

## Kinetics study of photocatalytic decolorization of Diamond green B in the presence of titanium dioxide nano particles

Shiva Joohari \*

Assistant Professor of Physical Chemistry, Department of Basic Sciences, Yasooj Branch , Islamic Azad University, Yasooj, Iran;  
sh.joohari@iauyasooj.ac.ir; shjoohari@yahoo.com

### Abstract

The photocatalytic degradation of Diamond green B, a triarylmethane dye, has been investigated in aqueous heterogeneous solutions containing TiO<sub>2</sub> nano- particles as photocatalysts. The factors effective on the degradation of Diamond green B, such as the amount of catalyst, the original concentration of dye, the effect of pH and illumination time were investigated under 400 W high pressure mercury lamp at room temperature. The disappearance of the organic molecule follows approximately pseudo- first order kinetics according to the Langmuir- Hinshelwood model. The photodegradation rate constants, adsorption constants and observed rate constants were evaluated in the ranges of (217.40- 30.30) × 10<sup>-2</sup> mg. min<sup>-1</sup>.L<sup>-1</sup>, (2.72- 44.70) × 10<sup>-2</sup> L. mg<sup>-1</sup> and (3.5- 5.70) × 10<sup>-2</sup> min<sup>-1</sup> respectively.

**Key words:** Kinetics, Diamond green B, Decolorization, Nano- photocatalyst

### Highlights

- Photolysis of Diamond green B was carried out at various aqueous buffer pHs.
- Photocatalysis of Diamond green B was done using nano- titanium dioxide.
- The photodegradation processes obeyed from first order kinetic.

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\*Corresponding author

## Introduction

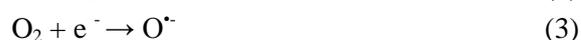
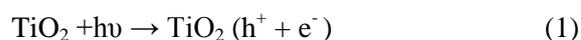
Azo dyes constitute an important class of synthetic, colored, organic compounds, which are characterized by the presence of one or more azo bonds (N=N). They represent about 50% of the worldwide dye production and are widely used in the textile industry and are therefore common industrial pollutants (1 & 2). Generally, presence of aromatics ring, metal ions and halides, especially chlorides in dyes structure increase their toxicity, carcinogenicity, genotoxicity, mutagenic and teratogenic property to living beings (3). They are produced in large amounts and may enter the environment during production and manufacturing process. Due to the stability of modern dyes, conventional biological treatment methods for industrial wastewater are ineffective, resulting often in an intensively colored discharge from the treatment facilities. Additionally, they are readily reduced under anaerobic conditions to potentially hazardous aromatic amines, etc (4 & 5).

Diamond green B has numerous industrial applications (dye used in fish farming industry as a fungicide, ectoparasiticide, disinfectant and using for dyeing of silk, leather, plastics paper and others) (6). This type of dyes may be easily reduced to their leuco forms, which have shown carcinogenic activity by producing toxicity to respiratory system and reduced fertility in humans (7).

For all these reasons, the development of new technologies of wastewater purification leading to complete destruction

of the contaminants becomes essential as the most suitable solution of the problem (8- 12).

Recently a number of research groups have dealt with the heterogeneous photocatalytic decomposition of this class of materials in the presence of UV- visible light with very encouraging results (13 & 14). Advanced Oxidation Processes include photo catalysis systems such as a semiconductor (TiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, etc.) and UV light (15). Among these semiconductor TiO<sub>2</sub> (with band gap energy 3.2 eV) and ZnO (with band gap energy 3.17 eV) were one of the best materials because of their suitable band gap energy and low cost. The general scheme of the photocatalytic destruction of organic compounds begins with its excitation by suprabandgap photons. When the semiconductor is irradiated with ultra violet light with photon energy greater or equal to the band gap energy of the semiconductor, valence band electrons are excited to the conduction band leaving a hole behind. These electrons and holes are considered the main species involved in the photodegradation process. Superoxide anion radicals O<sub>2</sub><sup>•-</sup> and hydroxyl radicals OH<sup>•</sup> produced by electron hole pairs in the aqueous medium are responsible to accelerate the oxidation of pollutants (Equation 1 - 3) (16- 18).



In this research we wish to report assisted Diamond green B decolorization in non- buffer solutions using  $\text{TiO}_2$  nanoparticles in a photocatalytic reactor under 400W high pressure mercury lamp and the influence of various parameters such as the effect of pH, irradiation time and catalyst dosage under air bubbling through the solutions is finally presented.

