

# **Equilibrium, isothermal, Kinetic and Thermodynamic studies for the removal of Lissamine green dye using Titanium nanoparticles**

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## **Abstract**

Rapid industrialisation has increased the use of dyes in a variety of industrial applications in order to meet rising consumer product demand. The toxicity level of a specific dye is critical due to the diverse effects it has on the environment and living organisms. Among all dye removal techniques, adsorption and photocatalysis are two important processes that have received a lot of attention in recent years. The maximum adsorption of LG dye (90 %) onto Ti Nps is observed from the current investigation from equilibrium studies also reveals the endothermic nature of sorption as  $\Delta H$  is positive (14.62842 J/mole), irreversible nature of sorption as  $\Delta S$  is positive (59.52846 J/mole.K) and spontaneity of sorption as indicated by negative  $\Delta G$  (-18022.5 J/mole).

**Keywords:** Biosorption, Ti Nps, Thermodynamics, Kinetics, Isothermal studies.

## **1. Introduction**

Because of their high toxicity and slow degradation, organic dyes are the most common pollutants in aquatic environments. When dyes from the textile, paper, leather, food, and other industries are discarded, they contaminate and pollute the environment, making it necessary to remove these coloured compounds from industrial effluents [1-2]. For the removal of dyes from wastewater, various methods and processes have been used.[3-6]. The two most important methods are (1) adsorption and (2) photocatalysis. The first method is a non-destructive process that transfers solutes from one phase to another, requiring regeneration before reuse. The second method, photocatalysis, is an advanced oxidation process in which dye molecules are decomposed by ultraviolet and visible light. The most widely used photocatalyst for this purpose is titanium dioxide due to its high activity, chemical stability, low toxicity and low cost. However, titanium dioxide has two main drawbacks. 1) It is difficult to separate the photocatalyst from the wastewater after

decomposition, and 2) At high concentrations, titanium dioxide particles tend to aggregate, reducing efficiency. Therefore, supported titanium oxide photocatalysts have been given great importance in order to alleviate the above problems. A significant portion of the research done so far has been It is an adsorption and photocatalytic process, demonstrating the potential for wastewater treatment[7-8].

**2. Experimental Procedure**

**2.1 Preparation of the Nanoparticle solution**

Collect the leaves of the *Quisqualis indica* plant nearby, wash thoroughly to remove dust, and boil in distilled water to obtain a broth solution. The broth solution obtained from the leaves is mixed with the 0.05M TiO<sub>2</sub> solution and then the mixture is heated at 60°C for 15 minutes to form nanoparticles.

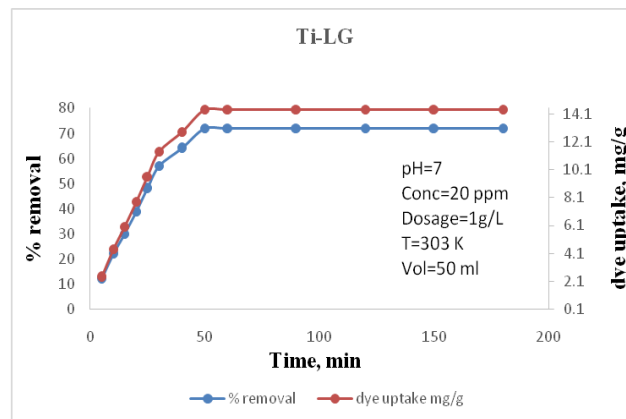
**2.2 Preparation of Dye solution**

To prepare the initial solution, take 1 g of dye powder per 1000 ml of distilled water to obtain a dye solution with a concentration of 1000 ppm and use a concentration of 20 ppm for the process. A periodic equilibrium study was performed to remove the LG dye to determine its bioadsorption capacity.

