

Thermodynamic Study of The Adsorption of Some Azo Dyes on Activated Carbon

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Abstract

This work is concerned with studying the adsorption of some azo dyes better on commercial activated carbon. The dyes were synthesized by considering the resorcinol as constant part in their structure which is reacted with a number of *para* substituted aniline via dizonium ions and used as adsorbate for achieving this study. These dyes were identified by a number of physical tests and the available spectroscopic methods. Three models of adsorption isotherms namely, Freundlich, Langmuir, and Tempken are applied to fit the experimented data of adsorption at equilibrium in the range of concentration (1×10^{-4} - 5×10^{-4})M at various temperatures (292-328)K, and using (1gm/L) of the Adsorbent (Activated Carbon). The results showed that, the Freundlich isotherm is better fitted to the experimental data of the studied systems, although Langmuir isotherm exhibited good fit. This work included performing thermodynamic, depending on calculating the equilibrium constants by different methods, which represented by Freundlich constant K_f , Langmuir constant (K_L) and finally is described by Tempkin constant (T_K). The results showed good consistency among the four sets of functions in terms of their values and physical meaning. This consistency gave good indication for the accuracy of such kind of calculation.

Key words: adsorption, azo dye, Adsorption isotherms, Thermodynamic study.

دراسة ترموديناميكية لإمتزاز بعض أصباغ الأزو باستخدام الكربون المنشط

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الخلاصة

تضمن هذا البحث دراسة إمتزاز عدد من أصباغ الأزو على الكربون المنشط التجاري . وحضرت هذه الصبغات بإعتماد مركب الريسورسينول كجزء رئيسي فيها مع إضافة عدد من مركبات الأمينات الأروماتية عليها من خلال تفاعلات الأزوتة والاقتران وقد تم تمييز الصبغات المحضرة من خلال دراسة بعض مواصفاتها الفيزيائية وبالطرائق الطيفية المتوفرة لدينا. وبعد تحديد الظروف المثلى لأفضل إمتزاز طبقت البيانات العملية للإمتزاز على عدد من الايزوثيرمات المعروفة مثل أيزوثيرم فرنديش ولانكماير وتيمكن في مدى من التراكيز (1×10^{-4} - 5×10^{-4}) مولاري وفي مدى من الدرجات الحرارية (292-328) مطلقة، وباستخدام (1غم / لتر) من المادة المازة، وقد اظهرت الدراسة إنطباق البيانات العملية المحصل عليها بشكل أفضل على ايزوثيرم فرنديش على الرغم من انطباقها بشكل جيد أيضا على ايزوثيرم لانكماير. وقد اشتمل البحث على دراسة ترموديناميكية تمت بالإعتماد على حساب ثابت فرنديش K_F و ثابت لانكماير K_L وثابت تيمكن T_K كدوال على ثابت الإتران.

الكلمات المفتاحية: الأمتزاز، ايزوثيرمات الأمتزاز، أصباغ الأزو، دراسة ترموديناميكية .

Introduction

Due to their good solubility in water, synthetic dyes are frequently found in industrial wastewater as common water pollutants. The removed of such dyes from wastewater has become a vital task, since they have wide application and uses in many industrial fields such as on textiles, paper, plastics, rubber, cosmetics and food industries. Pollution of water due to the discharge of effluents from dyeing industries affects the environment due to their toxicity since these effluents containing many harmful chemicals that pose series problems to human being and aquatic life [1, 2]. It is therefore, environmental pollution control has been a concern issue in many countries.

Various techniques have been employed for the removal of dyes from wastewater. The common methods for color effluents from water include chemical precipitation, ion exchange, ozonation,

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osmosis, solvent extraction, membrane filtration, and adsorption. Adsorption is considered to be superior to other techniques [3, 4]. Activated carbon is widely used as an adsorbent due its high adsorption abilities in removal of organic and inorganic pollutants from wastewater. [5] The growing interest in using low cost naturally abundant substances as a raw material for the production of activated carbon as adsorbent made the adsorption as a promising technique. The efficiency of the adsorption process depends on the conditions under which the adsorption is carried out such as contact time, initial concentration of adsorbate, and pH of the medium of adsorption system [6].

The type of adsorption system and the nature of bonds controlling the process is usually determined by studying the adsorption at equilibrium and fitting the experimental data into Langmuir and Freundlich equations and determine the best isotherm correlation [6]. The thermodynamic data are valuable for determining the period required to reach equilibrium and assessing the adsorbent performance for effluent species adsorption. These data also help to understand the type and nature of the adsorption which is essential for improving the efficiency of such processes. For these reasons, a great attention has been paid for such studies [7]. The main aim of this investigation is to study the adsorption desorption equilibrium that affect the related data for a number of azo dye molecules which vary in both type and position of their functional groups [8].

