

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

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Abstract: In this work, Light Green SF Yellowish (LGSF) dye was removed from aqueous solution at normal pH equal to 7.3 in the presence of bulk and nanoTiO₂ 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 TiO₂ and commercial nano TiO₂ were found to be 48.676 kJ mol⁻¹ and 37.032 kJ mol⁻¹ respectively. Further, thermodynamic studies showed that the photocatalytic decolourization of this dye is an endothermic and non-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) dye with the structural formula C₃₇H₃₄N₂Na₂O₉S₃, 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 dyeing 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 bulk titania 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 TiO₂ – Degussa P25 (particle of ca. 44 nm) was supplied by Fluka-Germany, while the commercial nano TiO₂ (particle size of ca. 18 nm) 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.

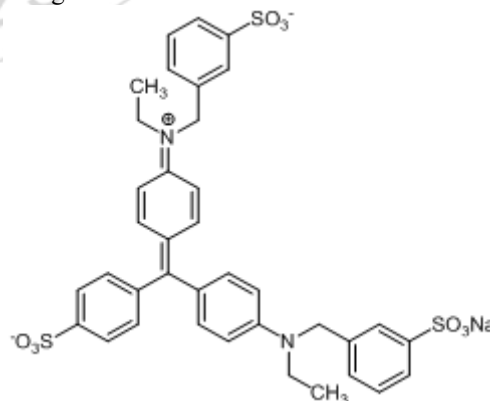


Figure 1: Chemical structure of LGSF.

2.1. Light source and photoreactor

400 cm³ cylindrical glass reactor was used to perform irradiation, which was provided by 400W high pressure mercury lamp (HPML) (Radium, 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. Photocatalytic experiments

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 stirred 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 transferred 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 decolorization 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]:

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

where: C_0 is an initial concentration of used dye at time of irradiation equal to 0 min. C_t is a concentration of the same dye at time t of irradiation.

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

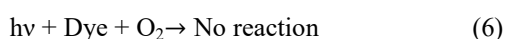
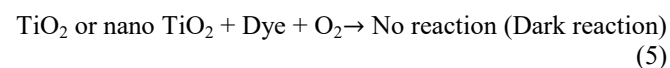
The photocatalytic decolorization efficiency [20] was determined using equation (3).

$$\% \text{ Efficiency} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (3)$$

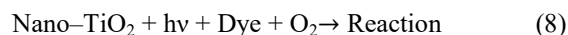
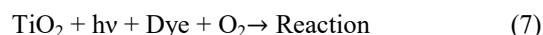
where: C_0 = the concentration of LGSF dye solution at time equal to 0 min, and C_t is the concentration of dye solution after time equal to t min.

3.2. Preliminary experiments

Series of preliminary experiments were performed and the results are expressed in figure 2. In the absence of UV light and photocatalyst (dark reaction) and under environmental O_2 gas, the reaction was never taken place, that proved no electron-hole pairs created. On the 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].



In the photocatalytic reaction under environmental O_2 gas, the dye solution decolorized as 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].



The photocatalytic reaction using bulk titania or nano titania to decolorize LGSF dye followed the first order plots.

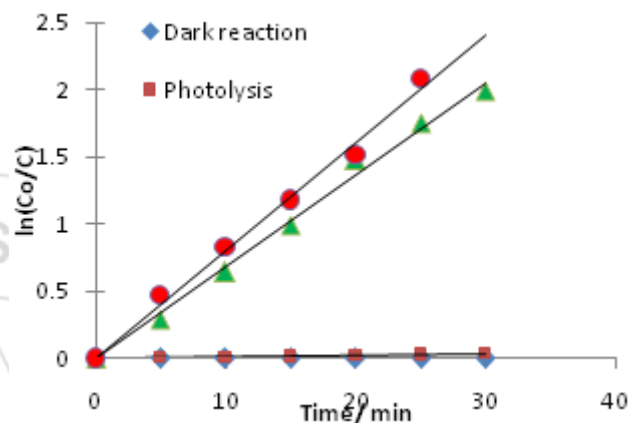


Figure 2: Preliminary experiments, with catalyst dose of Bulk TiO_2 and Nano TiO_2 equal to 175 mg/100ml with 30 ppm and 20 ppm of LGSF dye respectively, $T=293.15$ K.

3.3. Effect of Dye Concentration

The photocatalytic decolorization 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 $t_{1/2} / \text{min}$
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 $t_{1/2} / \text{min}$
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 decolorization 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].

