دراسة امتزاز عدد من أصباغ الازو على الكربون المنشط النانوي المحضر من جذوع اشجار الكالبتوس

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Adsorption Study of A Number of Di-Azo Dyes On A Nano Activated Carbon ; Prepared From Stem of Eucalyptus Tree

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الملخص:
تضمن هذا البحث دراسة الاتزان والديناميكية الحرارية لامتصاص صبغتين من اصباغ الازو على الكربون المنشط المحضر من أوراق شجر الكالبتوس المتساقطة التي تم جمعها من غابات مدينة الموصل الواقعة في الجزء الشمالي من العراق. وبعد عملية التحضير تم تحفيز الكاربون المنشط حراريا وتم تقدير كفاءة وسعة الامتزاز وتعين الظروف المثلى لنظام الامتزاز مثل تأثير كمية المادة المازة (الجرعة) ووقت التلامس ودرجة الحرارة والتركيز الأولي. تضمن البحث تطبيق ثلاثة أنواع من منحنيات الامتصاص على نظام الامتزاز قيد الدراسة وهي منحنيات لانكماير وفريندلك وفلوري-هجينز (FH)، حيث أن معادلة منحنيات الامتصاص لفريندلك هي الأكثر ملاءمة للبيانات العملية لامتزاز الأصباغ المدروسة عند جميع درجات الحرارة المشار إليها بقيم معاملات الارتباط (R2) والتي تراوحت بين (0.9999 – 0.9924) وهذا يشير إلى إمكانية تكوين امتزاز متعدد الطبقات موزع على مساحة سطح غير متجانسة. كما أجريت دراسة ثرموديناميكية عند تراكيز أولية مختلفة (35، 87، 140، و197 ملغم/لتر)، كل تركيز في نطاق درجات حرارة (293-333 كلفن). أثبتت النتائج أن قيم ثابت التوازن (K) تتناقص مع زيادة درجة الحرارة وهذا يتفق مع الطبيعة الفيزيائية لعملية الامتزاز. أثبتت قيم الدوال الديناميكية الحرارية أن نظام الامتزاز قيد الدراسة تلقائي، وأن القوى المسيطرة على الاتصال بين جزيئات الصبغة والمواقع النشطة على سطح الكربون فيزيائية بطبيعتها. تؤدي عملية الامتزاز إلى نظام أكثر تنظيمًا عند تركيز 35 ملغم/لتر، بينما كانت النتائج عند تركيزات أعلى عشوائية (لا انتظام) لكلا الصبغتين (D1 وD2). ويمكن إرجاع ذلك إلى حقيقة مفادها أن زيادة التركيز يزيد من عدد الجزيئات المتبقية في محاليل الصبغة، وبالتالي زيادة عشوائية النظام، وخاصة بعد التوازن.

الكلمات المفتاحية: الكربون المنشط، الامتزاز، اصباغ ثنائي مجموعة الأزو، أوراق الكالبتوس، الديناميكا الحرارية.

Abstract:
This work included equilibrium and thermodynamic studies of the adsorption of two azo dyes on activated carbon prepared from Fallen eucalyptus leaves collected from the forests of Mosul city which is located in the north part of Iraq. The preparation is followed by thermal stimulation where the efficiency and capacity of adsorption were estimated. The optimal conditions of the adsorption system such as; effect of amount of adsorbent (dose), contact time, temperature and initial concentration were conducted. The research included the application of three types of isotherms to the adsorption system under study, namely Langmuir, Freundlich, and Flory-Huggins (FH), The Freundlich isotherm equation is better fitted to the practical data of adsorption of the studied dyes at all temperatures indicated by the values of the correlation coefficients (R^2) that, ranged between (0.9999 –0.9924) and this pointing to the possibility of the formation multi-layer adsorption distributed on a heterogeneous surface area. Thermodynamic study was also conducted at various initial concentration (35, 87, 140, and 197 mg/L), each concentration at range of temperatures (293-333 Kelvin). The results proved that, the values of equilibrium constant (K) decreases with increasing temperature. This is agree with the physical nature of the adsorption process. The values of the thermodynamic functions proved that adsorption system under consideration are spontaneous, the forces dominate the connection between the dye molecules and the active sites on the carbon surface are physical in nature. The adsorption process leads to more ordered system at a concentration of 35 mg/L, while at higher concentrations the results were more random order for both dyes (D1 and D2). This can be attributed to the fact that increasing the concentration increases the number of remaining molecules in the dye solutions, thus increasing the randomness of the system, especially after equilibrium.
Keywords: Activated Carbon, Adsorption, Di-azo Dyes, eucalyptus leaves, Thermodynamics Thermodynamics.