Experimental part

The dyes used in this research synthesized *via* diazonium salts by two main steps:

Preparation of diazonium salts

- A.** (2.14g) of Aniline was dissolved in 15 ml HCl in a beaker using continuous magnetic stirring while maintaining the solution temperature in the range of (0-5°C).
- B.** In another beaker, (1.0g) of sodium nitrite (NaNO_2) was dissolved in (5 ml) distilled water while keeping temperature between (0-5°C), and then this solution is gradually was added to solution (A) with continuous stirring while keeping the mixture temperature between (0-5°C). [9]

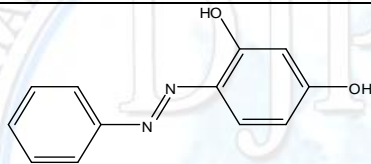
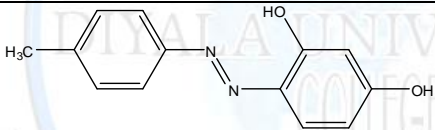
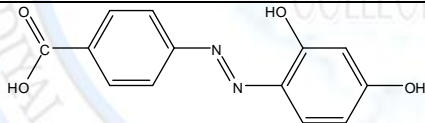
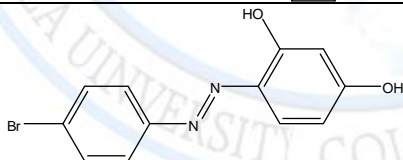
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Preparation of the resorcinol solution

9 ml of sodium hydroxide solution of 10 %. (3.9g) of resorcinol was dissolved in while preserving the solution temperature (0-5°C). Then the solution prepared in the first step is added to that of the second step solution slowly with the continuous stirring until the crystals of the desired material are formed, mixed for half an hour, then filtered and wash with distilled water and dried. The other dyes used in the study, are shown in Table (1), were prepared in the same manner. [9]

Table 1: Names, structure, colors, melting point and λ_{\max} of the prepared dyes structures

Dye	Structure	Color	Melting point (°C)	λ_{\max} (nm)
Phenyl azo resorcinol (PAR)		Red -orange	162-166	378
p-methyl phenyl azoresircinol (p-MAR)		orange	175-177	382
p-carboxy phenyl azo resorcinol (p-CAR)		Light orange	Decomp.	392
p-bromo phenyl azo resorcinol (p-BAR)		A reddish orange	150-153	386

Results and Discussion

Adsorption isotherms

The equations of isotherm are mathematical relationships that are derived or adapted to describe the adsorption system in equilibrium and the nature of the relationship between the adsorbed substance and the surface of the adsorbent by taking into consideration a number of assumptions that were adopted when deriving the mathematical equation that varied with the different

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principle on which each isotherm was based [10]. This study included the calculation of K_f , K , n , Q_{max} , b and K_T , B_T constants and their practical values. [10, 11]

1. Freundlich isotherm

It assumes that the energies of the effective sites on the surface of adsorbent are unequally energy-efficient and that the bonding of the adsorbate on the surface can be formed by the formation of multiple layers [12]. The equation of Freundelchcan be given As follows [13]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (1)$$

K_f and n are called freundlich isotherm constants which are related to adsorption capacity and intensity respectively. The value of K_f and n can be obtained from the values of the intercept and the slope, of the linear relationship plot between $\log q_e$ (adsorption capacity) versus $\log C_e$ (equilibrium concentration). The study and the straight lines drawn from this relationship are listed in figure (1):