**3. Results and Discussion**

**3.1. Effect of Contact time**

Lissamine green removal rate with respect to contact time in Fig. 1, from the plot, we can see that the removal rate increases continuously in the first 50 minutes of stirring. After a contact time of 50 minutes, the change in LG dye removal rate is almost constant. Therefore, the equilibrium contact time is 50 minutes. In the current study, the contact time was increased from 5 minutes to 180 minutes, 50 ml of aqueous solution, 0.04 of bacterial culture, and 0.01 g of nanoparticles were added, and 12% to 72% of contact was 5 to 50 times



**Fig. 1 Effect of Contact Time on LG dye**

**3.2. Effect of pH**

Fig. 2 is plotted between the removal rate of lissamine green and the pH value of aqueous solution. As the pH increases from 2 to 7, a sharp increase in LG removal is observed, and as the pH increases further above 7, a decrease in removal is observed. In the current study of pH with the addition of 50 ml aqueous solution, nanoparticles and organisms, the removal rate increased from 52% to 72% and the dye uptake was 10.4 to 14.4 mg / g in the pH range of 2 to 7.

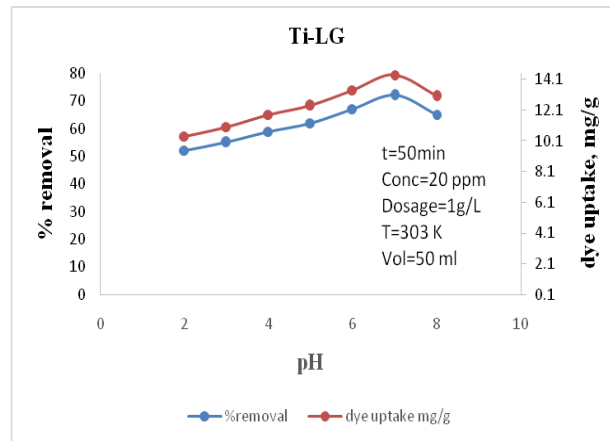


Fig. 2 Effect of pH on LG dye

3.3. Effect of Concentration

Fig. 3 shows the effect of the initial concentration of lissamine green in aqueous solution on the removal rate at optimal contact time. By increasing the LG dye concentration from 20 to 100 mg/L, the removal rate gradually decreases from 72% to 63.6% and the dye uptake goes from 14.4 mg/g to 63.6 mg/g.

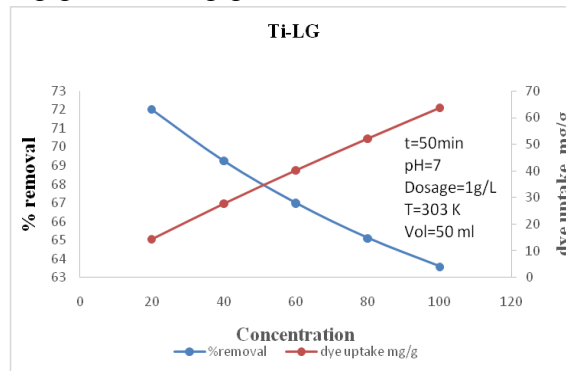


Fig. 3 Effect of Concentration on LG dye

3.4. Effect of Dosage

Fig. 4 shows the change in the removal rate of lissamine green from aqueous solution with the biosolvent dose. Increasing the dose from 1 g/L to 5 g/L increases the removal rate from 72% to 91%. Removal rate from solution increases by with increasing dose of bioadsorbent.. The increase in removal rate is not noticeable (89 to 91%) as the dose increases.

