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Adsorption Isotherms and Thermodynamic Study of Direct Blue2 (DB_2) Dye on Y_2O_3 Nanoparticles

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Abstract

In this work, the adsorption of DB2 dye on yttrium oxide (Y_2O_3) nanoparticles was investigated under various experimental conditions. The effect of temperatures and pH were studied, it was noted that the increasing in temperatures increases the adsorption quantity, which is increased in icidic medium and decreased in basic medium. The isotherm models (Langmiur, Freundlich, Temkin, Halsey and Harkins-Jura) were applicated and the isotherms can be arrange according to its high correlation-coefficients as follows: Freundlich (0.969) > Harkins-Jura (0.957) > Halsey (0.944) > Temkin (0.942) > Langmiur (0.902), the Freundlich isotherm model is suitable for the adsorption process. Thermodynamic Parameters such as ΔH, ΔG and ΔS were calculated from the slops and intercepts of the linear variation of lnk against 1/T, where noted that the adsorption of DB2 dye on Y_2O_3 nanoparticles is (endothermic reaction)

Keywords: *Adsorption Isotherms, DB2 Dye, Y_2O_3 Nanoparticles.*

Introduction

Dyes can be described as substances which, when used on a substrate give color by a method, which altersat least briefly, any crystal shaped by the colored substances .Such substances with massive coloring capability are wide applied in the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries [1]. azo dyes are the most important class of commercial dyes, which constitute more than half of the dye chemistry [2]. Azo dyes are common synthetic colorants released into the environment [3]. They institute the largest class of dyes used in industry [4, 5], are widely used to dye numerous materials such as leather, plastics [6], textiles, food, paper, and cosmetics [7, 8] and they are utilized in high tech applications such as “lasers and non-direct optical frameworks", “warm exchange printing and fuel cells”, “dye sensitized solar cells”, “photodynamic treatment”, and “metallo chromic indicators” [9]. Adsorption have been reported as a good method to remove organic dyes from wastewaters [10] because of its straight forwardness, cost viability and extraordinary proficiency Numerous kinds of both regular and manufactured adsorbents have been evaluated for the expulsion of colors and elective toxins from

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wastewater [11] . In this research used yttrium oxide nano particles (Y_2O_3) as adsorbent, Yttrium oxide is one of the most common compounds of rare earth and has been used in a wide variety of fields such as optics, advanced ceramics, optoelectronics, and practical composite additives [12], due to their attractive properties, including high corrosion resistivity, wide optical transmission range, good thermal stability and high melting point of around 2410 C° [13]. (Fig. 1) shows the geometric structure of the dye:

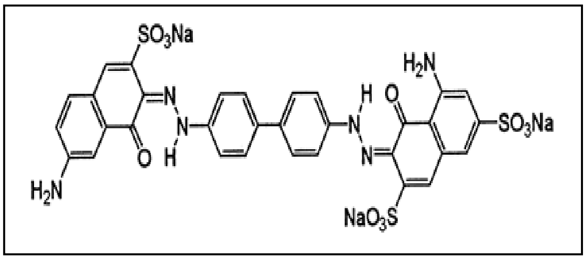

Fig. 1. The Structure of Direct Blue 2 (DB_2) Dye

Experimental

Materials

Direct blue 2 (DB_2) dye was collected from Baghdad's factory textile industry and Y_2O_3 nanoparticles was purchased from Sigma (Sigma–Aldrich).

Methods:

Determination of Calibration Curve:

To determine the calibration curve for DB2 dye at constant wavelength (λmax= 566nm) by using (Bear-Lambert Law): (A=ε.b.c) to determine the molar absorbance coefficient (ε= 0.012) and (R^2 = 0.999). (Fig. 2) shows this relation:

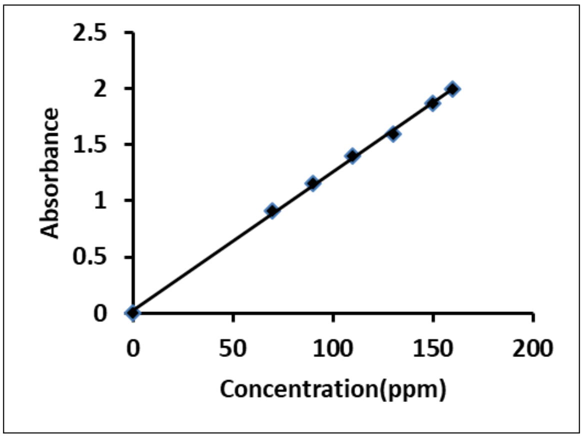

Fig. 2. Calibration Curve of DB2 Dye

Characterization of Y_2O_3 Nanoparticles:

X-Ray diffraction (XRD) was used for Y_2O_3 nanoparticles characterization and Debye-Scherrer equation was used to calculate the crystal size (D) of Y_2O_3 nanoparticles:

$$D = \frac{0.94\lambda}{\beta Cos\theta} \quad \text{.... (1)}$$

"λ is the wavelength in angstrom, β is the maximum full widith and θ the angle obtained from 2θ values corresponding to maximum intensity peak in XRD pattern" [14]. The mean crystal size of Y_2O_3 nanoparticles was (33.36 nm). (Fig. 3) shows the XRD spectra of Y_2O_3 nanoparticles.

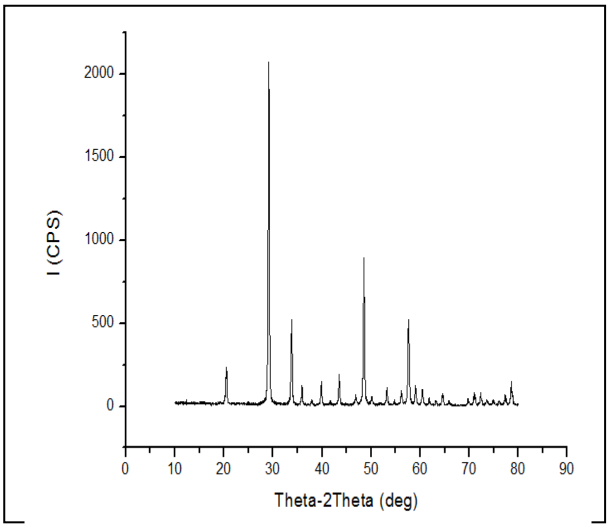

Fig. 3. XRD Spectra of Y_2O_3 Nanoparticles

Adsorption Experiments:

Solutions Preparation:

DB2 its formula is $C_{32}H_{21}N_6Na_3O_{11}S_3$, its M.Wt. is 830.7 g/mol. Stock solution of 1000 mg·L^{-1} was prepared by distilled water.

Batch Experiments:

The adsorbent dose of 0.1 g has been added to 100 mL conical flasks that accept 7.5 ml of DB2 dye band - aid of accepted concentrations (70, 90, 110, 130, 150 and 160) mg.L^{-1}. The flasks were placed under the set altitude of acquaintance time (30 min), afraid acceleration (182 rpm) and temperature (24.5 C^o). A foresaid altitude of accumulation abstracts were kept connected during the improvment of assorted ambit furnishings on the DB2 dye adsorption abundance of Y_2O_3 nanoparticles. The temperature furnishings, pH on the adsorption abundance of Y2O3 nanoparticles were activated within (25–50) C^o. After the accumulation experiment, the clarify was analyzed at 566 nm amicableness for DB2 application UV / VIS spectrophotometer. The abundance of DB2 dye adsorbed on Y_2O_3 nanoparticles was affected application Equation 2:

$$Q_e = (\frac{C_o - C_e}{m})V \quad \text{..... (2)}$$

"C_o and Ce are the concentrations of initial and equilibrium (mg·L^{-1}), respectively, Q_e is the adsorption quantity of DB2 dye (mg·g^{-1}), V the solution volume (L) and m is the adsorbent mass (g)" [15].

Results and Discussion

UV Spectroscopy:

In (Fig. 4) the UV spectra of DB2 dye shows bands at (231, 314 and 566) nm:

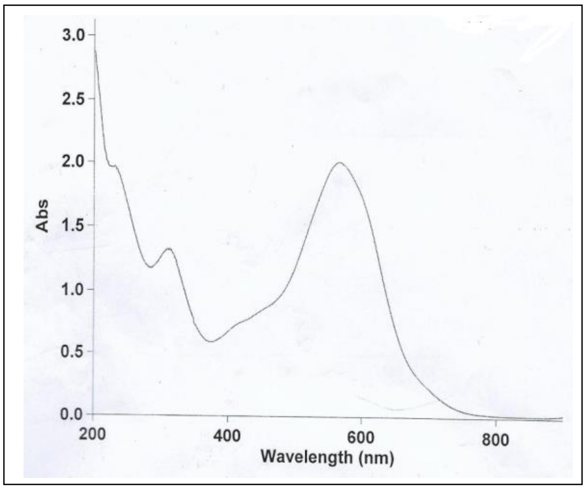

Fig. 4. UV Spectra of Direct Blue 2 (DB2) Dye.