### Material and Method

**Chemicals and Instruments:** This study was an applied- experimental research which was performed in laboratory scale in the environmental chemistry laboratory of University of Yasouj. The Diamond green B, (C.I. Basic Green 4 C.I.) with classification Number of 42, 000, chemical formula of  $\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_{12}$  (M.W. = 927.00)  $\lambda_{\text{max}}$  of 617 nm was supplied by Sigma- Aldrich (M) Sdn Bhd, Malaysia and used as received.  $\text{TiO}_2$  nano- particles were provided from Sigma- Aldrich. Images of SEM and TEM for  $\text{TiO}_2$  (Fig. 1- 2) indicates randomly distributed nanoparticles with an average diameter of 70 nm for  $\text{TiO}_2$ . Other chemical materials used in these experiments were purchased from Merck Company, Germany. Concentration of dye was measured using spectrophotometer (UV/ Vis JASCO V-570). A photochemical set containing 400W high pressure mercury lamp was applied for photodecolorization experiments Diamond green B. Separation of photocatalyst from suspension was carried out with Sigma 301 centrifuge. pH measurements were made using F60 pH-meter.

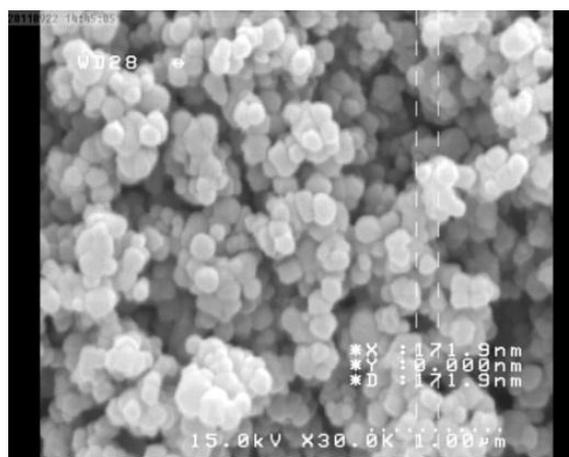


Fig. 1- SEM of nano- titanium dioxid used as photocatalyst

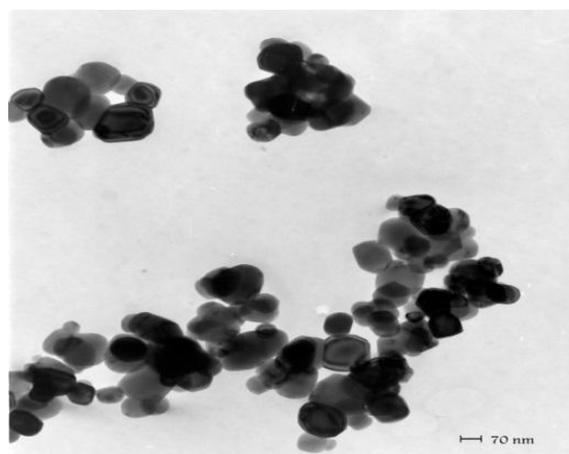


Fig. 2- TEM of nano- titanium dioxid used as photocatalyst

### General photo experiment method

Photocatalytic tests were performed in a Pyrex glass with a volume of 30 mL. The temperature was almost constant during the experiments (23- 25°C). An electrical magnetic stirrer with magnetic bar was used continuously so that reaction mixture can be uniformly. Since in various studies, different maximum wavelengths have been mentioned for Diamond green B dye, in order to determine the maximum wavelength of the given dye ( $\lambda_{\text{max}}$ ), UV/ V is spectrophotometer was used, and

Diamond green B dye absorption spectrum was prepared in the scope of 617nm. The reactions were performed using an immersion reactor fitted with a high pressure 400W mercury lamp. In all cases during the experiments, 30 ml of the Diamond green B solution containing the appropriate amount of the semiconductor powder was used. Initial concentrations of 25 ppm of dye were used for photo experiments at pHs of 5, 7 and 9 in non-buffer pH<sub>s</sub> solutions respectively. The required pH was adjusted by addition of diluted aqueous solution of HCl or NaOH. In this research, the amounts of catalyst, the original concentration of dye, the effect of pH and illumination time were measured.