Introduction

Water pollution is one of the most important topics that have attracted the attention of scientists interested in this field. And no organism can live without it, regardless of size, shape and type. In addition, water occupies 70% of the land area and many industries such as textile, paper making, plastics and food are known to generate large quantities of contaminated waste water. Among these pollutants are dyes which are of the most disturbing pollutants in the environment due to their toxicity as well as their biodegradation product, those, have an aesthetic effect in addition, they work to block sunlight in the current and reduce the photosynthesis reaction [1-3] because of the high solubility of dyes in water and low ability to decompose under natural conditions [2-4]. The complex compositions of industrial dyes, waste water in the textile industry is very difficult to be treated by traditional methods due to its high cost. It is also not as efficient as it. Is due to the wide range of dyes found in industrial waste water. Many conventional techniques have been developed to decontaminate industrial waste water, such as sedimentation, evaporation, filtration, ion exchange and other processes such as membrane osmosis and coagulation[5,6]. The fusion of any of the above, is a complex methods that are economically difficult to implement. The adsorption is considered as one of the most important and efficient methods in the treatment of pollution, which has been widely used in a number of applications more than the rest of the other methods[7,8]. The adsorption method is rather simple. The application, and most importantly, its ability to recover the adsorbate materials in addition to mention methods that, it does not leave deposits or sludge that may itself be colored and burdensome on the will environment, as is the case in chemical precipitation processes, as well as in coagulation and fusion processes [9-12]. The

need to provide absorbents, efficient and cheap materials has become urgent[13]. Among the most lead to important of these materials that used as an adsorbent materials are locally prepared activated carbon which were widely used and synthesized from modifications of residual[14-16].This study included testing the efficiency of (activated carbon) to remove two di azo dyes from their aqueous solutions. The used dyes were prepared in our laboratories. The prepared activated carbon was thermally treated in the range (350-550 ^{o}C) and then its efficiency was tested. The prepared carbon was employed to find the optimal conditions for the system under study. Equilibrium (adsorption isotherms) and thermodynamic studies were achieved.

1. Equilibrium Studies

1.1. Langmuir Isotherm

The Langmuir isotherm assumes that the adsorption process occurs as a monolayer of molecules distributed on pores surfaces with homogeneous energies and performed at the same temperature and at a range of concentrations[17-20]. The linear form of the Langmuir isotherm equation shown in Equation No (1). The Langmuir constants (b and Q_{max}) for both dyes under study can be determined by plotting the relationship between Ce/qe and Ce.

$$Ce/qe = 1/(Q_{max} \ b) + 1/Q_{max} \ Ce \ ....(1)$$

The success of applying this isotherm to the adsorption data of the studied system can be estimated by the strength of the linear relationship obtained, indicated by the value of the correlation coefficient that should be close to unity (R^2).

1.2.Freundlich Isotherm

In this isotherm, Freundlich assumed heterogeneous distribution of active site and pores on the adsorbent surface. Fundamental changes were achieved and the experimental equation was modified. In which he gave it a great importance[20]. It became more suitable for describing the practical results of adsorption, but it does not contain any indication of the adsorption capacity of a single layer as in the Langmuir isotherm. The linear form of Freundlich model is expressed by the following equation:

$$Log \ qe = 1/ \ n \ logCe + logK_F \ ....(2)$$

where $K_F(mg.g^{-1})$, and n (dimensionless) are the Freundlich constants related to the capacity and intensity of the adsorption respectively. The values of the constants K_F and n are determined from the intercept and the slope of the straight line obtained from plotting lnqe versus ln Ce, respectively. R^2 is used as a measure for fitting the experimental adsorption data to this model.

1.3- Flory - Huggins isotherm (FH):

This model assumes the degree of coverage of the adsorbate molecules on the surface of the adsorbent. It expresses the simplicity and spontaneity of the adsorption process. The degree of coverage of the adsorbent surface is indicated as (θ).The linear form of this isotherm is given as in equation(3)[20,21].

$$Log(\theta/Ci) = n_{FH} \ log(1-\theta) + logK_{FH} \ ....(3)$$

The value of the degree of coverage is determined by equation (4),

$$\theta = (1-Ce/Ci) \ ....(4)$$

K_{FH} is the equilibrium constant of (Flory-Huggins) ($L.mg^{-1}$), K_{FH} and n_{FH} are the FH isotherm constants, and θ represent the coverage factor of the adsorbent surface.

Plotting the values of log(θ/Ci) against log(1-θ) should give a straight line with a slope equal to (n_{FH}) and an intercept equal to K_{FH}. The factor K_{FH} can be used to calculate the adsorption spontaneity by calculating the values of the free energy of Gibbs [21,22] by using equation(5).

$$\Delta G^{o} = -nRTlnK_{FH} \ ....(5)$$

EXPERIMENTAL
1.Adsorbate Material
Two di-azo dyes derived from para and meta phenylene di-amines as a central part combined with two resorcinol molecules. These dyes are insoluble in water, but can be dissolved in ethanol or a mixture of ethanol-water. The two dyes were prepared and diagnosed by our researchers group[23] in our laboratories from their starting materials, via diazonium salts these dyes are shown as in Table (1).

Table (1): The dyes used in this study and some of their physical properties.

