Kinetic and Thermodynamic Study of the Photocatalytic Decolourization of Light Green SF Yellowish (Acid Green 5) Dye using Commercial Bulk Titania and Commercial Nanotitania

Mohammed T. Eesa[1], Amer M. Juda[2], Luma M. Ahmed[3]

[1, 2]Chemistry Department, College of Science, Kufa University, Najaf, Iraq

[b]Chemistry Department, College of Science, Kerbala University, Kerbala, Iraq

Abstract: *In this work, Light Green SF Yellowish (LGSF) dye was removed from aqueous solution at normal pH equal to 7.3in the presence of bulk and nanoTiO$_2$ under UV-A light. The decolourization process of this dye at optimum conditions obeyed pseudo-first order kinetics. Based on the kinetic study, the activation energies for decolorization of dye employing the commercial bulk TiO$_2$and commercial nano TiO$_2$were found to be 48.676 kJ mol^{-1} and 37.032kJ mol^{-1} respectively. Further, thermodynamic studies showed that the photocatalytic decolourization of this dye is an endothermic andnon-spontaneous reaction.*

Keywords: Light Green SF Yellowish dye, Titania, Photocatalysis, Decolourization, Treatment of organic pollutants.

1. Introduction

Triphenylmethane (TPM) dyes belong to the class of polymethine dyes. This class contains two aryl rings and R group bonded to the central methine carbon creating the branches, in which the polymethine chain is combined [1], [2].Moreover, these dyes have auxochromic and bathochromic groups such as hydroxyl and amino groups in a para position to the methane carbon, hence, these dyes absorb strongly in the visible region and have brilliant colours ranging from red to blue shades.[3], [4].

At the outset, these dyes were prepared without knowledge of their constitution principle. In 1859 Verguin developed the first industrial production process for Fuchsin[2].

Light Green SF Yellowish (LGSF) dyewith the structural formula $C_{37}H_{34}N_2Na_2O_9S_3$, also known as Acid green 5 and Lissamine green SF, is an acidic triarylmethane-type that dissociate to form a colored anion. Moreover, this dye is manufactured as a dyestuff for wool dying closely [5]–[7].

LGSF is widely utilized as a stain in cell, eye membranes, cytoplasm, retina, microorganisms, endoscope, proteins and hairs. It also has several biological applications and is used in cosmetics, sunscreen, oral hygiene products, detecting proteins and treating apolipoprotein E-related diseases. From the other hand, it has multiple industrial applications and is used in color filters, adhesives, detergents, inks, highlighters, photographic materials, recording materials, leathers and textiles. The disadvantages of using LGSF are acute toxicity, chronic toxicity, carcinogenicity, genotoxicity, mutagenicity and retinal toxicity [6], [7]. The removal of different kinds of Triphenylmethane dyes was reported in literatures by various alternative techniques such as adsorption [8]–[10], bacterial consortium [11], biodegradation using different plants[12], [13], photodegradation [14]–[16].

The present study focused on the investigation of the efficiency of a commercial bulktitania and commercial nanotitania as photocatalysts to decolourize Light Green SF Yellowish dye from aqueous solution, followed by the investigation of the thermodynamics functions and activation energy at the optimum conditions.

2. Experimental

The commercial TiO$_2$ – Degussa P25 (particle of ca.44 nm) was supplied by Fluka-Germany, while the commercial nano TiO$_2$ (particle size of ca.18nm) was purchased from Chemlab- China.

LGSF(M.wt = 792.85 g/mol, λ_{max} = 640 nm) was obtained from Avantor Performance Materials and used without further purification. The respective chemical structure is shown in Figure 1.
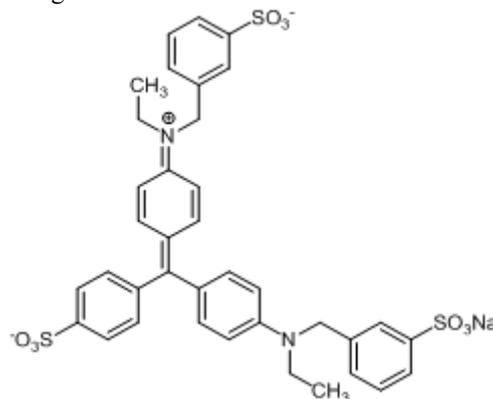
Figure 1: Chemical structure of LGSF.