**Diamond green B measurement:** The decolorization kinetics of Diamond green B irradiated solutions were followed using a UV- vis spectrophotometer. For each irradiation experiment, one sample (30 mL) was taken from the reactor and the final absorbance value was determined by aid of relative calibration curves that are easily obtained from drawing of absorbance-concentration plots for a series of standard non- buffer solutions of dye with above pHs at wave length of 617 nm.

## Results

**The effect of catalyst dosage:** Generally, increase in concentration of catalyst increases the number of active sites on the photocatalyst surface, which in turn increases the number of OH radicals. Beside, when the catalyst concentration increases to higher than the optimum value,

the degradation rate declines due to the interference of light by suspension (19- 22). So, choice of catalyst amount is important. The photocatalytic decolorization of Diamond green B solution in pHs of 5, 7 and 9 for non- buffer pH<sub>s</sub> with different dosages of nano TiO<sub>2</sub> was run for different times under high pressure 400W mercury lamp irradiation at room temperature. Fig. 3 shows absorbance as a function of irradiation time in the presence of different dosages of photocatalyst at all above pHs. It is observed that the absorbance is decreased with charging of photocatalyst so that the optimum dosages of photocatalyst are found at pHs of 5, 7 and 9 at 20, 15 and 15 mg respectively.

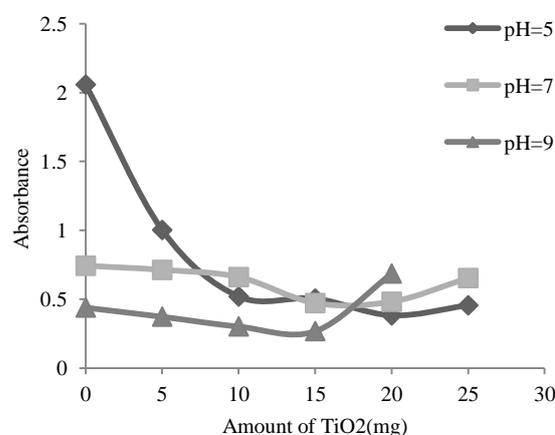


Fig. 3- The effect of photocatalyst dosage TiO<sub>2</sub> on the residual absorbance of Diamond green B (concentration: 25 ppm) in non- buffer pHs= 5, 7 and 9 at time= 60, 30 and 45 min.

**Absorbance- irradiation time discussion:** Effect of irradiation time on the removal of Diamond green B from aqueous solution by TiO<sub>2</sub> has been presented in Fig. 4. The experiments were carried out at room temperature, at 5, 7 and 9 none- pH<sub>s</sub> and the

dye concentration of Diamond green B was (25 mg / L). As the irradiation time increased, the residual absorbance of solution decreased to reach nearly total decolorization at non- buffer pHs= 5, 7 and 9 after 105, 50 and 70 min. Many compounds were decomposed entirely more than two hours [23], however, Diamond green B was decomposed almost entirely in less than two hours in this system for all pHs, it is suggested the catalyst is efficient for the degradation of this dye.

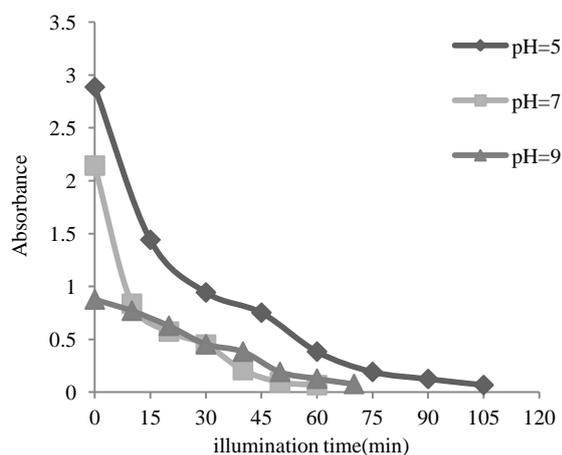


Fig. 4- The effect of irradiation time on photocatalytic decolorization of Diamond green B in non- buffer solution in present of TiO<sub>2</sub> (initial concentration: 25ppm)

**The effect of pH:** pH is one of the most important factors to control the removal of dye [24]. pH of the dye solution was studied with the change in pH. The pH of Diamond green B solution was adjusted in 5, 7 and 9 pHs. Fig. 5 depicts the percentage of decolorization of Diamond green B was found about 96% decolorization of dye at pH=7 in the presence of TiO<sub>2</sub> (50 min). It can be explained based on the higher concentration of hydroxyl radicals in this

neutral pH with respect to basic and acidic pHs [25]. The OH radicals produced have been considered to be the major active species responsible for the decolorization process and result in the enhancement of the efficiency of the process (26- 29).