Dye	Central part	R–part	L–part	Color	M.P	λmax (nm)	M.Wt g/mol	ε_{max} L.cm/mol
D1	p–phenylene di–amine	Resorcinol	Resorcinol	Gay Black	165.7	427	350	29460
D2	m–phenylene di amine	Resorcinol	Resorcinol	Black	207	390	350	25590

Where n is the number of moles, ΔG^o is the variation in the Gibbs free energy (kJ.mol^{-1}) at certain conditions [22].
2.Adsorbent
A new activated carbon was synthesized from Fallen eucalyptus leaves obtained from Mosul forests which located in the north of Iraq. The raw materials were washed with distilled water for several times in order to remove dust and impurity, then dried in an oven at (105-110 °C) for12 hours. It was then cut into pieces, crushed and thermally activated by heating into (350-550°C) for 3hs with 1:2.5 (wt:wt) of KOH in order to increase the surface area, and then washed by water till the pH of washing water reach (7). The obtained carbon was refluxed with (0.1N HCl) for 3h in order to remove ashes from pores, Then washed into pH =7, dried and saved in a closed container for subsequent studies. XRD, SEM, EDX and BET were used to study the crystalline regions, particle sizes, shapes, and the pores on the surface of the prepared carbon.
3.Estimation of adsorbate concentration
Since the study included colored materials (Dyes), the best analytical way to estimate the concentration of adsorbate is the spectrophotometric method. This method is the most efficient and accurate technique for estimating colored materials.
A double beam Uv-Vis spectrophotometer of the type (UV-1800) supplied by Shimadzu (Japan) is employed to achieve this study. The first step in this work is the determination of the maximum wavelength (λmax) for absorption of each dye under consideration. Then calibration curve is made by plotting the relationship between the absorption and various concentrations (C, mg/L) for each dye at its λmax within the detection limit of each dye according to Beer's law (eq.6) in order to estimate the concentration of the residual of the dye after adsorption. The concentration of the adsorbed dye (Cads., mg/liter) was determined from the difference between the initial (Ci) and residual (at any time (Ct), or at equilibrium (Ce)) concentrations (mg/liter), as in equation(6):
$A=\varepsilon\,C\,L$ .... (6)

Where: A; represents the dye absorption, (ε) = Molar absorption coefficient (Liter. cm. mol^{-1}), C= represents the molar concentration of the dye, and L is the cell width (the cell we used L=1).

The concentrations of the residual were estimated from applying the absorption of the remained dye on titration curve at any time (C_t) or at equilibrium (C_e) (mg/liter) by difference with the initial concentration (C_i) (mg/liter).

The adsorption capacity (qe, mg/g) which is represented by the number of mg of the dye per gram of carbon can calculated by using equation(7):-

$$qe = \frac{Ci - Ce}{m} \times V \ldots \ldots \ldots \ldots \ldots (7)$$

Where; m is the weight of the adsorbent (carbon, g), and V (Liter) is the volume of solution used in adsorption. The percentage of the adsorbed dye (adsorption efficiency) is determined, by using equation(8):-

$$\%Adsorption = \frac{Ci - Ce}{Ci} \times 100 \ldots \ldots \ldots \ldots . (8)$$

4.Batch method

This work was achieved by shaking specific amounts of dye solutions of different concentrations, and equal amounts of adsorbent (activated carbon) using sealed conical flasks. The conditions of the experiments were varied as required in the study under consideration. The conical flasks were shacked in a temperature programmed water bath vibrator of the type (Julabosw23) at a constant speed (100 (cpm) cycle/minute) after adjusting the temperature required for the study.

RESULTS AND DISCUSSION

1.Analytical method

The most important requirement of this study is to find precise analytical method in order to estimate the amount of adsorbate before and after the adsorption process.

The spectral method is one of the most important methods that can be used to achieve the desired purpose, and this method is characterized by high accuracy as well as its sensitivity to low concentrations, and it does not involve any interference with other materials that may be present in the studied system.

Figure (1): Calibration curve for dye (D1and D2) at wavelength 390 and 421 respectively in solvent 50:50 ethanol: water.
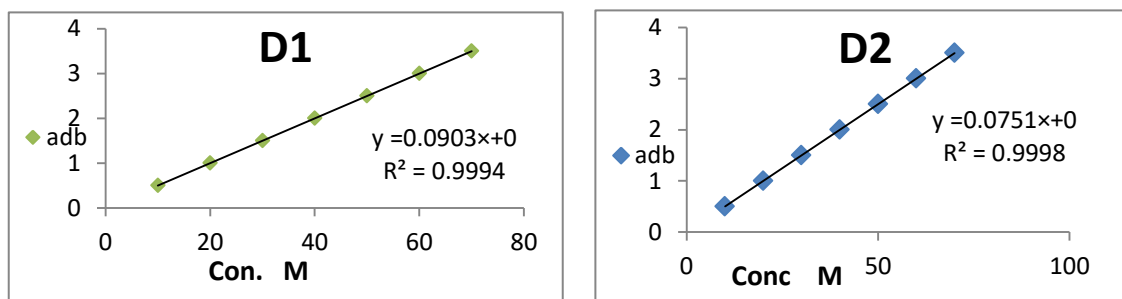Figure (1): Calibration curve for dye (D1and D2) at wavelength 390 and 421 respectively in solvent 50:50 ethanol: water.
Calibration curves were made for the dyes at the value of (λmax) for each of them within the limits of detection of each dye and according to Beer's law, and the correlation coefficient value was high (R = 0.9994 and 0.9998) respectively

2.Adsorbent

In this study, a new type of modified activated carbon was prepared from Fallen eucalyptus leaves, as mentioned in the practical part. The prepared carbon was characterized and its specifications were studied in the following ways:

3.Using the X-ray diffraction (XRD) technique

The X-ray diffraction of the prepared activated carbon has been recorded, Two distinct bands were observed. A major region appeared in which the diffraction is confined between (16-34)2θ and there is a very small region between(41-46)2θ. it is clear this measurement that, the prepared sample has no crystalline surface (Fig. No. 2). This surface support that, there is a defect which means the prepared carbon has an amorphous shape which support the high adsorption efficiency.
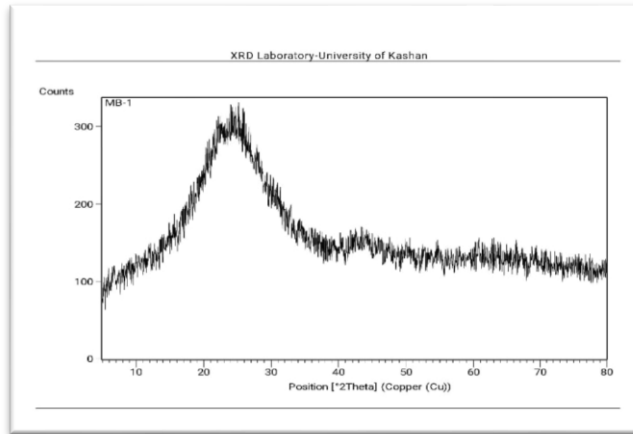
Figure (2): X-ray diffraction (XRD) of prepared carbon

4.Scanning Electron Microscope Measurement:- (SEM)

A scanning electron microscope was used to study the morphology of the surface area of the prepared carbon before and after adsorption, in order to identify the nature of the granular and porous shape of carbon surface and the effect of the adsorption process on these properties. It was found that, the pores were (Fig. 3) distributed all over the carbon surface before the adsorption as fine granules, all of which were less than (100 nm), and these granules had gathered to form larger parts, and this also indicates a good surface area of carbon through the distribution of pores on its parts.

The adsorption process, through observing the images of carbon before the adsorption process, led to a clear decrease in the appearance of pores than before the adsorption process, and this corresponds to an increase in the value of (pore size) when measuring the model by the (BET) method. As can be seen in Table (2).

Table (2): Calculation of surface area and pore volume by BET and Langmuir methods before and after adsorption

Measurement of active Carbon Samples					
Samples	BET Surface Area (m^2/g)	Langmuir Surface Area (m^2/g)	Pore Size (nm)	pore volume (cm^3/gm)	Average Particle size(nm)
AC-M $_1$ Before	224.000	888.410	5.38815	0.1080245	26.7875
AC-M $_2$ After	66.7954	581.9953	8.0339	0.1786835	89.8265
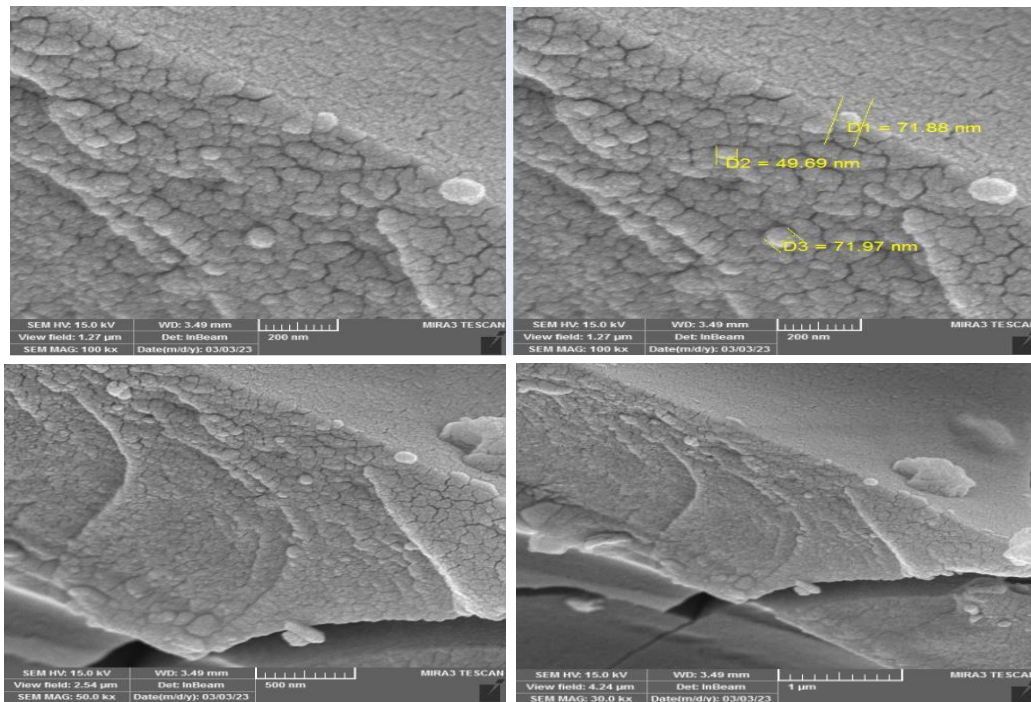
Figure (3): A scanning electron microscope image of the prepared activated carbon

Table No. (2) shows that, the surface area of activated carbon decreased from (224,000nm) in the sample before the adsorption process to (66,7954nm) after the adsorption process. This is clear as the adsorption process of the dye under study filled the pores of the activated carbon, and thus led to a decrease in the surface area. This was also proved, since when observing the surface area values measured by the Langmuir method, the surface area value of activated carbon was reduced.