2.1. Light source and photoreactor

400 cm^3 cylindrical glass reactor was used to perform irradiation, which was provided by 400W high pressure mercury lamp (HPML) (Rudium, China).

Photon flux of the UV radiations reaching the reactor was measured through chemical actinometry [21] and was found to be 1.409×10^{-7} Einstein s^{-1}.

2.2. Photocatalyticexperiments

Definite amount of the photocatalyst (bulk titania or nano titania) and 100 cm^3 of aqueous solutions of Light Green SF Yellowish dye were mixed in a 400 cm^3 beaker and stirrred by Labtech magnetic stirrer. The suspension was stirred in darkness for 30 min in order to reach the adsorption desorption equilibrium. Subsequently, the suspension was exposed to UV-A light. At regular intervals; about 3 cm^3 of reaction mixture was sampled and centrifuged for 15 min at 4000 rpm. The supernatant was carefully transformed into a new plastic tube and centrifuged again at the same speed and time to ensure the total removal of fine TiO$_2$ particles from the solution. The docolourization of LGSF solution was monitored via measuring absorbance with a UV-Vis spectrophotometer (model: Cary 100Bio)at the maximum wavelength 640 nm.

3. Results and Discussion

3.1. Photocatalytic Kinetic Analysis

Langmuir-Hinshelwood (L-H) model was crucial to estimate the order of photoreaction, and the apparent rate constant (k$_{app}$) was determined using the following equations [17]–[19]:

$$C_t = C_0 \exp^{(-k_{app} \cdot t)} \qquad (1)$$

where: C$_o$ is an initial concentration of used dye at time of irradiation equal to 0 min. Ct is a concentration of the same dye at time t of irradiation.

$$\ln \frac{C_0}{C_t} = k_{app} \cdot t \qquad (2)$$

The photocatalytic decolourization efficiency [20] was determined using equation (3).

$$\% \text{ Effeciency} = (\frac{C_0 - C_t}{C_0}) \times 100 \qquad (3)$$

where: C$_0$= the concentration of LGSF dye solution at time equal to 0 min, and C$_t$ is the concentration of dye solution after time equal to t min.

3.2. Preliminary experiments

Series of preliminary experiments were performed and the results are expressed in figure 2.In the absence ofUV light and photocatalyst (dark reaction) and under environmental O$_2$ gas, the reaction was never taken place, that proved no electron-hole pairs created.Onthe other hand, the results of the photolysis process (absence of the photocatalyst) explain a very slight reaction. These results are in good agreement with the interpretations reported in literature [22].

$$\text{TiO}_2 \text{ or nano TiO}_2 + \text{Dye} + \text{O}_2 \rightarrow \text{No reaction (Dark reaction)} \qquad (5)$$

$$h\nu + \text{Dye} + \text{O}_2 \rightarrow \text{No reaction} \qquad (6)$$
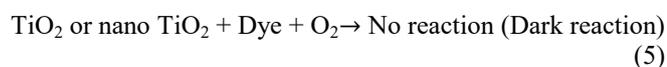
In the photocatalytic reaction underenvironmental O$_2$gas, the dye solution decolorizedas the time of illumination increased. The results proved that the presence of a photocatalyst and UV light are essential requirements for photo-decolorization of any dye [16], [23]–[24].