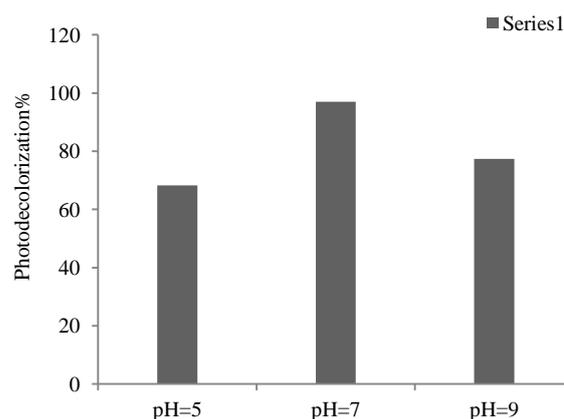


Fig. 5- The effect of non- buffer pHs on % photocatalytic decolorization of Diamond green B in present of TiO<sub>2</sub>.

**Kinetic investigation:** The photocatalytic decolorization of the Diamond green B in the presence of photocatalyst follows apparently pseudo- first order kinetics at low initial dye concentration and the rate expression is given by Eq. (4)

$$\ln \left( \frac{C_0}{C} \right) = K_{Obs} t \quad (4)$$

Where  $k_{obs}$  is the apparent first order rate constant (30 & 31).

The Diamond green B is adsorbed onto TiO<sub>2</sub> surfaces. Fig. 6 shows the plots of  $\ln(C_0/C_t)$  of Diamond green B versus irradiation time (where  $C_0$  is the initial concentration of Diamond green B, and  $C$  is its concentration at any time,  $t$ ) in non-buffer medias for TiO<sub>2</sub> catalyst that is found to be linear. According to equation

(4), the slopes of plots of  $\ln(C_0/C_t)$  of Diamond green B versus irradiation time are considered as observed rate constants ( $k_{obs}$ ) of photocatalytic process at various media. These evaluated rate constants have been summarized at Table 1. Among the acidic, neutral and basic media, the maximum value of  $k_{obs}$  for  $TiO_2$  is related to neutral media for non- buffer solution.

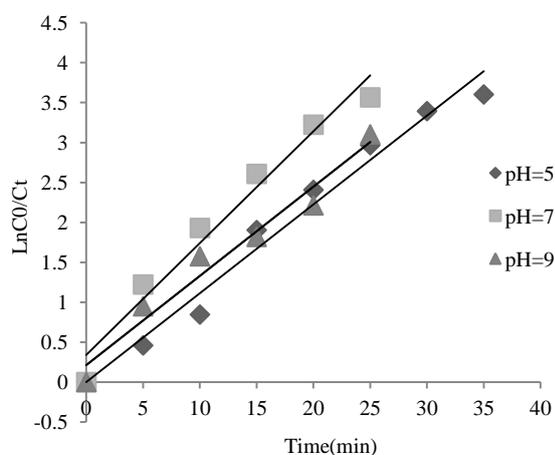


Fig 6- The plots of  $\ln C_0/C_t$  versus irradiation time at various non- buffer pHs in present of  $TiO_2$ .

The reaction mechanism of Diamond green B oxidation step has been well correlated by Langmuir–Hinshelwood (L–H) model, wherein the dye molecule is initially adsorbed on the catalyst surface and is further reacted by the first order reaction rate from the available active hydroxyl radicals.

The kinetic model is given as Eq.5.

$$R = k_r \frac{K_A C_0}{1 + K_A C_0} \quad (5)$$

Where  $k_r$  is the rate constant and the  $K_A$  is equilibrium adsorption constant.

The rate constant can be estimated by plotting data for reaction rate at different

initial concentration of Diamond green B. An equivalent expression for the Langmuir–Hinshelwood (L–H) kinetics is shown in Eq. 6.

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r} \quad (6)$$

Where R is the reaction rate and  $C_0$  is the initial concentration (32- 35).