5.EDX Measurements:
Elemental analysis is carried out by the energy dispersive X-ray spectroscopy (EDX) measurements of the synthesized carbon shown in Figure (4). It consists of (84.29%) carbon, (14.84%) oxygen, and a very small percentage of sulfur (0.087%). This results give an indication to the high purity of the activated carbon, as shown in the figure. (4).
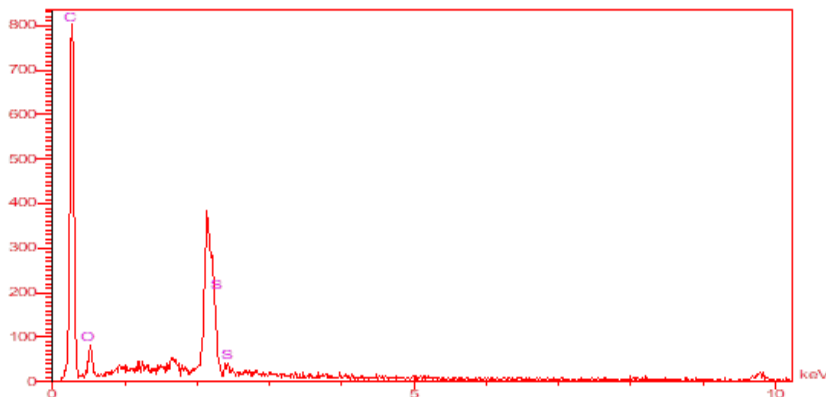
Figure (4): EDX test for prepared activated carbon

6.Effect of the amount of adsorbent:
The aim of this study is to choose the appropriate amount of prepared carbon to carry out the subsequent study.

Table(3) :Effect of amount of carbon on adsorption capacity and efficiency at pH=7 and a temperature of 293˚k.

Dye	C_i (mg/l)	Dose (gm/10ml) Of Adsorption	q_e(mg/gm)	Ads.%
D1	87	0.01	81.857	94.0885
		0.02	40.928	95.093
		0.04	20.464	97.875
		0.06	13.642	99.38
D2	192	0.01	154.66	80.552
		0.02	77.33	80.771
		0.04	38.665	86.879
		0.06	30.932	92.912

The selection of the amount of adsorbent dose does not depend on the value of the percentage of adsorption or the efficiency of adsorption, but rather aims to choose an appropriate percentage that can bear the increase and decrease at different conditions in subsequent studies so that it does not rise to the removal of the dye above (99%) and does not go below the percentage (50%) because In both cases, we will not be able to complete neither the kinetic nor the equilibrium studies. The amount of dye used for subsequent studied were chosen according to Table (3), (0.02) grams of the adsorbent in both dyes for all of the initial concentrations for comparison.

7.Effect of initial concentration:
The results obtained from studying the effect of the initial concentration of the two dyes on the adsorption of the carbon prepared by shaking (10 ml) of the dye solution at different concentrations within the range of (35-192 mg/L), at certain temperature within the range (298-333 K°), constant shaking speed (100rpm) and amount of adsorbent (0.02g). Results obtained are listed in Tables No (4,5,6 and 7).
The results indicate that, when increasing the initial concentration, the adsorption capacity and amount of adsorbed dyes are increased while the adsorbed dye ratio is decreased[18].
The increase of the initial dye concentration is accompanied by decrease in the adsorption efficiency due to the increase of the interaction among the adsorbate molecules attacking the adsorbent and with those already attached to the adsorbent surface.

8.Effect of Temperature
Studying the effect of temperature is one of the most important variables that gives an idea about the nature of the adsorption system under study and enables the researcher to calculate thermodynamic functions[20]. When looking closely at the Tables (4) and (5), It was found that the increase in temperature, at a fixed concentration, decreases the adsorption efficiency. This gives an indication to the physical nature that dominates the bonds between the dye and the carbon surface.