$$\text{TiO}_2 + h\nu + \text{Dye} + \text{O}_2 \rightarrow \text{Reaction} \qquad (7)$$

$$\text{Nano–TiO}_2 + h\nu + \text{Dye} + \text{O}_2 \rightarrow \text{Reaction} \qquad (8)$$
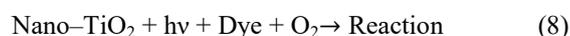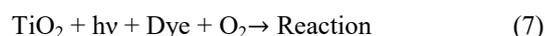
The photocatalytic reaction using bulk titania or nano titania to decolorize LGSF dye followed the first orderplots.
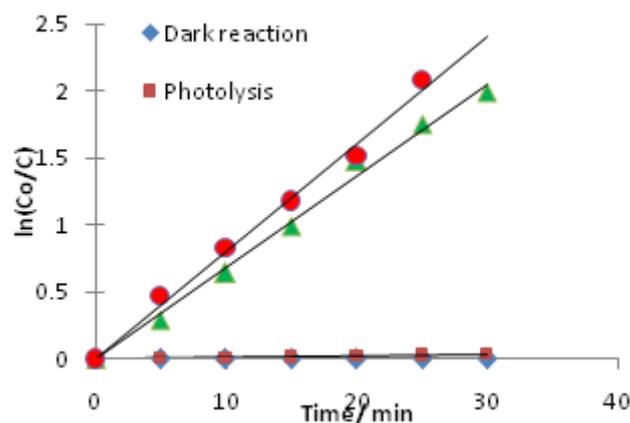
Figure 2: Preliminary experiments, with catalyst dose of Bulk TiO$_2$andNano TiO$_2$ equal to 175 mg/100ml with 30 ppm and 20 ppm of LGSF dye respectively, T=293.15 K.

3.3. Effect of Dye Concentration

The photocatalytic decolourization of LGSF dye has been determined in aqueous suspension of bulk TiO$_2$ and nano TiO$_2$ as a function of irradiation time.

Table 1: The relationship between conc. of LGSF dye with bulk TiO$_2$ as photocatalyst and apparent rate constant and half time

LGSF dye conc./ ppm	Apparent rate constant k/ min^{-1}	Half time $t_{1\backslash 2}$ / min
20	0.0599	11.5717
30	0.0594	11.6691
40	0.0402	17.2424
50	0.0374	18.5333

Table 2: The relationship between conc. LGSF dye with nano TiO$_2$ as photocatalyst and apparent rate constant and half time

LGSF dye conc./ ppm	Apparent rate constant k/ min-1	Half time $t_{1\backslash 2}$ / min
15	0.0803	8.6319
20	0.0403	17.1996
25	0.0212	32.6956

The results listed in Tables 1 and 2 explain that the value of half time for the decolourization of 20 ppm of dye using nano TiO$_2$ is greater than that of using bulk TiO$_2$ (Degussa P25). The possible reason is that the bulk TiO$_2$ (Degussa P25) contains a mixture of rutile and anatase, which have absorption bands at < 415 nm for rutile and < 385 nm for

anatase, thereby they have bandgaps in the solid state at 3.05 eV for rutile and 3.29 eV for anatase respectively [25].
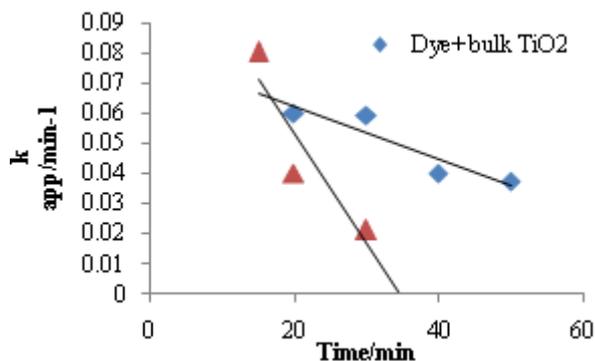
Figure 3: Pseudo-first order rate constant at varying dye concentration. Conditions: Bulk and Nano TiO$_2$ dosage 175 mg/100 mL, pH= 7.21, temperature 293.15 K, UV light intensity 1.409×10^{-7}ensien.s^{-1}.