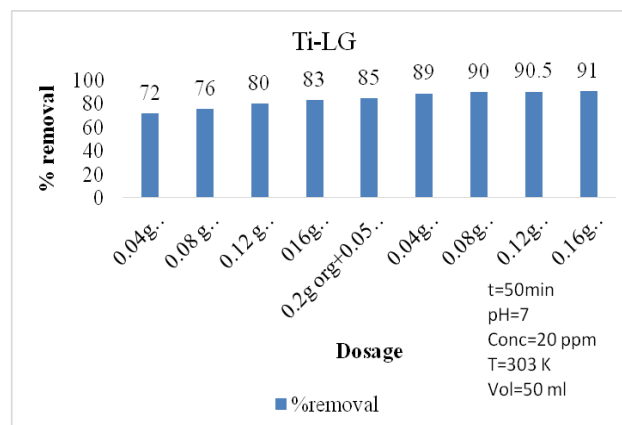
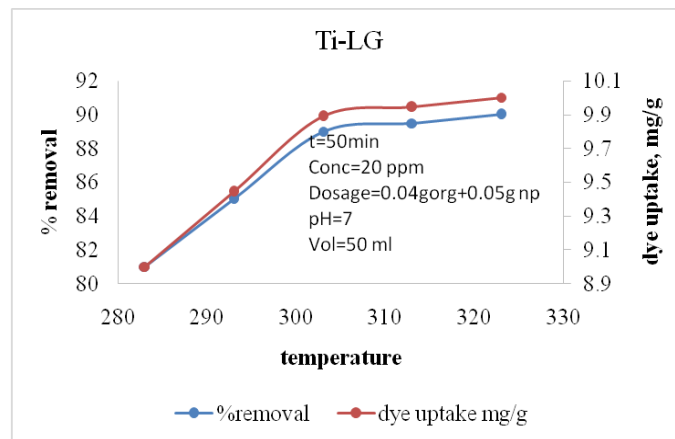


Fig. 4 Effect of Dosage on LG dye

**3.5. Effect of Temperature**

The temperature effect on optimal dye absorption was important. Fig. 5 shows the effect of temperature changes on the uptake of LG dyes. The results show that the QI adsorption limit of LG dyes increases with temperature. Increasing the temperature from 283K to 323K increased the removal rate from 81% to 90%. Therefore, temperature affects the removal process



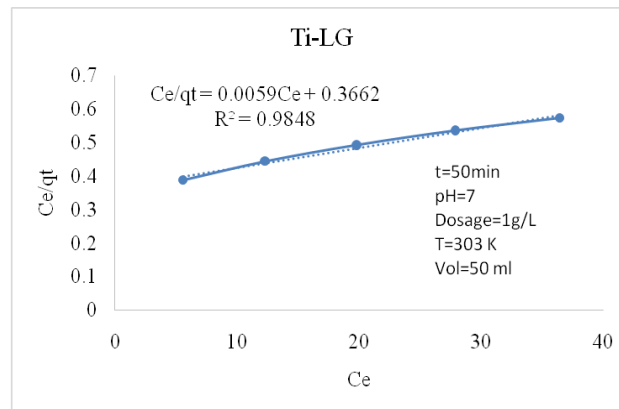
**Fig. 5 Effect of Temperature on LG dye**

**3.6. Isotherms**

**3.6.1 Langmuir Isotherm**

The Langmuir isotherm is drawn between  $C_e / q_e$  and  $C_e$  in Fig. 6 for current data. The resulting formula is equation 1 is

$$C_e / q_e = 0.0059 C_e + 0.3662 \quad \text{--- (1)}$$



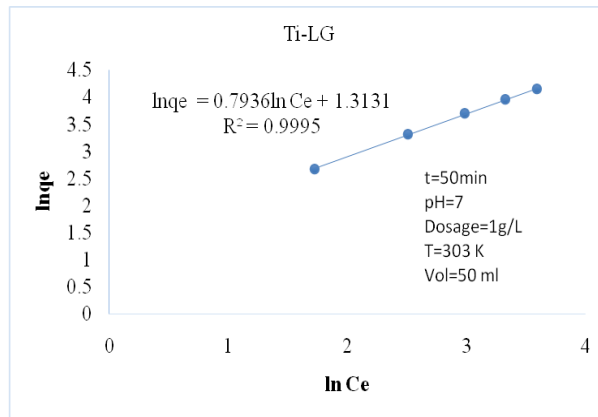
**Fig. 6 Langmuir Isotherm for LG dye**

(Correlation coefficient 0.9848) confirms strong binding of lissamine green ions to the surface of the Ti Nps.