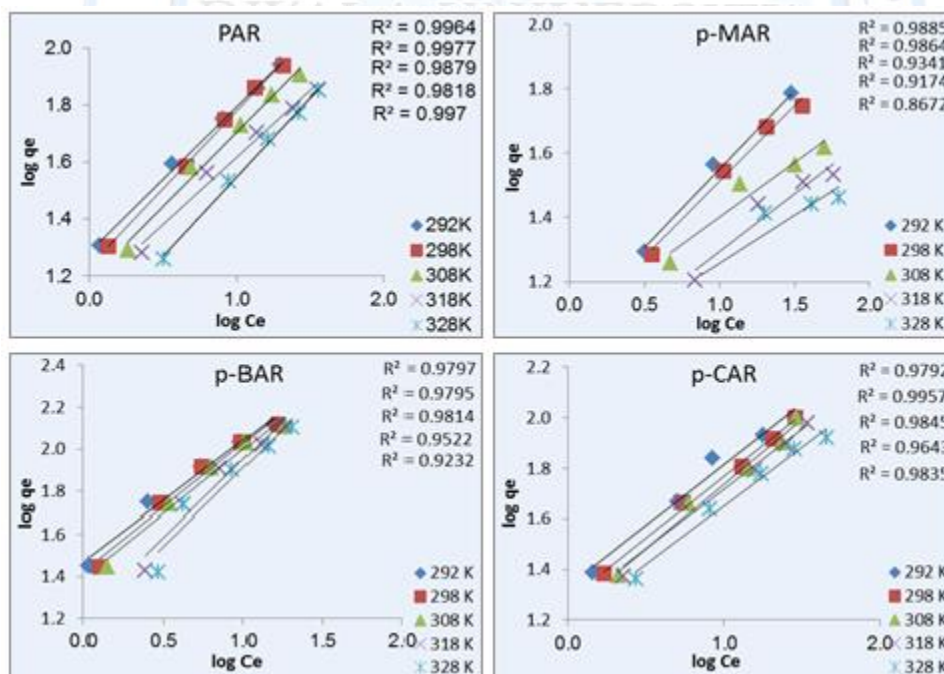


Figure 1: Application of Freundlich Isotherm on adsorption of dyes under study

The results were obtained from the fitting equation (1) to the experimental data of adsorption systems fee are included in Table (2), and showed in Figure (1).

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Table 2: Values of Freundlich Isotherm coefficients resulting from applying the experimental data the isotherm equation

dye	Temp. K°	n	K _f (mg/g)	R ²
PAR	292	1.962	19.222	0.9964
	298	1.837	17.155	0.9977
	308	1.919	15.233	0.9879
	318	2.124	13.960	0.9818
	328	1.796	9.767	0.997
p-MAR	292	2.043	11.548	0.9885
	298	2.124	11.036	0.9864
	308	2.942	11.487	0.9341
	318	2.788	8.650	0.9174
	328	3.359	9.122	0.8672
P-CAR	292	2.064	21.439	0.9792
	298	2.045	18.993	0.9957
	308	1.948	16.788	0.9845
	318	2.118	17.713	0.9643
	328	2.160	15.421	0.9835
p-BAR	292	1.764	29.895	0.9797
	298	1.676	27.051	0.9795
	308	1.653	24.843	0.9814
	318	1.367	16.669	0.9522
	328	1.370	15.164	0.9232

From the observation of the results in Table (2) we find that, the values of n is limited to (1-10) and in all the temperature degrees in the studied range, indicating that the adsorption system under study is of a physical nature. These results are supported by the values of Freundlich constant K_f, which is related to the adsorption capacity. The equation of Freundlich isotherm is found to be applicable to practical adsorption data.

2. Langmuir isotherm

The Langmuir equation is often used in single-layer adsorption systems. This isotherm assumes that the particles of adsorbate are adsorbed on a fixed number of energetically equal and well-defined gaps on the surface of the solid surface, and that each gap can carry only one adsorbed molecule [14] The linear form of the Langmuir isotherm can be given as follows [15]:

$$\frac{C_e}{q_e} = \frac{1}{b Q_{max}} + \frac{C_e}{Q_{max}} \dots\dots\dots(2)$$

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Where, q_e (mg / g) is the adsorption capacity, and represents the amount of the dye (mg) for each (g) of the adsorbent equilibrium, and Q_{max} is the maximum theoretical adsorption capacity, which represents the amount of the dye (mg). per gm of adsorbent at equilibrium maximum, C_e (mg/L) represents the concentration of the remaining dye in the solution at equilibrium. Drawing the relationship between C_e/q_e versus C_e , straight lines were obtained with good coefficients as shown in Figure (2).