Adsorption study:

Effect of Temperature:

The adsorption of DB_2 dye on Y_2O_3 nanoparticles using different temperatures (25, 40 and 50) C^o at constant concentration of dye solution were studied and the study results shows in (Fig. 5)

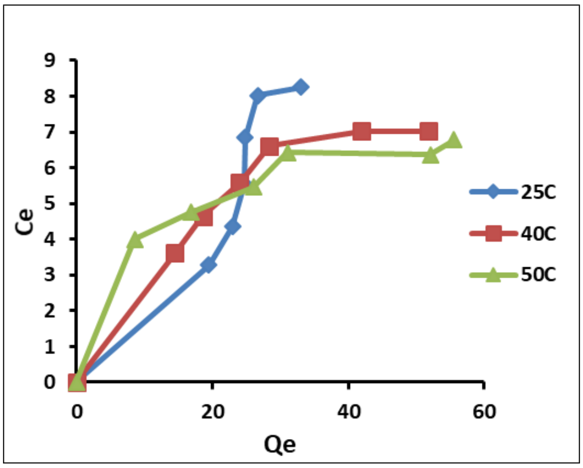

Fig. 5. Effect of Temperature on adsorption quantity of DB_2 dye on Y_2O_3 nanoparticles

From (Fig. 5) observed that the adsorption quantities were increased when the temperatures increased.

Effect of pH:

The adsorption of DB_2 dye on Y_2O_3 nanoparticles at different pH (1.6, 3, 6.5, 8 and 10) using constant concentration of dye solution and constant temperature 30C° was studied for 30min and the study results shows in (Fig. 6).

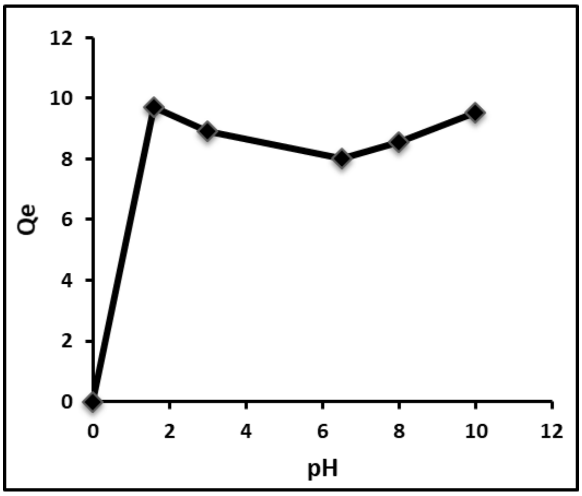

Fig. 6. Effect of pH on adsorption quantity of DB_2 dye on Y_2O_3 nanoparticles

From (Fig. 6) observed that the adsorption quantities of DB_2 dye on Y_2O_3 nanoparticles were increased in the acidic medium and decreased in basic medium.

Adsorption Isotherms:

Table 1 shows the laws of adsorption isotherm models. Figures 7, 8, 9, 10 and 11 shows the relations of adsorption isotherm models:

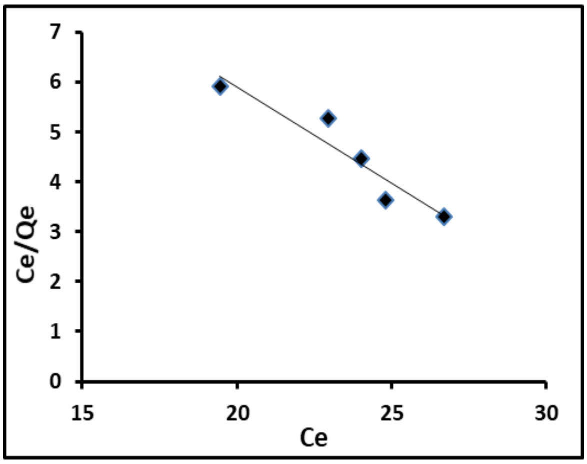

Fig. 7. Adsorption Isotherm Model of Langmiur

TABLE 1. The Laws of Adsorption Isotherm Models

Isotherm	Linear Form	Plot of Linear Form	Parameters
Langmuir[16]	$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{1}{q_m} \times C_e$	C_e *vs* C_e/q_e	q_m , K_L
Freudlich[17, 18]	$Logq_e = LogK_F + \frac{1}{n} LogC_e$	Log C_e *vs* log q_e	K_F
TTemkin[19]	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	Ln C_e *vs* q_e	b , K_T
Halsey[20]	$\ln q_e = \frac{1}{n_H} \ln K_H + \frac{1}{n_H} \ln C_e$	Ln C_e *vs* ln q_e	K_H, n_H
Harkins-Jura[21]	$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log C_e$	Log C_e *vs* $1/q_e^2$	B_{HJ}, A_{HJ}