**3.6.2 freundlich Isotherm**

The Freundlich isotherm is drawn between  $\ln C_e$  and  $\ln q_e$  in the figure. As a result of Fig. 7, the following equation 2 was obtained.

$$\ln q_e = 0.7936 \ln C_e + 1.3131 \quad \text{----(2)}$$



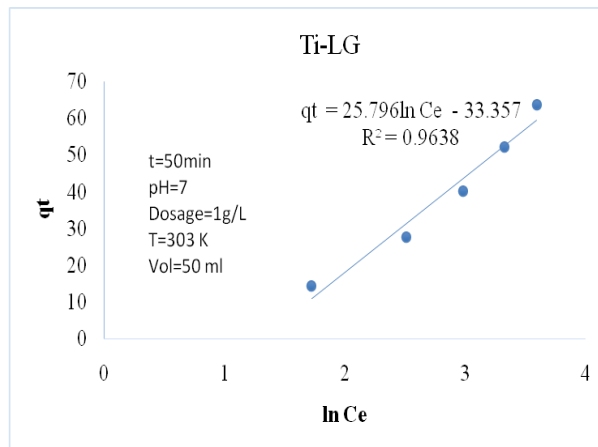
**Fig. 7 Freundlich isotherm for LG dye**

The correlation coefficient for this equation is 0.9995. A 'n' value of 0.76 indicates a preferred distance that satisfies condition.

**3.6.3 Temkin Isotherm**

Figure 8 shows the diagram between  $q_e$  and  $\ln C_e$ . The removal formula for Lissamine Green is shown in equation 3

$$q_e = 25.796 \ln C_e - 33.357 \quad \text{----- (3)}$$



**Fig. 8 Temkin Isotherm for LG dye**

**Table 1 Equations and Isotherm constants for LG dye**

Langmuir isotherm $C_e/q_e = 0.0059C_e + 0.3662$	Freundlich isotherm $\ln q_e = 0.7936 \ln C_e + 1.3131$	Temkin isotherm $q_e = 25.796 \ln C_e - 33.357$
$q_m = 169.4915 \text{ mg/g}$	$K_f = 3.717681 \text{ mg/g}$	$A_T = 0.40436 \text{ L/mg}$
$K_L = 0.016111$ $R_L = 0.917243$	$n = 0.76$	$b_T = 97.6563$
$R^2 = 0.9848$	$R^2 = 0.9995$	$R^2 = 0.9638$

Table 1 gives the isotherm constants along with the correlation factors of Isotherms are given by 0.9848, 0.9995, 0.9638

**3.7. Kinetics**

**3.7.1 Lagrangren First Order Kinetics**

The lagrengan equation is obtained from the Fig. 9 which is plotted against time and  $\log(q_{e,t} - q_t)$  and the equation 4 is given below

$$t/q_t = 0.026t + 2.0015 \quad \text{---(4)}$$

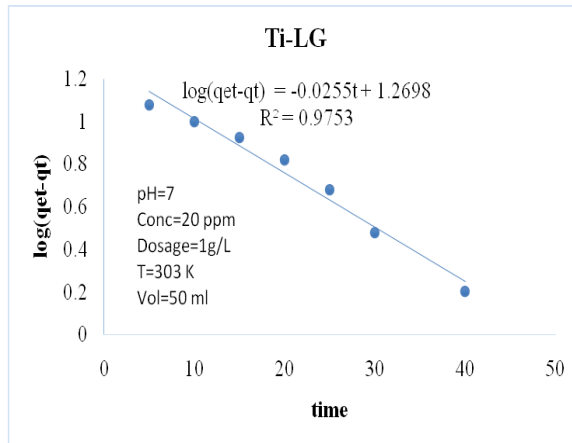


Fig. 9 Lagrangren First order for LG dye

3.7.2 Pseudo Second Order Kinetics

If pseudo-quadratic kinetics is applicable, plotting (t / qt) against `t` yields a linear relationship in which qe and K can be calculated from Fig 10 and equation 5 is given below