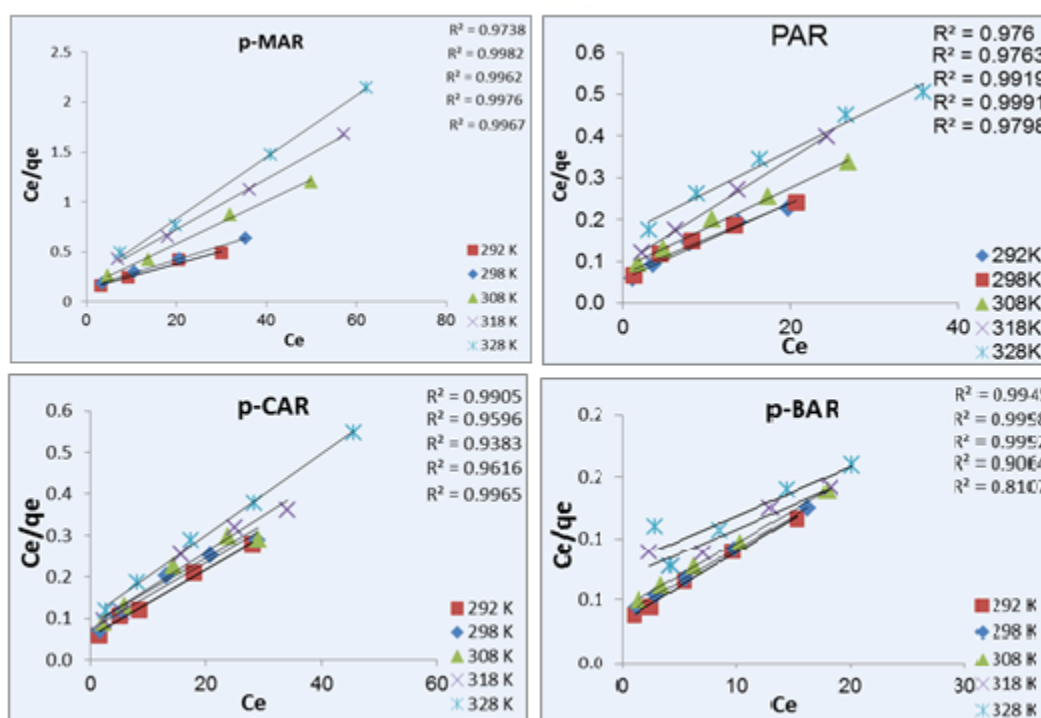


Figure 2: Applicatin of Langmuir Isolation of the experimental data of studied dyes

The values of the Langmuir constants, those calculated from the slope and the intercept of straight lins are included in Table (3) and correlation.

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Table 3: Values of Langmuir Isotherm coefficients resulting from the application of isotherm to practical adsorption data

Dye	Temp. K°	Q _{max} (mg/g)	b (L/mg)	R ²
PAR	292	111.111	0.153	0.976
	298	117.647	0.122	0.9763
	308	104.167	0.114	0.9919
	318	86.957	0.111	0.9936
	328	99.010	0.062	0.9798
p-MAR	292	79.365	0.094	0.9738
	298	71.942	0.0976	0.9982
	308	46.948	0.136	0.9962
	318	39.841	0.111	0.9976
	328	32.468	0.143	0.9967
P-CAR	292	123.457	0.142	0.9905
	298	125.000	0.108	0.9596
	308	125.000	0.0924	0.9383
	318	114.943	0.103	0.9616
	328	102.041	0.095	0.9965
p-BAR	292	178.571	0.171	0.9945
	298	185.185	0.144	0.9998
	308	185.185	0.127	0.9992
	318	208.333	0.085	0.9833
	328	192.308	0.443	0.9232

Table (3) shows that, the maximum adsorption capacity Q_{\max} is decreased with temperature increase with some exceptions and is in compliance with practical adsorption capacity. Q_{\max} values are higher than the values of practical adsorption capacity. This is due to the actual repulsion and occurrence of discrepancies resulting among the molecules of dye, which are not considered in the calculation of theoretical values, compete with Q_{\max} values as high as 298 in most dyes. This gives a positive indication in terms of the economic factor. On the other hand, the Langmuir b constant, which is strongly related to surface-bonding, is also decreasing with increasing temperature (with some fenders). All of this supports the physical nature of the studied systems and type of the bonds that bind the dye to the solid surface.

3. Tempkin isotherm

This isotherm assumes that the adsorption temperature decreases linearly with the increased coverage of the solid surface, which causes increased competition among the molecules to bind to the remaining sites, thereby increasing the interaction between the adsorbed and non-

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adsorbend molecules and thereby weakening the bonding strength of the molecules absorbed with the surface thereby reducing the adsorption temperature [16].

The linear form of this equation can be given as follows [17]:

$$q_e = B_T \ln K_T + B_T \ln C_e \dots\dots\dots (3)$$

Where B_T represents the Tempkin constant that related to the surface capacity to adsorb the dye for each unit of energy and computes its value from the mathematical relationship:

$$B_T = RT / b \dots\dots\dots (4)$$

(T) is the absolute temperature (K), R is the gas constant and its value ($8.314 \text{ j.mol}^{-1}.\text{K}^{-1}$) and b is a constant related to the adsorption temperature (J/mol). K_T (L / mg) is the bonding equilibrium constant and indicates the maximum B_T bonding power. In drawing the relationship between q_e versus $\ln C_e$, it is possible to find the value of the B_T and K_T constants by the values of the slope and the intercept of the straight line, respectively.