The results illustrated in Figure 3 show clearly that the apparent rate constant of LGSF dye decolourization in the presence of TiO$_2$ was depressed with increasing in the initial dye concentrations at range (15-50) ppm, hence the high dye concentrations inhibit light penetration [26], [27], which increase the competition between the dye molecule and hydroxyl group to react with valance band leading to a decline in the amount of the formed hydroxyl and superoxide radicals, hence the decolorization efficiency was reduced, and this result is in agreement with the reported results of Ahmed and coworkers [28].
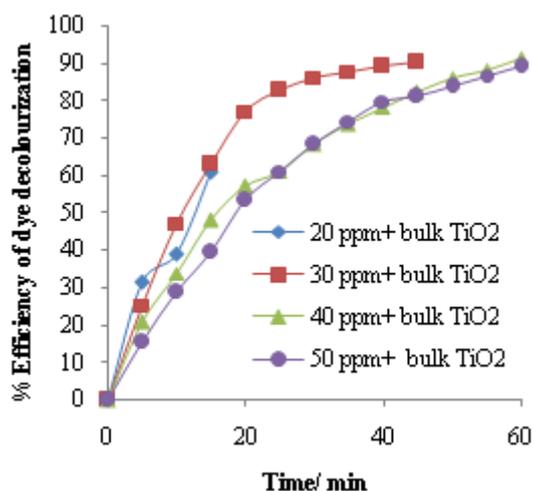
Figure 4: Effect of initial dye concentration on the efficiency of dye decolourization (Dye (15-50)ppm, Bulk TiO$_2$ dosage 175 mg/100 mL, pH 7.3, Temp. 293.15 K, UV light intensity 1.409×10^{-7}ensien.s^{-1}).
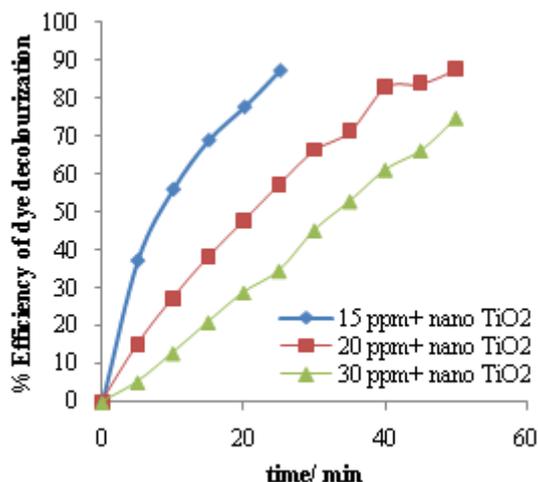
Figure 5: Effect of initial dye concentration on the efficiency of dye decolourization (Dye (15-50) ppm, Nano TiO$_2$ dosage 175 mg/100 mL, pH 7.3, Temp. 293.15 K, UV light intensity 1.409×10^{-7}ensien.s^{-1}).

Figure (4 and 5) shows that the efficiency of decolorization for this dye is 90.2 % with bulk TiO$_2$ at 45 min and 30 ppm of dye, and is equal to 83.8 % for nano TiO$_2$ at 45 min and 20 ppm of dye.

3.4. Effect of temperature

The effect of various temperatures in the range 283.15-2981.15 K was shown in Figures 5 and 6. It was observed that the photo-decolourization of the studied dye was increased with increasing temperature and produced a linear relationship that fitted the graph of the Arrhenius equation (eq. 9) and Eyring equation (eq. 10).

The obtained results for the apparent activation energy and the other thermodynamic functions are listed in Tables 3 and 4. Equation 9 was used to determine the apparent activation energy for this reaction [24], [29].