Kinetic parameters of photodegradation of Diamond green B were obtained based on Langmuir- Hinshelwood (L- H) from the diagram of  $1/R$  versus  $1/C_0$  at various non- buffer pHs (Fig. 7) the slope and intercept of these diagrams are attributed to basic data for calculation of  $K_A$  (absorption constants) and  $k_r$  (photocatalytic degradation rate constants).

The obtained parameters from the diagrams of Fig. 7 have been collected in Table 1. The maximum of  $k_A$  is related to basic pH. The maximum of  $k_r$  is related to neutral pH.

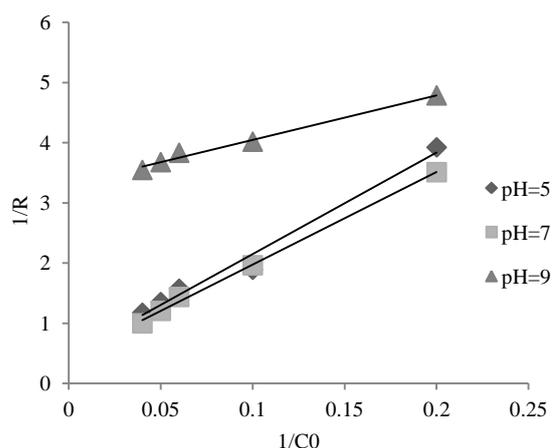


Fig.7 - The plots of  $1/R$  vs.  $1/C_0$  at various non- buffer pHs= 5, 7 and 9 at time= 15, 15 and 15 min (Langmuir- Hinshelwood kinetics model) in present of  $TiO_2$ .

Table 1 - Kinetic and thermodynamic parameters in photodegradation of Diamond green B in present of nano- titanium dioxide in non- buffer pH<sub>s</sub>

Parameter	pH=5	pH=7	pH=9
$K_A$ (L. mg <sup>-1</sup> )	$2.72 \times 10^{-2}$	$2.86 \times 10^{-2}$	$44.70 \times 10^{-2}$
$k_r$ (mg. min <sup>-1</sup> .L <sup>-1</sup> )	$217.40 \times 10^{-2}$	$227.30 \times 10^{-2}$	$30.30 \times 10^{-2}$
$k_{obs}$ (min <sup>-1</sup> )	$3.50 \times 10^{-2}$	$5.70 \times 10^{-2}$	$3.50 \times 10^{-2}$

## Discussion and Conclusion

In this study, photocatalytic assisted decolorization of Diamond green B in the presence of nano- titanium dioxide in some non- buffer solutions under irradiation by 400W high pressure mercury lamp has been reported. The effects of catalyst amount, non- buffer pHs and irradiation time on photocatalytic process were investigated. Pseudo- first- order rate constants at various non- buffer pHs were extracted. At the end, Langmuir- Hinshelwood parameters including  $K_A$  (adsorption-desorption constant) and  $k_r$  (decolorization rate constant) were evaluated at various buffer pHs.