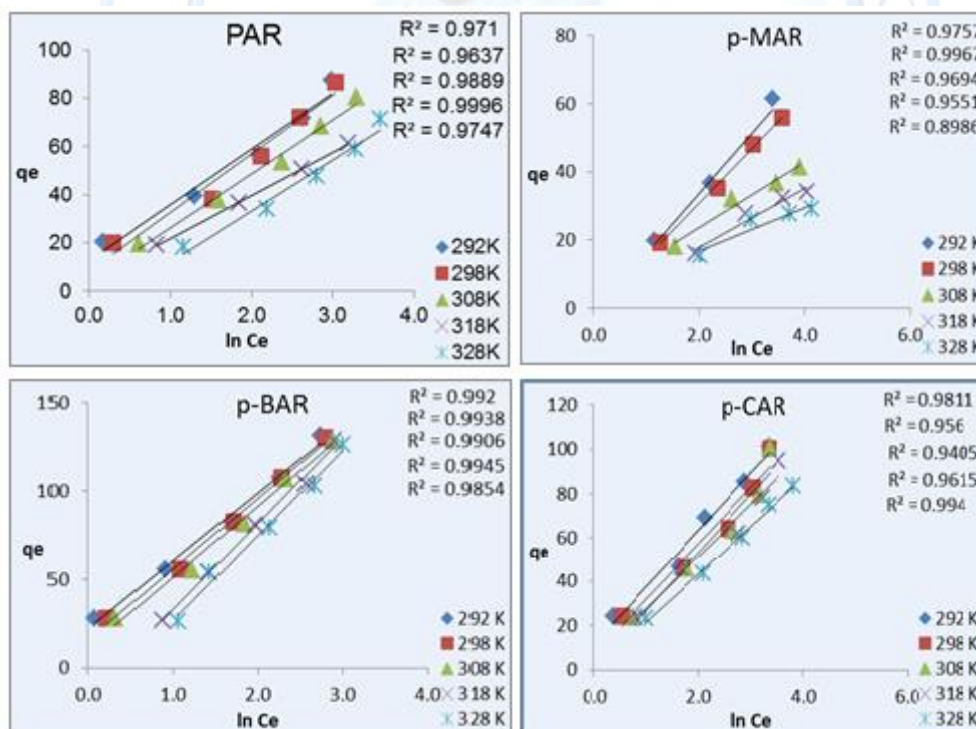


Figure 3: Application of Tempkin isotherm on the adsorption data of studied dyes

The Tempkin parameters calculations from Figure (3) are listed in Table (4).

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Table 4: Values of Tempkin constants (B_T and K_T) and correlation coefficients from application of practical adsorption data

dye	Temp. K°	$B_T(KJ/mol)$	$K_T(L/mg)$	R^2
PAR	292	23.029	1.741	0.971
	298	24.324	1.398	0.9637
	308	22.377	1.305	0.9889
	318	18.701	1.155	0.9911
	328	21.281	0.438	0.9747
p-MAR	292	17.557	1.087	0.9757
	298	16.093	1.098	0.9967
	308	9.521	1.617	0.9694
	318	8.599	1.090	0.9551
	328	6.377	1.8620	0.8986
p-CAR	292	26.061	1.551	0.9811
	298	25.549	1.277	0.956
	308	26.468	1.017	0.9405
	318	24.005	1.135	0.9615
	328	21.875	1.017	0.994
p-BAR	292	38.222	0.589	0.992
	298	40.024	0.3995	0.9938
	308	40.123	0.2737	0.9906
	318	48.433	0.3158	0.9945
	328	48.024	0.4396	0.9854

Looking at Table (4), the values of correlation coefficients (R^2) indicate that, the Tempkin isotherm is less applicable to experimental data of adsorption of the studied systems, when compared with the Freundlich and Langmuir isotherms. It was observed that the value of the K_T constant is inversely proportional to the temperature, which supports the physical nature of the bond between the dye and the surface. The value of the B_T constant which is absorb the dye for each energy calculated from (eq. 4). The value of B_T has been found to be inversely proportional to the temperature.

The results of the above discussion, medicate that Langmuir and Tempkin isotherm constants can be changed by a certain pattern and are consistent with the variation between temperature and adsorption capacity as well as bond energy. Thus, they can be used as well as Freundlich isotherm to derive and calculate the thermodynamic functions of the studied system.

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Thermodynamic study

Recording to Van't Hoff equation, thermodynamic parameters i.e. the standard adsorption Gibbs free energy ΔG° , enthalpy ΔH and entropy ΔS° can be calculated from the variations of the thermodynamic equilibrium constant K , which was determined using the method from literature [18], The thermodynamic Functions can be calculated from Van't Hoof equation (eq.5) which describes the relation between the variation of equilibrium constant with the temperature.

$$\ln K = \ln K_o e^{-\Delta H/RT} \dots\dots\dots(5)$$

The calculation of the value of (ΔH), the thermodynamic functions (ΔG° and ΔS°) can be calculated from the following equations:

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \dots\dots\dots(6)$$

$$\Delta S^\circ = (\Delta H - \Delta G^\circ) / T \dots\dots\dots(7)$$

The value of (ΔH) was calculated by plotting the relationship between ($\ln K$) versus the ($1/T$), which gives a straight line with slope equal to ($-\Delta H/R$). R is the gas constants $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ and $T(\text{K})$ is the absolute temperature. In a new attempt, the value of K is determined by the values of the isotherm constant those described earlier and as follows:

The thermodynamic Functions are determined from Freundlich constant (K_f) derived from eq.1, which was calculated in the concentration range of $(1-5) \times 10^{-4}$.

Since K_f is related to the adsorption capacity, so it can be good representative of the equilibrium constant, and can be used for estimating the thermodynamic function. The calculated values of, the values of the equilibrium constant are well expressed and the thermodynamic functions (ΔH , ΔS° and ΔG°) using K_f are shown in Table (5).