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \quad (9)$$

where: E$_a$ is an apparent activation energy, k$_{app}$ is an apparent rate constant, R is gas constant, T is temperature of reaction and A is frequency constant.
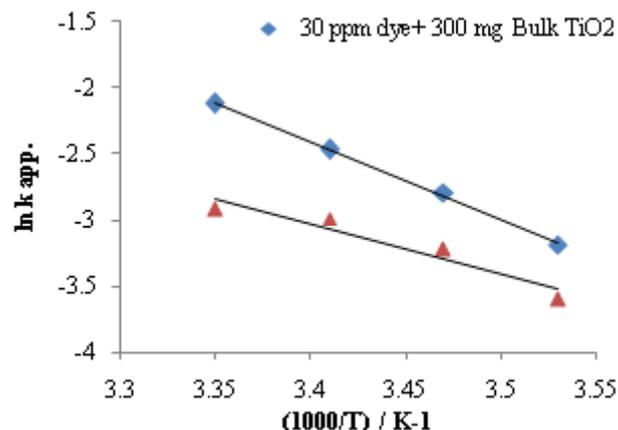
Figure 6: Pseudo-first order rate constant at varying temperature. Conditions: pH= 7.3, temperature (283.15-2981.15) K, UV light intensity 1.409×10^{-7}ensien.s^{-1}, dye

conc. 30 ppm, 20 ppm, semiconductor dosage 300 mg/100 mL from Bulk TiO_2 and 175 mg/100 mL from Nano TiO_2.

In order to calculate the thermodynamic parameters such as the change in activation enthalpy ΔH, the change in activation entropy ΔS, Eyring equation (eq. 10) was plotted in Figure 6. Besides, the change in activation free energy ΔG was calculated employing Gibbs equation (eq. 11) [28], [29].

$$\ln \frac{k_{app}}{T} = \frac{-\Delta H}{RT} + (\ln \frac{k_B}{h} + \frac{\Delta S}{R}) \qquad (10)$$

where: k_B is Boltzmann's constant, h is Plank's constant, R is gas constant and T is the temperature of reaction.

$$\Delta G = \Delta H - T \Delta S \qquad (11)$$
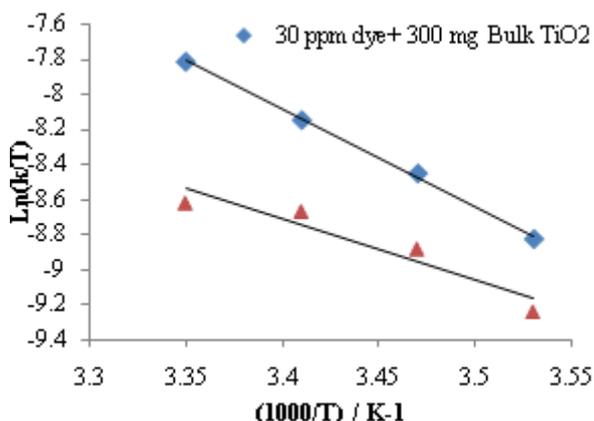
Figure 7: Eyring plot of (ln(K_{obs}/T)) vs.1/T. Conductions: pH= 7.3, temperature (283.15-2981.15) K, UV light intensity 1.409×10^{-7}ensien.s^{-1}, dye conc. 30 ppm, 20 ppm, semiconductor dosage 300 mg/100 mL from Bulk TiO_2 and 175 mg/100 mL from Nano TiO_2.

Table 3: The activation kinetic and thermodynamic parameters of the decolorization of LGSF dye using commercial TiO_2.

E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	$\Delta G_{288.15}$ (kJ mol^{-1})
48.676	46.292	-0.107	78.847

Table 4: The activation kinetic and thermodynamic parameters of the decolorization of LGSF dye using commercial nano TiO_2.

E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	$\Delta G_{288.15}$ (kJ mol^{-1})
37.032	34.667	-0.152	80.664

The results of thermodynamic study were itemized in Tables 3 and 4. It was observed that as the value of activation energy in the presence of nano TiO_2 is less than that in the presence of bulk TiO_2. This can be rationalized due to the small size of the Nano TiO_2particles (*ca.*18 nm), which agrees with the results reported by Jiang and coworker [30].

