to 8.22 mW cm<sup>2-1</sup>, several studies were conducted to study the impact of light intensity on the photocatalytic degradation of crystal violet dye. At a given mass of titanium dioxide nanoparticle ( $0.14 \text{ g} 100 \text{ cm}^{3-1}$ ), 15 ppm of crystal violet dye, a pH of 6.4, and a flow rate of an air bubble of 10 cm<sup>3</sup> min<sup>-1</sup> at room temperature, the rate of photodegradation of crystal violet dye rose with an increase in light intensity, as shown in figure 6. This may be explained by the increased electron-hole creation that was necessary for the titanium dioxide nanoparticle's electron transfer from the valence band to the conduction band; as a result, electron-hole recombination is minimal [21, 22]. The amount of light was 8.22 mW.



**Figure 5.** Photocatalytic degradation of crystal violet dye at variation initial pH using UV radiation, initial orange G dye concentrations = 15 ppm, amount of photocatalyst titanium dioxide nanoparticles = 0.14 gm/100 cm<sup>3</sup>,



Figure 6. The change of ( $A_t / A_0$ ) with irradiation time at the different light intensity with 0.14 gm/100cm<sup>3</sup> of titanium dioxide nanoparticles, pH=6.4, on photocatalytic degradation of crystal violet dye.



**Figure 7.** The change of Photocatalytic Degradation Efficiency with irradiation time at different light intensity, initial crystal violet dye concentrations=15 ppm, the amount of photocatalyst titanium dioxide nanoparticles=0.14 gm/100 cm<sup>3</sup>, and pH =6.4.

# CONCLUSION

- The photo degradation of Rohdamine B not degraded in absent of catalyst.
- The degradation of dye successfully degraded when used the catalyst with the light.
- The optimum condition for the Photocatalytic degradation of Rohdamine B (0.14 g 100 mL<sup>-1</sup> mass of TiO<sub>2</sub> and 15 ppm concentration of crystal violet dye.
- Photocatalytic Degradation Efficiency (P.D.E %) was 93.89 %.

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# REFERENCES

- M. A. Rosana, C. C. Maria, N. E. Marcos, F. J. Wilson, Catalyst deactivation in the gas phase destruction of nitrogen-containing organiccompounds using TiO<sub>2</sub>/UV–Vis, *Applied Catalysis B: Environmental*, 2000, 793, 1-9.
- [2]. M. Z. Mukhlish, F. Najnin, M. M. Rahman, M. J. J. Uddin, Photocatalytic Degradation of Different Dyes Using TiO<sub>2</sub> with High SurfaceArea: A Kinetic Study, *Sci. Res.*, 2013, 5(2), 301-314.
- [3]. V. Maria, A. Luminita, D. Anca, Fly ash-TiO<sub>2</sub> nanocomposite material for multi-pollutants wastewater Treatment, *Journal of Environmental Management*, **2015**, 150, 336-343.
- [4]. V. Maria, D. Anca, Methyl-orange and cadmium simultaneous removal using fly ash and photo-Fenton systems, *Journal of Hazardous Materials*, **2013**, 244, 773–779.
- [5]. A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, **1972**, 238, 37-38.
- [6]. A. Yadollah, H. A. Abdul, Z. Zulkarnain, A.Y. Nor, Photodegradation of o-cresol by ZnO under UV irradiation, *Journal of American Science*, **2011**, 7(8).
- [7]. M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, Ch. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review, *Chemical Engineering Journal*, **2016**, 284, 582–598.
- [8]. M. Abouzlam, R. Ouvrard, D. Mehdi. F. Pontlevoy, B. Gombert, N. VelLeitner, S. A. Boukari,  $H_{\infty}$  control for optimizing the advanced oxidation processes-Case of a catalytic cozonation reactor, *Control Engineering Practice*, **2015**, 44, 1–9.
- [9]. H. Suzuki, S. Araki, H. Yamamoto, Evaluation of advanced oxidation processes (AOP) using O<sub>3</sub>, UV, and TiO<sub>2</sub>for the degradation of phenol in water, *Journal of Water Process Engineering*, 2015, 7, 54–60.
- [10]. Z. Jeirani, A. Sadeghi, J. Soltan, B. Roshani, B, Rindall Effectiveness of advanced oxidation processes for the removal of manganese and organic compounds in membrane concentrate, *Separation and Purification Technology*, **2015**, 149, 110-115.
- [11]. M. Aline, S. Sales, A. Carlos, H. Martínez, G. Sergi, E. Abdellatif, B. Enric, Application of electrochemical advanced oxidation processes with a boron-doped diamond anode to degrade acidic solutions of Reactive Blue 15 (Turquoise Blue) dye, *Electrochimica Acta*, 2016, 197, 210–220.
- [12]. U. Akpan, B. Hameed, Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>based photocatalysts: A review, *Journal of Hazardous Materials*, **2009**, 170, 520–529.
- [13]. S. Yang, L. Lou, X. Wu, Y .Chen, Reaction sit and mechanism in the UV or visible light induced TiO<sub>2</sub> photodegradation of orange G, *Journal of Environmental Sciences*, 2006, 18(1), 180-183.
- [14]. H. Lachhe, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, M. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl

Red, Congo Red, Methylene Blue) in water by UV-irradiatedtitania, *Appl. Catal. B: Environ*, **2002**, 39, 75–90.

- [15]. M. Rachita, S. Menka, Comparative study of photo-degradation of dye Acid Orange-8 by Fenton reagent and Titanium Oxide- A review, *Pharma Chemica*, **2012**, 4(1), 311-319,
- [16]. Y. A. Hazim, The effect of coupled titanium dioxide and cobalt oxide on photocatalytic degradation of malachite green, *International Journal of Chem Tech Research*, 2016, 9(2), 227-235.
- [17]. H. Peidong, L. Mingce, Cobalt-catalyzedsulfate radical-based advanced oxidation: A review of heterogeneous catalysts and applications, *Applied Catalysis B: Environmental*, **2016**, 181, 103– 117.
- [18]. S. Jianguo, X. Zhen, L. Wei, C. Chang-Tang, KBrO<sub>3</sub> and graphene as double and enhanced collaborative catalysts for the photocatalytic degradation of amoxicillin by UVA/TiO<sub>2</sub> nanotube processes, *Materials Science in Semiconductor Processing*, **2016**, 52, 32–37.
- [19]. Y. A. Hazim, Y. M. Qasim, Prepared coupled ZnO-Co<sub>2</sub>O<sub>3</sub> then study the photocatalytic activities using crystal violet dye, *Journal of Chemical and Pharmaceutical Sciences*, 2016, 9(3), 1161-1165.
- [20]. L. Da-Rui, J. Yin –Shan, G. Gui-Mei, photocatalytic degradation of an azo dye using N-doped NaTaO<sub>3</sub> synthesized by one-step hydrothermal process, *Chemosphere*, **2011**, 83, 1546-1552.
- [21]. A. Yadollah, H. A. Abdul, Z. Zulkarnain, A. Y. Nor, Photocatalytic Degradation of p-Cresol by Zinc Oxide under UV Irradiation, *Int. J. Mol. Sci.*, **2012**, 13, 302-315.
- [22]. J. M. Herrmann, C. Guillard, P. Pichat, Heterogeneous photocatalysis: an emerging technology for water treatment, *Catalystiosday*, **1993**, 17, 7-20.