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Table 5: Thermodynamic functions obtained from Freundlich constants

Dye	Temp. K°	K _f (mg/g)	G°Δ (KJ.mol ⁻¹)	HΔ (KJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
PAR	292	19.222	-7.176	-9.342	-7.417
	298	17.155	-7.042		-7.718
	308	15.233	-6.974		-7.688
	318	13.96	-7.189		-6.564
p-MAR	292	11.548	-5.939	-6.194	-0.872
	298	11.036	-5.949		-0.822
	218	2.158	-5.704		-1.540
	328	9.122	-6.029		-0.504
p-CAR	292	44.294	-9.201	-19.338	-34.717
	298	38.833	-9.066		-34.469
	318	37.512	-9.282		-31.623
	328	33.313	9.269-		-30.698
p-BAR	292	29.895	-8.249	-22.129	-26.508
	398	27.051	-8.170		-26.237
	308	24.843	-8.226		-25.203
	318	16.669	-7.439		-26.888
	328	15.164	-7.414		-26.142

The values of the thermodynamic functions were calculated using the Langmuir K_L constant which was calculated from the following equation.

$$K_L = Q_{max} * b \dots\dots\dots(8)$$

Multiplying Q_{max} (the maximum theoretical capacity) by b will result in giving actual value close to the practical adsorption capacitance as K_L value [19]. Calculated values are included in Table (6), and the thermodynamic function values are calculated from this constant in the same way using eq. 5,6 and 7.

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Table 6: Thermodynamic functions obtained from Langmuir constants

Dye	Temp. K°	K _L (L/g)	G°Δ (KJ.mol ⁻¹)	HΔ (KJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
PAR	292	16.978	-6.875	-21.08	-48.647
	398	14.327	-6.596		-48.605
	308	11.905	-6.343		-47.848
	318	9.652	-5.994		-47.440
	328	6.105	-4.933		-49.227
p-MAR	292	7.484	-4.886	-14.974	-34.547
	298	7.022	-4.829		-34.044
	308	6.380	-4.746		-33.209
	318	4.41	-3.923		-34.750
p-CAR	292	17.513	-6.950	-12.305	-18.338
	308	11.547	-6.265		-19.611
	318	11.806	-6.527		-18.171
	328	9.681	-6.191		-18.641
p-BAR	292	30.581	-8.304	-13.974	-19.419
	398	26.596	-8.128		-19.617
	308	23.474	-8.081		-19.132
	318	17.731	-7.602		-20.038
	328	16.667	-7.672		-19.213

The values of thermodynamic functions were calculated using the T_K constant which derived according to the same principle as the Langmuir constant by multiplying the constants of the K_T and B_T according to the following equation:

Table 7: Thermodynamic functions obtained from the Tempkin constants

Dye	Temp K°	K _T (mg/g)	G°Δ (KJ.mol ⁻¹)	HΔ (KJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
PAR	292	40.1	-6.875	-29.221	-45.409
	298	34.01	-6.596		-45.247
	308	29.203	-6.343		-44.092
	318	9.652	-5.994		-44.331
	328	9.325	-4.933		-49.184
p-MAR	292	19.088	-7.159	-10.570	-11.680
	398	17.677	-7.116		-11.590
	308	15.393	-7.001		-11.588
	328	11.874	-6.747 -6.747		-11.654
p-CAR	292	40.41	-8.98	-12.557	-43.003
	398	32.613	-8.634		-42.138
	308	26.905	-8.431		-40.769
	328	22.24	-8.459		-38.284
p-BAR	292	22.513	-7.560	-33.107	-87.490
	398	15.99	-6.868		-88.051
	308	10.982	-6.136		-87.568

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$$T_K = K_T \cdot B_T \dots\dots\dots (9)$$

These two parameters, the B_T is related to the differential surface area of adsorption per each unit of energy. The K_T represents the constant of the bonding equilibrium, indicating the maximum bonding energy. T_K has been derived from them. This constant has been successfully applied for the first time in previous studies [16, 19]. The results obtained are listed in Table (7).

From Tables (5), (6) and (7) it can be concluded that:

- A) The values of K_L , K_f , and T_K are inversely related to the temperature, indicating that, the adsorption is of a physical nature.
- B) The values of the ΔG° adsorption indicate that the adsorption system tends to occur in the forward direction (surface link) and decreases with temperature increase.
- C) The negative values ΔH indicate that the adsorption is an exothermic reaction and the bond between the dye and carbon are physical in nature (less than 40 kJ / mol).
- D) Finally, the values of ΔS° are slightly differentiated by physical adsorption and indicate that the adsorption system at equilibrium is less random than the beginning of the process.

The above-mentioned methods applied for calculating thermodynamic Functions so far showed good consistency. To illustrate that, the simple comparison shown in table (8) can be used.