The obtained results for thermodynamic functions showed that the decolourization of LGSF dye was an endothermic and non-spontaneous process. The positive values of ΔH and $\Delta G_{288.15}$ indicate that the transition state between hydroxyl radicals and the studied dye molecules is highly solvated structure. On the other side, the small negative value of ΔS evidences that the intermediate complex is unstable, less ordered than reactants (dye molecules and hydroxyl radicals) and the bands are not strongly associated, which had supported the removal process of dye and produced simple products [17], [24], [31].

3.5. Suggested Mechanism

The mechanism of photocatalytic degradation of LGSF in aqueous solution depends on the formation of active species ($O_2^{-•}$, $^•O_2H$ and $^•OH$)[28].

The main source of hydroxyl radicals is the reaction between the holes and the surface-adsorbed water or hydroxyl ions. It is presumed that degradation of LGSF dye occurs mostly via attack by OH radicals on the *N*-ethyl groups of LGSF dyes under neutral and basic conditions, and through attack of OH radicals on the central carbon atom of LGSF to destruct the conjugated structure of the dye [32], as follows in Scheme 1.
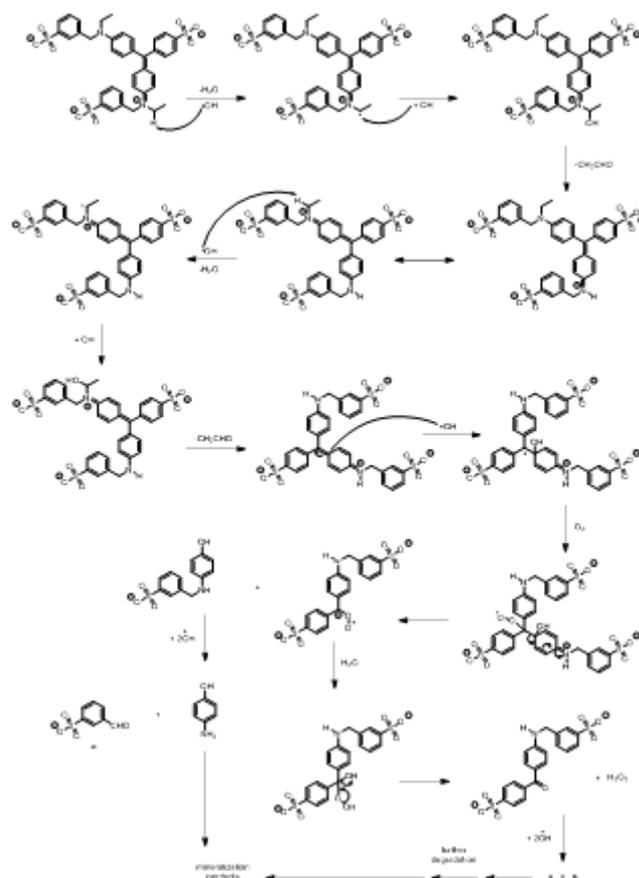
Scheme 1: Suggested mechanism for the degradation of LGSF dye. Adapted from reference [32].

4. Conclusions

In this work, the main conclusions can be summarized as follows:
1) The preliminary experiments explain that the presence of substrate (LGSF dye), photocatalyst (Bulk or Nano TiO_2), oxygen and UV light is regarded as essential requirements forphotodecolorization reaction of this dye.

2) The apparent activation energy values for both reactions in the presenceof Bulk and Nano TiO_2 decrease with decreasing the particle size.

3) Thermodynamic functions indicate that the decolorization of LGSF is a fast, endothermic and a non-spontaneous process.

References

[1] A. Tolmachev, "Polymethine Dyes, " *Kirk-Othmer Encyclopedia of Chemical Technology.* Wiley-Interscience, pp: 504–521, 2007.

[2] T. Gessner and U. Mayer, "Triarylmethane and Diarylmethane Dyes, " *Ullmann's Encyclopedia of Industrial Chemistry.* Wiley-VCH Verlag GmbH & Co. KGaA., pp: 425–478, 2012.