## References

- (1) Ollgaard H., Frost L., Gastler J., Hensen O.C. Survey of Azo- Colorants on Denmark: Milgo Danish Environmental Protection Agency, 1999, Project 509.
- (2) Stolz A. Basic and applied aspects in the microbial degradation of azo dyes. *Applied Microbiology and Biotechnology* **2001**, *56*, pp 69- 80.
- (3) Robinson T., McMullan. G., Marchant R., Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology* **2001**, *77* pp 247- 255.
- (4) Dogan Uluozlu O., Sari A., Tuzen M., Soylak M. Biosorption of Pb (II) and Cr (III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. *Bioresource Technology* **2008**, *99*, pp 2972- 2980.
- (5) Sari A., Mendil D., Tuzen M., Soylak M. Biosorption of Cd (II) and Cr (III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal* **2008**, *144*, pp 1- 9.
- (6) Bidhendi G.N., Torabian A., Ehsani H., Razmkhah N, Iran. Evaluation of industrial dyeing wastewater treatment with coagulants and polyelectrolyte as a coagulant aid. *Journal of Environmental Health Science and Engineering* **2007**, *4*, pp 29- 36.
- (7) Srivastava S., Rangana S., Roy D. Toxicological effects of malachite green. *Aquatic Toxicology* **2004**, *66*, pp 319- 329.
- (8) Gregorio C. Non- conventional low- cost adsorbents to dye removal: A review. *Bioresource Technology* **2006**, *97*, pp 1061- 1085.
- (9) Chen J., Liu M., Zhang L., Zhang J., Jin L. Application of nano TiO<sub>2</sub> towards polluted water treatment combined with electro- photochemical method. *Water Research* **2003**, *37*, pp 3815- 3820.
- (10) Gao B., Peng C., Chen G., Puma G. Photo- electro- catalysis enhancement on carbon nanotubes/ titanium dioxide (CNTs/ TiO<sub>2</sub>) composite prepared by a novel surfactant wrapping sol- gel method. *Applied Catalysis B Environmental* **2008**, *85*, pp 17- 23.
- (11) Xiu F., Zhang F. Preparation of nano- Cu<sub>2</sub>O/ TiO<sub>2</sub> photocatalyst from waste printed circuit boards by electrokinetic process. *Journal of Hazardous Materials* **2009**, *172*, pp 1458- 1463.
- (12) Zhang J., Fu D., Xu Y., Liu C. Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO<sub>2</sub> as photocatalyst by response surface methodology. *Journal of Environmental Sciences* **2010**, *22*, pp 1281- 1289.
- (13) Habibi M.H., Karimi. B. Doctor blade sol- gel deposition of a nano- composite copper- zinc oxide on borosilicate glass for advanced oxidative degradation of textile dye in water environment. *Iranian Journal of Environmental Technology* **2015**, *1(1)*, pp 31- 38.
- (14) Montazerzohori M., Malekhoseini M., Joohari S. Photolytic and photocatalytic decolorization of Lauth's violet using nano- titanium dioxide: A kinetics study. *Iranian Journal of Environmental Technology* **2015**, *1*, pp 39- 48.