8.1.Langmuir Isotherm
Application of the linear form of the Langmuir isotherm (equa.(1)). The Langmuir constants (b and Q_{max}) for both dyes under study can be determined by plotting the relationship between C_e/q_e and C_e. The results obtained are given in Tables 4 ad 5 for D1 and D2 respectively and portrayed in Figures (5and 6). The isotherm was first applied on different concentrations (35, 87, 140, 192 mg/ L) and constant temperature (293°K) . The isotherm was repeated at the same concentrations but various temperatures (303, 313, 323, 333° K).
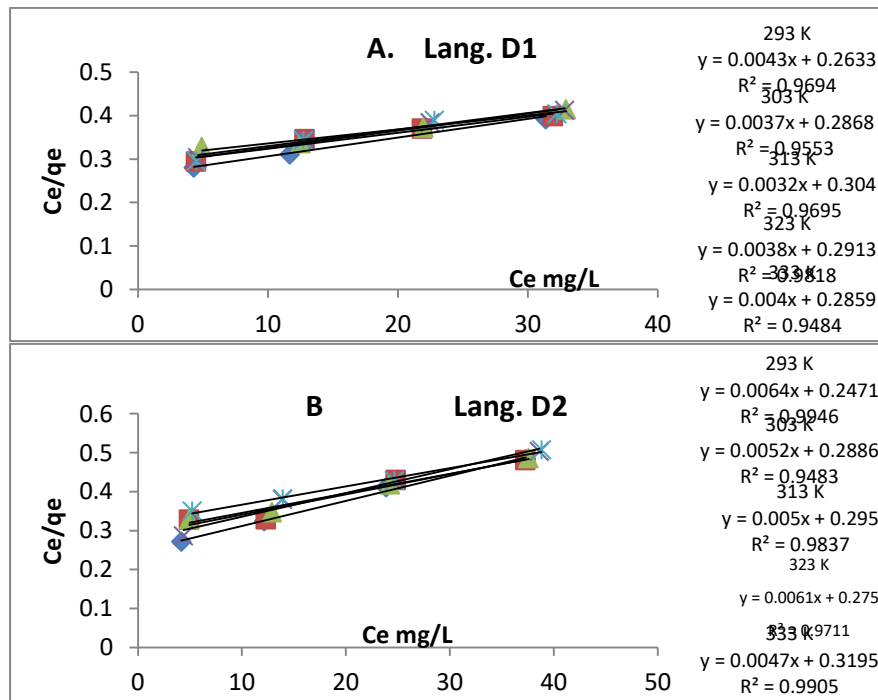
Figure (5):Plot of Langmuir isotherm at different concentrations and each time with a various temperature. A : for D1 and B: D2

Table(4) : Langmuir isotherm application on the experimental results of D1 at various temperatures

T °K	Ci mg/L	Ce mg/L	Cads mg/L	%	qe mg/g	Ce/qe	Qmax mg/gm	b	R_L
293	35	4.311	30.689	87.682	15.3445	0.280	232.558	0.0163	0.666
	87	11.690	75.31	86.563	37.655	0.310			0.413
	140	21.955	118.045	84.317	59.022	0.371			0.304
	192	31.399	160.601	83.646	80.300	0.391			0.241
303	35	4.491	30.509	87.168	15.254	0.294	270.270	0.0129	0.613
	87	12.841	74.159	85.240	37.079	0.346			0.389
	140	21.873	118.127	84.376	59.063	0.370			0.284
	192	31.939	160.061	83.365	80.030	0.399			0.224
313	35	4.926	30.074	85.925	15.037	0.327	312.5	0.010	0.641
	87	12.523	74.477	85.60575	37.2385	0.336			0.418
	140	21.994	118.006	84.29	59.003	0.372			0.308
	192	32.953	159.047	82.83698	79.5235	0.414			0.245
323	35	4.608	30.392	86.83	15.196	0.303	263.15	0.013	0.563
	87	12.855	74.145	85.22	37.07	0.346			0.342
	140	22.511	117.489	83.92	58.74	0.383			0.244
	192	32.855	159.145	82.88	79.57	0.412			0.190
333	35	4.499	30.501	87.145	15.250	0.295	250	0.014	0.660
	87	12.746	74.254	85.349	37.127	0.343			0.438
	140	22.821	117.179	83.699	58.589	0.389			0.327
	192	32.270	159.73	83.192	79.865	0.404			0.261

Table(5) : Langmuir isotherm application on the experimental results of dye D2 at various temperatures

T°K	Ci mg/l	Ce mg/l	Cads mg/l	%	qe mg/l	Ce/qe	Qmax	R_L	b
293	35	4.182	30.818	88.051	15.409	0.271	156.25	0.533	0.025
	87	12.157	74.843	86.026	37.421	0.324		0.314	
	140	23.896	116.104	82.931	58.052	0.411		0.222	
	192	37.340	154.66	80.552	77.33	0.482		0.172	
303	35	4.934	30.066	85.902	15.033	0.328	192.37	0.613	0.0180
	87	12.307	74.693	85.854	37.346	0.329		0.389	
	140	24.811	115.189	82.277	57.594	0.430		0.284	
	192	37.273	154.727	80.586	77.363	0.481		0.224	
313	35	4.954	30.046	85.845	15.023	0.329	200	0.641	0.016
	87	12.893	74.107	85.180	37.053	0.347		0.418	
	140	24.241	115.759	82.685	57.879	0.418		0.308	
	192	37.590	154.41	80.421	77.205	0.486		0.245	
323	35	4.391	30.609	87.450	15.30	0.286	163.93	0.563	0.0221
	87	13.920	73.08	84.000	36.54	0.380		0.342	
	140	24.706	115.294	82.35	57.647	0.428		0.244	
	192	38.631	153.369	79.87	76.684	0.503		0.190	
333	35	5.216	29.784	85.09	14.892	0.350	212.76	0.660	0.0147
	87	13.935	73.065	83.98	36.532	0.381		0.438	
	140	24.680	115.32	82.37	57.66	0.428		0.327	
	192	38.839	153.161	79.77	76.58	0.507		0.261	

Looking closely at Tables (4) and (5), it was found that, at a fixed concentration, the rising of temperature, decreases the percentage of adsorption, this indicates that, the forces dominates the bonds between the dye and the carbon surface are physical in nature. It is also noted that, the results mentioned in Tables (4 and 5) are as follow: All R_L values calculated at the initial concentration (35ppm) and at different temperatures were within the range of ($0<R_L<1$) and this indicates that, adsorption is of the favored type and tested to complete this study.
It was also noted that increasing the temperature decreases the value of (R_L). This may indicates that increasing the temperature leads to weakening the binding forces between dye and carbon and encouraging the process of reverse migration of dye molecules towards the solution.