Table 8: Comparison of adsorption enthalpies values for the isotherm, Freundlich, Langmuir and Tempkin

Dye	$H\Delta$ From (K_f)	$H\Delta$ From (K_L)	$H\Delta$ From (K_T)
PAR	-9.342	-21.08	-29.221
p-MAR	-6.194	-14.974	-10.570
p-CAR	-19.338	-12.305	-12.557
p-BAR	-22.129	-13.974	-33.107

When looking at the ΔH values listed in (Table 8) and obtained from the three isotherms, we find that they are in good agreement despite the different methods used in the calculations. This is a good achievement in the calculation of thermodynamic functions since, despite the difference in the principles adopted by the Isotherm and hypotheses on which they were given

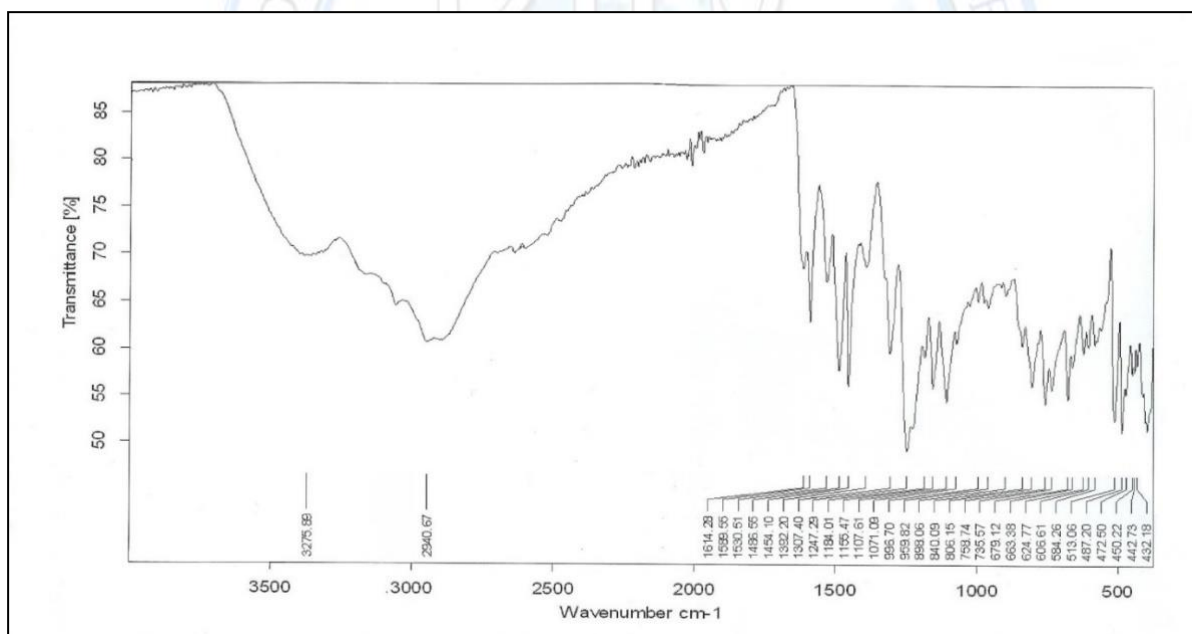
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Thermodynamic functions correspond to their range, direction of change and their correlations, and this is consistent with what was obtained in a previous study [20].