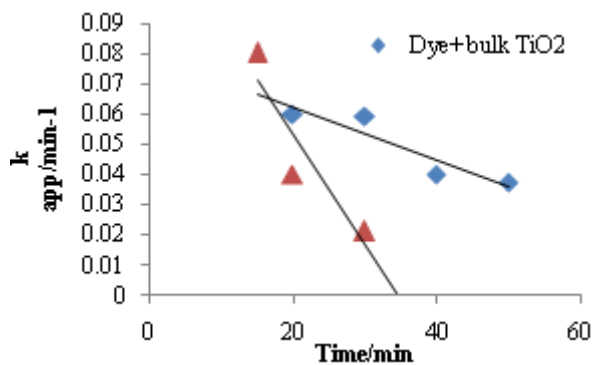


Figure 3: Pseudo-first order rate constant at varying dye concentration. Conditions: Bulk and Nano TiO₂ dosage 175 mg/100 mL, pH= 7.21, temperature 293.15 K, UV light intensity 1.409×10^{-7} ensien.s⁻¹.

The results illustrated in Figure 3 show clearly that the apparent rate constant of LGSF dye decolorization in the presence of TiO₂ 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].

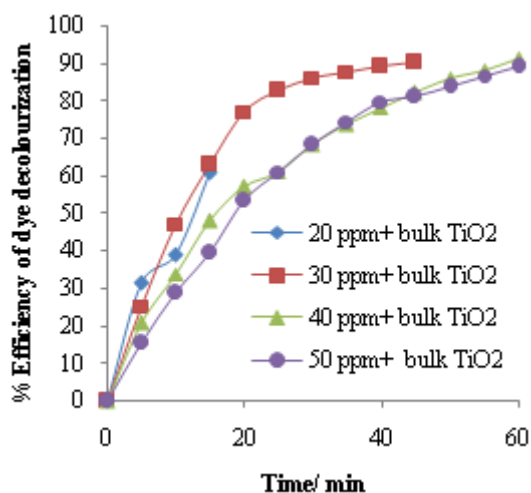


Figure 4: Effect of initial dye concentration on the efficiency of dye decolorization (Dye (15-50)ppm, Bulk TiO₂ dosage 175 mg/100 mL, pH 7.3, Temp. 293.15 K, UV light intensity 1.409×10^{-7} ensien.s⁻¹).

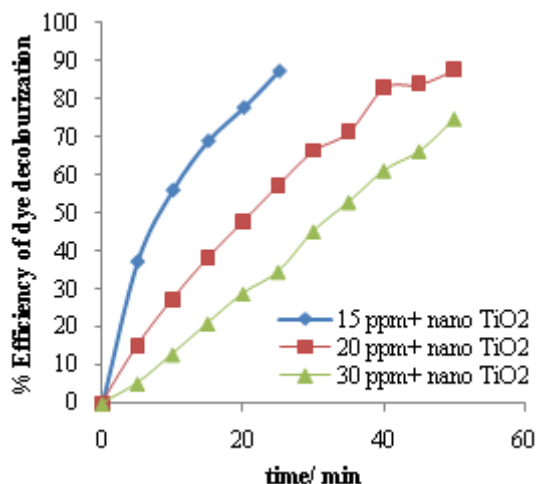


Figure 5: Effect of initial dye concentration on the efficiency of dye decolorization (Dye (15-50) ppm, Nano TiO₂ dosage 175 mg/100 mL, pH 7.3, Temp. 293.15 K, UV light intensity 1.409×10^{-7} ensien.s⁻¹).

Figure (4 and 5) shows that the efficiency of decolorization for this dye is 90.2 % with bulk TiO₂ at 45 min and 30 ppm of dye, and is equal to 83.8 % for nano TiO₂ 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-decolorization 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.

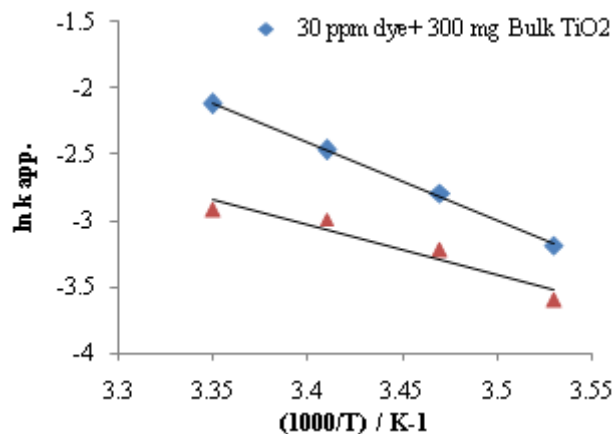


Figure 6: Pseudo-first order rate constant at varying temperature. Conditions: pH= 7.3, temperature (283.15-2981.15) K, UV light intensity 1.409×10^{-7} ensien.s⁻¹, dye

conc. 30 ppm, 20 ppm, semiconductor dosage 300 mg/100 mL from Bulk TiO₂ and 175 mg/100 mL from Nano TiO₂.