8.2.Freundlich Isotherm:

This isotherm (Equation No.2) is applied on the experimental data of the adsorption systems of D1and D2 under the same conditions as in Langmuir isotherm. The values of ln qe is plotted versus ln Ce. Great linear relationships were obtained indicated by values of R^2 close to unity. Freundlich constant (n and K_F)were determined from the slope and intercept of the straight lines respectively. The results obtained are shown in figure(6) and presented in Tables (4 and 5).
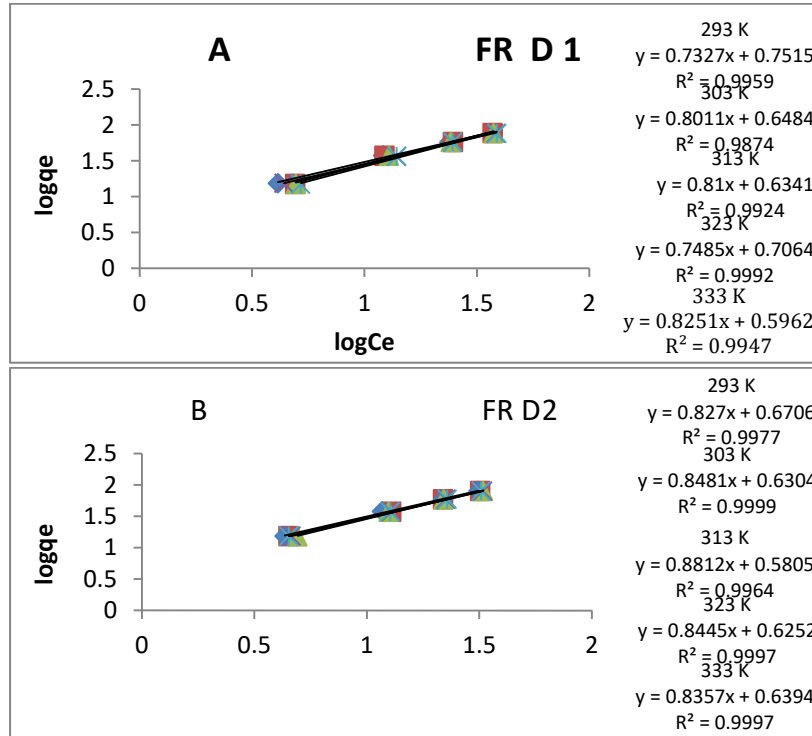
Figure (6):Plots of Freundlich isotherm at different concentrations and each time with a various temperature. A : for D1 and B: D2

Looking at the results presented in Tables (6 and 7), it can be concluded that, the fitting of the Freundlich isotherm equation to the practical data of adsorption of the studied dyes gave linear relationships at all temperatures indicated by the values of the correlation coefficients (R^2) that ranged between (0.9924 – 0.9999) and this pointing to the possibility of using this isotherm in the representation of the practical data of adsorption in the studied system successfully.

The value of (n) is related to the intensity of adsorption. All dyes at all temperatures were greater than (1) and less than (10) giving indication to preferable adsorption. It was also noted that, the values of (n) declined with the rise of temperature and this may give evidence that the adsorption is physical, that is, the intensity of physical adsorption decreases with increasing temperature.

The values of (K_F), is an energy value related to the adsorption capacity, It was found that, its values decrease with increasing temperature, which leads to weakness in the binding forces between dye and active site existing on carbon surface and encouraging the process of reverse migration of dye molecules towards the solution. This is also consistent with the change in the values of adsorption capacity (qe) or temperature. The weakening of the adsorption capacity with increasing temperature gives evidence that the adsorption process in the studied

system is of a physical nature. As a conclusion the Langmuir isotherm proved the single layer adsorption and Freundlich isotherm proved the heterogeneous distribution of pours on the carbon (adsorbent surface).

Table(6) :Freundlich isotherm application on the experimental results of dye D1 at various temperatures

T°k	Ci mg/L	Ce mg/L	Cad mg/L	%	qe mg/gm	logqe	logCe	K_F	n
293	35	4.311	30.689	87.682	15.344	1.185	0.634	4.683	1.209
	87	11.69	75.31	86.563	37.655	1.575	1.067		
	140	21.955	118.045	84.317	59.022	1.771	1.341		
	192	31.399	160.601	83.646	80.300	1.904	1.496		
303	35	4.491	30.509	87.168	15.254	1.183	0.652	4.269	1.179
	87	12.841	74.159	85.240	37.079	1.569	1.108		
	140	21.873	118.127	84.376	59.063	1.771	1.339		
	192	31.939	160.061	83.365	80.030	1.903	1.504		
313	35	4.926	30.074	85.925	15.037	1.177	0.692	3.806	1.134
	87	12.523	74.477	85.605	37.238	1.570	1.097		
	140	21.994	118.006	84.290	59.003	1.770	1.342		
	192	32.953	159.047	82.836	79.523	1.900	1.517		
323	35	4.608	30.392	86.834	15.196	1.181	0.663	4.218	1.184
	87	12.855	74.145	85.200	37.072	1.569	1.109		
	140	22.511	117.489	83.920	58.744	1.768	1.352		
	192	32.855	159.145	82.888	79.572	1.900	1.516		
333	35	4.499	30.501	87.145	15.250	1.183	0.653	4.359	1.196
	87	12.746	74.254	85.349	37.127	1.569	1.105		
	140	22.821	117.179	83.699	58.589	1.767	1.358		
	192	32.27	159.73	83.192	79.865	1.902	1.508		