Spectral diagnosis

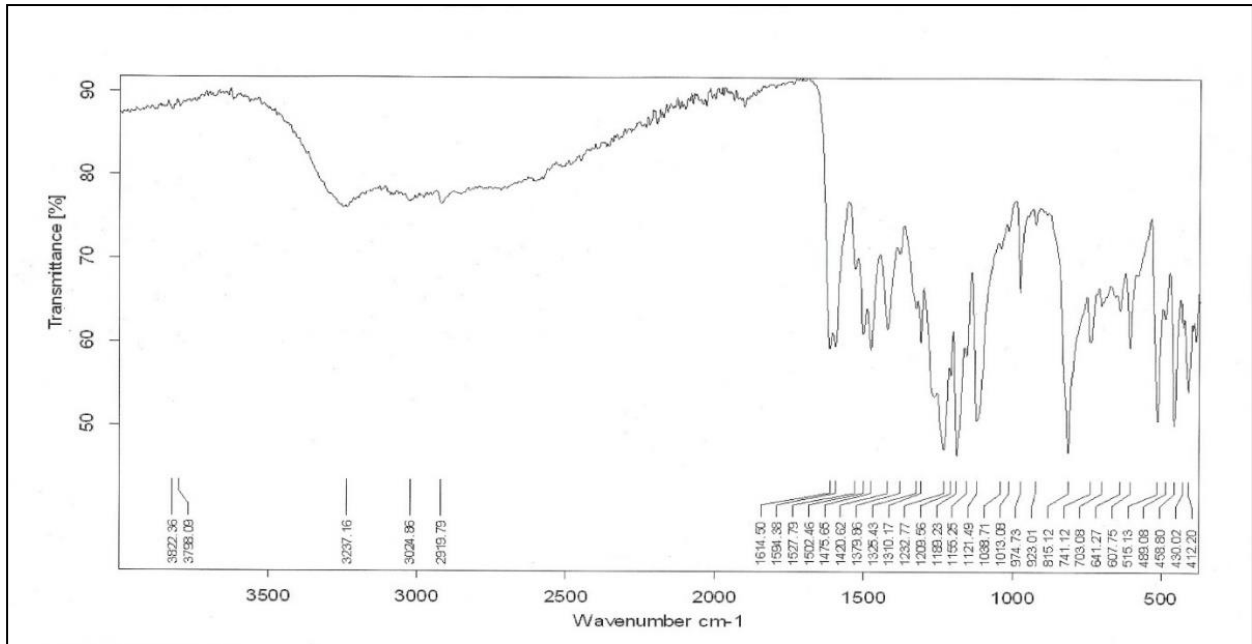
(N = N) was tested using infrared spectroscopy (IR). There was a distinctive package of the ISO range between (1475.65-1549.59) which appeared in the dye spectrum after the disappearance of NH₂ in the primary amino acid each dye was prepared indicating the formation of the Dye. The forms of IR spectra drawn for the dyes are shown in Appendixes (1) to (3). As well as other indications such as the composition of solid compounds and colors distinct from the colors of the primary compounds prepared by each dye, as well as the emergence of distinctive packages of studied Dyes such as (O-H), and (C-O), (C-N) and (C-H). all of these are shown in Table (1) in the research.



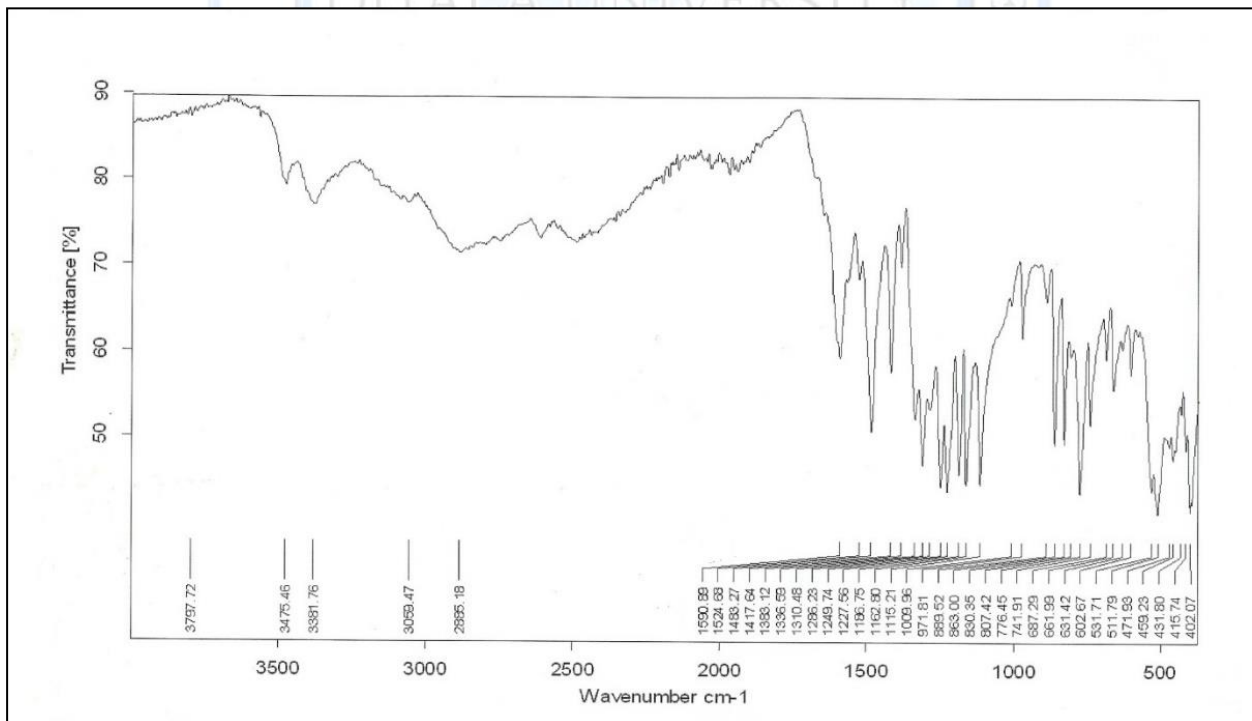
Appendix 1: Infrared spectrum of dye (PAR)

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Appendix 2: Infrared spectrum of dye (p-MAR)



Appendix 3: Infrared spectrum of dye (p-CAR)

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