- (15) Awitor K., Rafqah S., Gérantona; G., Sibaud Y., Larson P., Bokalawela R., et al. Photocatalysis using titanium dioxide nanotube layers. *Journal of Photochemistry and Photobiology A: Chemistry* **2008**, 199, pp 250- 254.
- (16) Gaya U. I., Abdullah A. H. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2008**, 9, pp 1- 12.
- (17) Gaya U. I., Abdullah A. H., Zainal Z., Hussein M. Z. Photocatalytic Degradation of 2, 4- dichlorophenol in Irradiated Aqueous ZnO Suspension. *International Journal of Chemistry* **2010**, 2, pp 180- 189.
- (18) Chakrabarti S., Dutta B. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *Journal of Hazardous Materials* **2004**, 112, pp 269- 278.
- (19) Chen Y. B., Wang X. X., Fu X. Z., Li Y.L. Photocatalytic degradation process of azo dye congo red in aqueous solution. *Journal of Catalysis*. **2005**, 26, pp 37- 42.
- (20) Chakrabarti S., Dutta B. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *Journal of Hazardous Materials* **2004**, 112, pp 269- 278.
- (21) Huang M., Xu C., Wu Z., Huang Y., Lin J., Wu J., Photocatalytic discolorization of methyl orange solution by Pt modified TiO<sub>2</sub> loaded on natural zeolite. *Dyes and Pigments* **2008**, 77, pp 327- 334.
- (22) Konstantinou I., Albanis T. TiO<sub>2</sub>- assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. *Applied Catalysis B: Environmental* **2004**, 49, pp 1- 14.
- (23) Yang Y., Guo Y. H., Hu C. W., Wang E. B. Lacunary Keggin- type polyoxometalates- based macroporous composite films: preparation and photocatalytic activity. *Applied Catalysis A: General* **2003**, 252, pp 305- 314.
- (24) Zhu X., Yuan C., Bao Y., Yang J., Wu Y., Mol. J. Photocatalytic degradation of pesticide pyridaben on TiO<sub>2</sub> particles. *Journal of Molecular Catalysis A* **2005**, 229, pp 95- 105.
- (25) Matthews R. W. Photocatalytic oxidation and adsorption of methylene blue on thin films of near- ultraviolet- illuminated TiO<sub>2</sub>. *Journal of Chemical Society Faraday Transaction 1* **1989**, 85, pp 1291- 1302.
- (26) Ishibashi K., Fujishima A., Watanabe T., Hashimoto, K. Detection of active oxidative species in TiO<sub>2</sub> photocatalysis using the fluorescence technique. *Electrochemical Communication* **2002**, 2, pp 207- 210.
- (27) Ishibashi K., Fujishima A., Watanabe T., Hashimoto K. Quantum yields of active oxidative species formed on TiO<sub>2</sub> photocatalyst. *Journal of Photochemistry and Photobiology A: Chemistry* **2000**, 134, pp 139- 142.
- (28) Xiang Q., Yu J., Wong P. K. Quantitative characterization of hydroxyl radicals produced by various photocatalysts. *Journal of Colloid Interface Sciences* **2011**, 357, pp 163- 167.
- (29) Xiang Q., Yu J., Cheng B., Ong H.C. Microwave- hydrothermal preparation and visible- light photoactivity of plasmonic photocatalyst Ag- TiO<sub>2</sub> nanocomposite hollow spheres. *Chemistry an Asian Journal* **2010**, 5, pp 1466- 1474.
- (30) Grzechulska J., Morawski A.W. Photocatalytic decomposition of azo- dye acid black 1 in water over modified titanium dioxide. *Applied Catalysis B: Environmental* **2002**, 36, pp 45- 51.
- (31) Sapawe N., Jalil A.A., Triwahyono S. One- pot electro- synthesis of ZrO<sub>2</sub>- ZnO/ HY nanocomposite for photocatalytic decolorization of various dye- contaminants. *Chemical Engineering Journal* **2013**, 225, pp 254- 265.
- (32) Basu S., Brockmana A., Gagareb P., Zhenga Y., Ramachandranb P.V., Delgassb W.N. Chemical kinetics of Ru- catalyzed ammonia borane hydrolysis. *Journal of Power Sources* **2009**, 188, pp 238- 243.
- (33) Ahsan Habib Md., Ibrahim Ismail I. M., Mahmood A. J., Rafique Ullah Md. Photocatalytic decolorization of Brilliant Golden Yellow in TiO<sub>2</sub> and ZnO suspensions. *Journal of Saudi Chemical Society* **2012**, 16, pp 423- 429.
- (34) Palominos R.A., Mora A., Mondaca M.A., Perez-Moya M., Mansilla H.D. Oxolinic acid photo- oxidation using immobilized TiO<sub>2</sub>. *Journal of Hazardous Materials* **2008**, 158, pp 460- 464.
- (35) Sun J., Wang X., Sun J., Sun R., Sun S., Qiao L., Photocatalytic degradation and kinetics of Orange G using nano- sized Sn (IV)/ TiO<sub>2</sub>/ AC photocatalyst. *Journal of Molecular Catalysis A: Chemistry* **2006**, 260, pp 241- 246.

## مطالعه سینتیک رنگ زدایی نور کاتالیزوری دیاموند گرین در حضور نانوذرات تیتانیم دی اکسید

شیوا جوهری\*

استادیار شیمی فیزیک، واحد یاسوج، دانشگاه آزاد اسلامی، یاسوج، ایران، sh.joohari@iauyasooj.ac.ir

### چکیده

در پژوهش حاضر، تخریب نور کاتالیزوری رنگ دیاموند گرین در حضور کاتالیزور تیتانیوم دی اکسید نانوساختار بررسی شد. عامل‌های مؤثر بر فرآیند تخریب مانند مقدار فوتوکاتالیزور، غلظت رنگ، اسیدیته محیط و زمان تابش تحت تابش لامپ پر فشار جیوه در دمای محیط بررسی شد. نتایج نشان داد، حذف رنگ از معادله لانگمویر-هینشل وود تبعیت می‌کند. ثابت‌های سرعت تخریب، ثابت‌های جذب و ثابت‌های سرعت مشاهده شده به ترتیب در محدوده‌های  $10^{-2} \text{ mg. min}^{-1} \cdot \text{L}^{-1}$  (۳۰/۳۰ - ۲۱۷/۴۰)،  $10^{-2} \text{ L. mg}^{-1}$  (۲/۷۲ - ۴۴/۷۰) و  $10^{-2} \text{ min}^{-1}$  (۳/۵ - ۵/۷۰) ارزیابی شدند.

**واژه‌های کلیدی:** سینتیک، دیاموند گرین، رنگ زدایی، نانو فوتوکاتالیزور

\* نویسنده مسؤول مکاتبات، shjoohari@yahoo.com

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