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].

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

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

$$\Delta G = \Delta H - T \Delta S \quad (11)$$

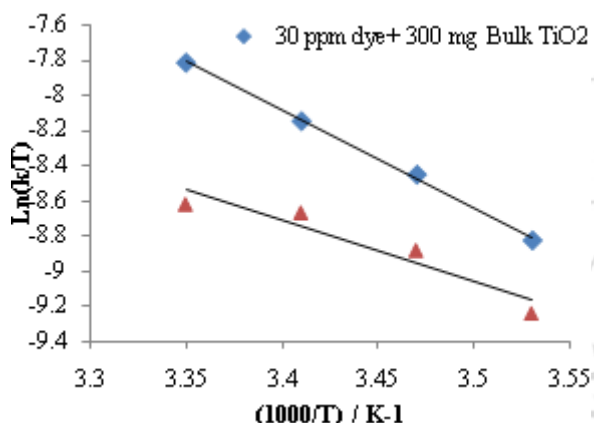


Figure 7: Eyring plot of $\ln(K_{obs}/T)$ vs. $1/T$. Conditions: pH=7.3, temperature (283.15-2981.15) K, UV light intensity 1.409×10^{-7} ensien.s⁻¹, dye conc. 30 ppm, 20 ppm, semiconductor dosage 300 mg/100 mL from Bulk TiO₂ and 175 mg/100 mL from Nano TiO₂.

Table 3: The activation kinetic and thermodynamic parameters of the decolorization of LGSF dye using commercial TiO₂.

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 TiO₂.

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 TiO₂ is less than that in the presence of bulk TiO₂. This can be rationalized due to the small size of the Nano TiO₂ particles (*ca.* 18 nm), which agrees with the results reported by Jiang and coworker [30].

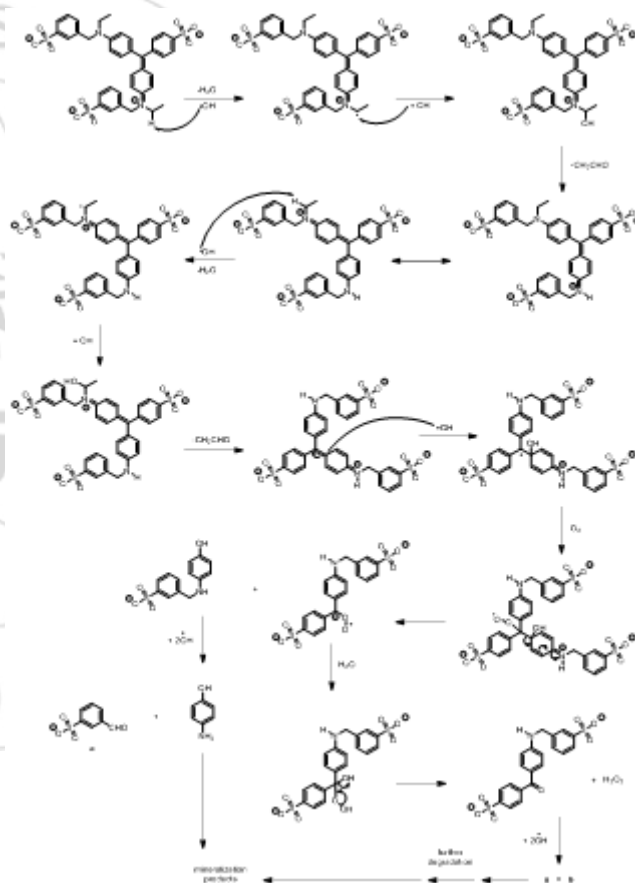
The obtained results for thermodynamic functions showed that the decolorization of LGSF dye was an endothermic and non-spontaneous process. The positive values of ΔH and $\Delta G_{288.15}$ indicate that the transition state between hydroxyl radicals and the studied dye molecules is highly solvated

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 ($O_2^{\bullet-}$, $\bullet O_2H$ and $\bullet OH$) [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 TiO₂), oxygen and UV light is regarded as essential requirements for photodecolorization reaction of this dye.

- 2) The apparent activation energy values for both reactions in the presence of Bulk and Nano TiO₂ decrease with decreasing the particle size.
- 3) Thermodynamic functions indicate that the decolorization of LGSF is a fast, endothermic and a non-spontaneous process.

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