[3] V.G. Witterholt, Triphenylmethane and related Dyes In: *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd, Vol. 20. John Wiley & Sons, Wilmington, pp: 672–737, 1969.

[4] Z. Barghouthi1 and S. Amereih, "Spectrophotometric determination of fluoride in drinking water using aluminium complexes of triphenylmethane dyes" *Water SA*, vol.38, n.4, pp:543-548, 2012.

[5] R. W. Sabnis, Handbook of Biological Dyes and Stains: Synthesis and Industrial Applications. New Jersey: John Wiley & Sons, Inc., 2010.

[6] E. G. Kelley and E. G. Miller, "Reactions of Dyes with Cell Substances: I. Staining of Isolated Nuclear Substances", *J. Biol. Chem,* vol.110, pp:113-118, 1935.And reference there in.

[7] J. A. L. Gorringe, "Lissamine green as a protein stain in paper electrophoresis, " *Clin. Chim. Acta*, vol. 2, no. 5, pp: 353–371, 1957.

[8] A. Mittal, J. Mittal, A. Malviya, D. Kaur and V.K. Gupta, " Decoloration treatment of a hazardous triarylmethane dye, Light Green SF (Yellowish) by waste material adsorbents ", Journal of Colloid and Interface Science, vol. 342, pp: 518–527, 2010.

[9] S. Alam, F. Mabood, M. Sadiq, Noor-ul-Amin, andF. K. Bangash." Removal of Triphenylmethane Dye from Aqueous Solution by Carbonaceous Adsorbent. Tenside Surfactants Detergents": Vol. 48, No. 2, pp:134-142, 2011.

[10] R. Srivastava and D. C. Rupainwar, "Removal of hazardous triphenylmethane dye through adsorption over waste material-mango bark powder", Indian Journal of chemistry Technology, vol. 18, pp:469-474, 2011.

[11] J. Cheriaa, M. Khaireddine, M. Rouabhia and A. Bakhrouf, "Removal of Triphenylmethane Dyes by Bacterial Consortium", The Scientific World Journal, pp:1-9, 2012.

[12] A. Török, E. Buta, C. Indolean, S. Tonk, L. Silaghi-Dumitrescu1 and C. Majdik, " Biological Removal of Triphenylmethane Dyes from Aqueous Solution by Lemna minor ", Acta Chim. Slov., vol. 62, pp: 452–461, 2015.

[13] R. Yogita, S. Simanta, S.Aparna and S. Kamlesh, " Biodegradation of malachite green by wild mushroom of Chhatisgrah ", J. Exp. Sci., vol. 2, no. 10, pp: 69-72, 2011.

[14] H. K. Egzar, M. S. Mashkour and A. M. Juda, " Study the Photodegradation of Aniline Blue dye in aqueous Phase by using Different Photocatalysts ", Asian Transactions on Basic and Applied Sciences, vol. 3, no. 2, pp:23-28, 2013.

[15] C.C. Chen, C.S. Lua, Y.C. Chung and J.L. Jan, " UV light induced photo degradation of malachite green on TiO_2 nanoparticles", Journal of Hazardous Materials, vol. 141, pp: 520–528, 2007.

[16] E.S. Fathal and L. M. Ahmed, "Optimizationof PhotocatalyticDecolorization of Methyl Green Dye Using Commercial Zinc Oxide as catalyst", *J. of Kerb. Univ.,* Vol. 13, No. 1, pp: 53-63, 2015.

[17] A. Giwa, P.O. Nkeonye, K.A. Bello, E.G. Kolawole and A.M.F. Oliveira Campos, "Solar Photocatalytic Degradation of Reactive Yellow 81 and Reactive Violet 1 in Aqueous Solution Containing Semiconductor Oxides", *International Journal of Applied Science and Technology,* vol. 2, no. 4, pp: 90-105, 2012. And references there in.

[18] M. Montazerozohori, M. Nasr-Esfahani and S. Joohari, "Photocatalytic Degradation of An Organic Dye In Some Aqueous Buffer Solutions Using Nano Titanium Dioxide: A Kinetic Study ", *Env. Prot. Eng.*, vol. 38, no. 3, pp:45-55, 2012. And reference there in.