$$t/q_t = 0.026t + 2.0015 \quad \text{---(5)}$$

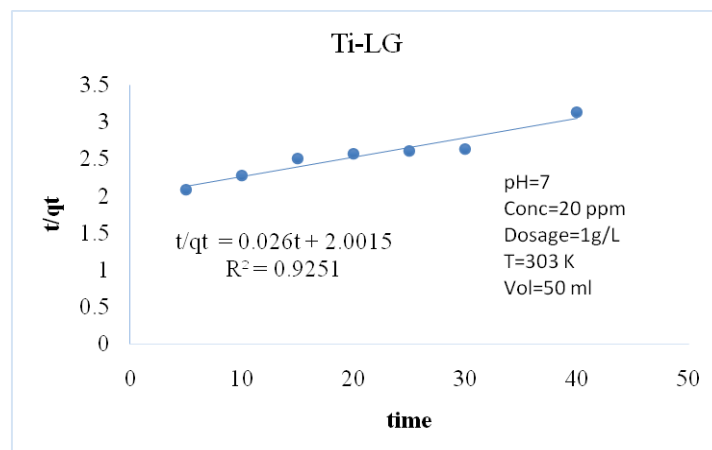


Fig. 10 Pseudo second Order for LG dye

Table 2 Equations and rate constants

Order	Equation	Rate constant	R <sup>2</sup>
Lagergren first order	log (qe-qt) = -0.0255t + 1.2698	0.058 min <sup>-1</sup>	0.975
Pseudo second order	t/qt = 0.026t + 2.0015	0.0003 g/(mg-min)	0.925

Table 2 summarizes the rate constant and correlation factors obtained from kinetics for LG dye is 0.975 and 0.925.

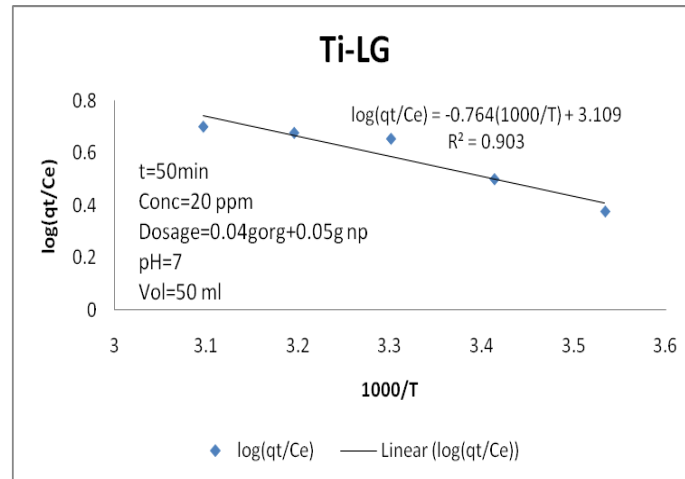
3.8. Thermodynamics

The ΔG, ΔS, and ΔH values of LG dye ions at different temperatures and different concentrations are shown given Fig 11.and the equation 6 is given

$$\log(qe/C_e) = -0.764 (1000/T) + 3.109 \quad \text{----(6)}$$

The thermodynamic parameters of the LG dye removal process are calculated from the logarithmic (qe / Ce) vs. 1000 / T graph. The values of ΔH and ΔS are calculated from the

slope and intercept of the axis. The  $\Delta G$  estimate of  $-18022.5$  J/Mol indicates that the removal of LG dye by the QI leaf can occur unexpectedly. Higher temperatures improved removal and increased equilibrium removal capacity. A positive  $\Delta H$  of  $14.62842$  J/Mol K indicates the endothermic property of removal, and a positive  $\Delta S = 59.52846$  J/Mol K indicates the ease of removal of the LG dye.



**Fig. 11 Vant Hoff's plot for LG dye**

**4. Conclusion**

The maximum sorption of LG dye (90 %) onto Ti Nps is observed when the optimum parameters are set as:  $t = 50$  min,  $pH = 7$ ,  $w = 1.8$  g/L,  $C_o = 20$  mg/L and  $T = 303$  K. The thermodynamic data show that % sorption of CV dye is increased with increase in temperature. The investigation also reveals the endothermic nature of sorption as  $\Delta H$  is positive ( $14.62842$  J/mole), irreversible nature of sorption as  $\Delta S$  is positive ( $59.52846$  J/mole.K) and spontaneity of sorption as indicated by negative  $\Delta G$  ( $-18022.5$  J/mole).

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