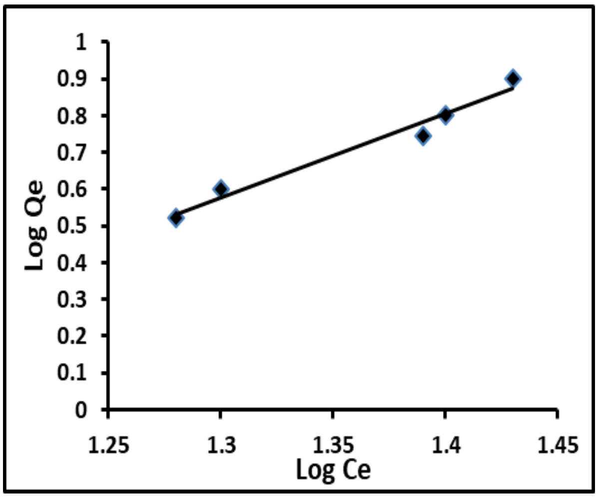

Fig. 8. Adsorption Isotherm Model of Freundlich

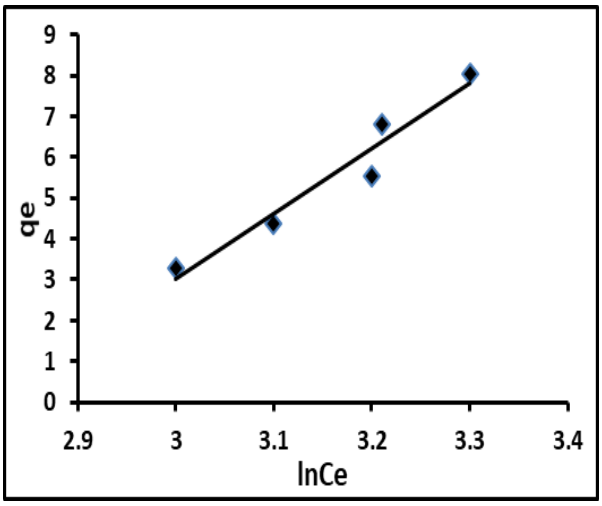

Fig. 9. Adsorption Isotherm Model of Temkin

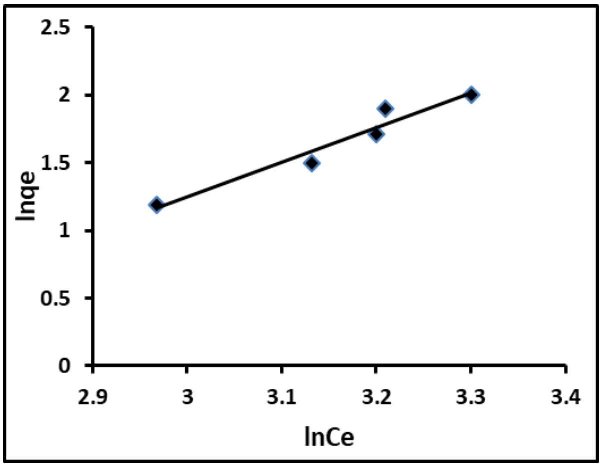

Fig. 10. Adsorption Isotherm Model of Halsey

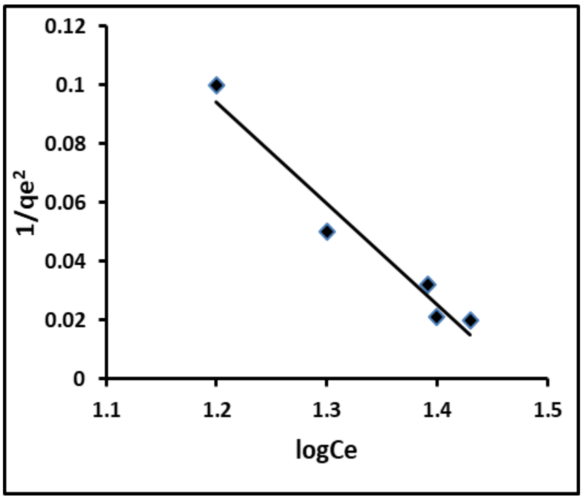

Fig. 11. Adsorption Isotherm Model of Harkins-Jura

Table 2 shows the parameters of adsorption isotherm models of DB_2 dye on Y_2O_3 nanoparticles:

TABLE 2. Parameters of Adsorption Isotherm Models of Adsorption DB_2 dye on Y_2O_3 nanoparticles

Model	**Parameters**	
Langmiur	q_m	2.583
	K_L	0.028
	R^2	0.902
Freundlich	1/n	2.282
	K_F	0.091
	R^2	0.969
Temkin	b	155.822
	K_T	16.621
	R^2	0.942
Halsey	n_H	0.391
	K_H	0.081
	R^2	0.944
Harkins-jura	A_{HJ}	2.898
	B_{HJ}	1.472
	R^2	0.957

It is found from the table above that the freundlich isotherm model is appropriate for the adsorption of DB2 dye on nanoparticles Y2O3.

Thermodynamic Study:

Thermodynamic parameters were calculated to study the effects of temperature on the adsorption quantity of DB2 onY_2O_3 nanoparticles. The coefficient of distribution K_d was calculated from Equation 8:

$$K_d = \frac{q_e}{C_e} \qquad .....(8)$$

The enthalpy, ΔH (kJ·mol⁻¹) and entropy ΔS (kJ·mol⁻¹) were calculated from the Van't Hoff [21] plot by equation 9

$$\ln K_d = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \qquad ..... (9)$$

(Fig. 12) shows the relation between $\ln K_d$ and 1/T :

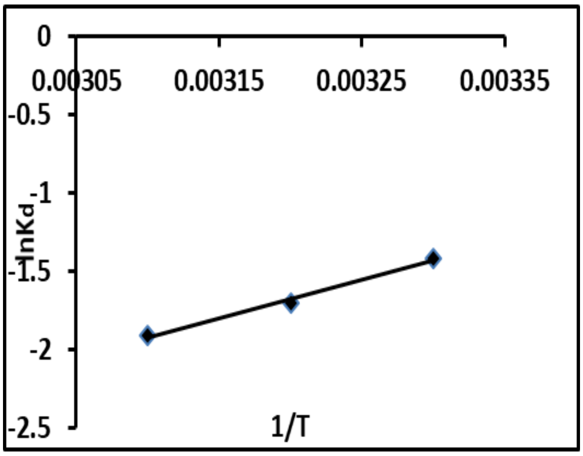

Fig. 12. The relation between $\ln K_d$ and 1/T

The free energy change (ΔG) ($kJ \cdot mol^{-1}$) values were obtained from Equation 10 [22].

$$\Delta G = \Delta H - T\Delta S \qquad ..... (10)$$

The thermodynamic parameters for the adsorption of DB2 on Y_2O_3 nanoparticles are shown in table 3:

TABLE 3. Thermodynamic Parameters for The Adsorption of DB2 Dye on Y_2O_3 Nanoparticles

ΔHº (kJ.mol⁻¹)	**ΔSº (kJ.mol⁻¹.K⁻¹)**	**ΔG_1^o (kJ.mol⁻¹)**	**ΔG_2^o (kJ.mol⁻¹)**	**ΔG_3^o (kJ.mol⁻¹)**
20.327	-0.0789	43.839	45.022	45.811

The positive value of ΔHº showed that it was (endothermic reaction) the adsorption of DB2 dye on Y_2O_3 nanoparticles.

Conclusions

We concluded in this work that the adsorption isotherm model (Freundlich isotherm) is suitable for the adsorption of DB2 dye on Y_2O_3 nanoparticles and this reaction is endothermic reaction because of the positive value of ΔHº.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgments

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