[19] S. Khezrianjoo and H. D. Revanasiddappa, "Langmuir-Hinshelwood Kinetic Expression for the Photocatalytic Degradation of Metanil Yellow Aqueous Solutions by ZnO Catalyst", *Chem. Sci. J.*, pp: 1-7, 2012. And reference there in.

[20] H. Nadi, M. Alizadeh, M. Ahmadabadi, A. R. Yari and S. Hashemi, "Removal of Reactive Dyes (Green, Orange, and Yellow) from Aqueous Solutions by Peanut Shell Powder as a Natural Adsorbent ", *Arch. Hyg. Sci.*, vol.1, no. 2, pp: 41-47, 2012.

[21] S. Ahmed, "Photo electrochemical study of ferrioxalate actinometry at A glassy carbon electrode", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 161, pp:151-154, 2004.

[22] L. Ahmed, F. Hussein and Ali Mahdi, "Photocatalytic Dehydrogen-ation of Aqueous Methanol Solution by Bare and Platinized TiO_2 Nanoparticles", *Asian Journal of Chemistry;* vol. 24, no. 12, pp:5564-5568, 2012.

[23] M. Mashkour, A. Al-Kaim, L. Ahmed and F. Hussein, "Zinc Oxide Assisted Photocatalytic Decolourization of Reactive Red 2 Dye", *Int. J. Chem. Sci.,* vol. 9, no.3, pp: 969-979, 2011.

[24] S. I. S. Zuafuani and L. M. Ahmed, "Photocatalytic Decolourization of Direct Orange Dye by Zinc Oxide under UV Irradiation", *I. J. of chemistry science*, Vol. 13, No. 1, pp: 187-196, 2015.

[25] AEROXIDE®, AERODISP® and AEROPERL, Titanium Dioxide as Photocatalyst, Technical Information, pp: 1-12, 2015.

[26] K.Byrappa, A.Subramani, S. Ananda, K. Rai, R. Dinesh and M. Yoshimura, "Photocatalytic degradation of rhodamine B dye using hydrothermally synthesized ZnO ", *Bull. Mater. Sci.,* vol. 29, no. 5, pp: 433–438, 2006.

[27] J. Chanathaworn, C. Bunyakan, W. Wiyaratn and J. Chungsiriporn, "Photocatalytic decolorization of basic dye by TiO_2 nanoparticle in photoreactor", *Songklanakarin J. Sci. Technol.*, vol. 34, no. 2, pp:203-210, 2012.

[28] L. M. Ahmed, F. T. Tawfeeq, M. H. Abed Al-Ameer, K. Abed Al-Hussein and A. R. Athaab, " Photo-Degradation of Reactive Yellow 14 Dye (A Textile Dye) Employing ZnO as Photocatalyst", *Journal of Geoscience and Environment Protection,* vol. 4, pp: 34-44, 2016.

[29] M. A. Tabbara and M. M. Jamal, "A kinetic study of the discoloration of methylene blue by Na_2SO_3, comparison with NaOH", *J. of the Uni. of Chem. Tech. and Metall.*, vol. 47, no. 3, pp: 275-282, 2012.

[30] Q. Jiang, S.H. Zhang and J.C. Li, "Grain size-dependent diffusion activation energy in nanomaterials ", *Solid State Communications*, vol. 130, pp: 581–584, 2004.

[31] S. B. Gajbhiye, "Photocatalytic Degradation Study of Methylene Blue Solutions and Its Application to Dye Industry Effluent", *IJMER*, vol. 2, Issue.3, pp.1204-1208, 2012.

[32] C. Chen and C. Lu, "Photocatalytic degradation of basic violet 4: Degradation efficiency, product distribution, and mechanisms, " *Journal of Physical Chemistry C*, vol. 111, no. 37, pp. 13922–13932, 2007.