Table(7) :Freundlich isotherm application on the experimental results of dye D2 at various temperatures

T°K	Ci	Ce	Cads	%	qe	logqe	logCe	K_F	n
293	35	4.128	30.872	88.205	15.436	1.188	0.615	5.642	1.364
	87	12.157	74.843	86.026	37.421	1.573	1.084		
	140	23.896	116.104	82.931	58.052	1.763	1.378		
	192	37.340	154.660	80.552	77.330	1.888	1.572		
303	35	4.934	30.066	85.902	15.033	1.177	0.693	4.427	1.246
	87	12.307	74.693	85.854	37.346	1.572	1.090		
	140	24.811	115.189	82.277	57.594	1.760	1.394		
	192	37.273	154.727	80.586	77.363	1.888	1.571		
313	35	4.954	30.046	85.845	15.023	1.176	0.694	4.306	1.234
	87	12.893	74.107	85.180	37.053	1.568	1.110		
	140	24.241	115.759	82.685	57.879	1.762	1.384		
	192	37.59	154.410	80.421	77.205	1.887	1.575		
323	35	4.391	30.609	87.454	15.304	1.184	0.642	5.086	1.336
	87	13.920	73.080	84.000	36.540	1.562	1.143		
	140	24.706	115.294	82.352	57.647	1.760	1.392		
	192	38.631	153.369	79.879	76.684	1.884	1.586		
333	35	5.216	29.784	85.097	14.892	1.172	0.717	3.946	1.211
	87	13.935	73.065	83.982	36.532	1.562	1.144		
	140	24.68	115.320	82.371	57.660	1.760	1.392		
	192	38.839	153.161	79.771	76.580	1.884	1.589		

8.3.FH Isotherm
Isotherm FH (Equation No.3) is applied on the experimental data of the adsorption systems of D1and D2 under the same conditions as in Langmuir and Freundlich isotherms. The values of log θ/Ci is plotted versus log(1-θ). Weak linear relationships were obtained indicated by values of R^2 far from unity. FH (n_{FH} and K_{FH})were determined from the slope and intercept of the straight lines respectively. The results obtained are shown in figure(7) and presented in Tables (8 and 9).

Table (8): Application of the FH isotherm on experimental data of D1

T K°	Ci mg/L	Ce mg/L	Cad mg/L	%	θ	log θ/Ci	Log $(1-\theta)$	K_{FH}	n_{FH}	R^2	ΔG^O
293	35	4.182	30.818	88.050	0.880	-1.599	-0.920	4.934	3.549	0.9522	-3.887
	87	12.157	74.843	86.020	0.860	-2.005	-0.853				
	140	23.896	116.104	82.930	0.829	-2.227	-0.767				
	192	37.340	154.66	80.550	0.805	-2.377	-0.709				
303	35	4.934	30.066	85.902	0.860	-1.609	-0.853	4.429	2.892	0.1937	-3.748
	87	12.307	74.693	85.85	0.858	-2.006	-0.847				
	140	24.811	115.189	82.277	0.822	-2.231	-0.749				
	192	27.273	164.727	85.795	0.857	-2.35	-0.844				
313	35	4.954	30.046	85.845	0.858	-1.61	-0.847	5.837	4.818	0.8520	-4.590
	87	12.893	74.107	85.180	0.851	-2.009	-0.826				
	140	24.241	115.759	82.685	0.826	-2.229	-0.759				
	192	37.59	154.410	80.421	0.804	-2.378	-0.707				
323	35	4.391	30.609	87.454	0.825	-1.627	-0.756	5.252	4.251	0.2813	-4.450
	87	13.920	73.080	84.000	0.840	-2.015	-0.795				
	140	24.706	115.294	82.352	0.824	-2.23	-0.754				
	192	38.631	153.369	79.879	0.799	-2.38	-0.696				
333	35	5.216	29.784	85.090	0.850	-1.614	-0.823	6.245	5.470	0.8673	-5.071
	87	13.935	73.065	83.980	0.839	-2.015	-0.793				
	140	24.680	115.320	82.370	0.823	-2.23	-0.752				
	192	38.839	153.161	79.770	0.797	-2.381	-0.692				

FH D1   A   log(1-θ)

293K
y = -3.5491x - 4.9348
R² = 0.9522
303K
y = -2.8919x - 4.4297
R² = 0.1937
313K
y = -4.8184x - 5.8377
R² = 0.852
323K
y = -4.2514x - 5.2526
R² = 0.2813
333K
y = -5.4708x - 6.2451
R² = 0.8673

FH D2   B   log(1-θ)

y = -0.1646x - 1.1778
R² = 0.9384
y = -0.1446x - 1.121
R² = 0.9964
y = -0.108x - 1.0355
R² = 0.8047
y = -0.1489x - 1.1215
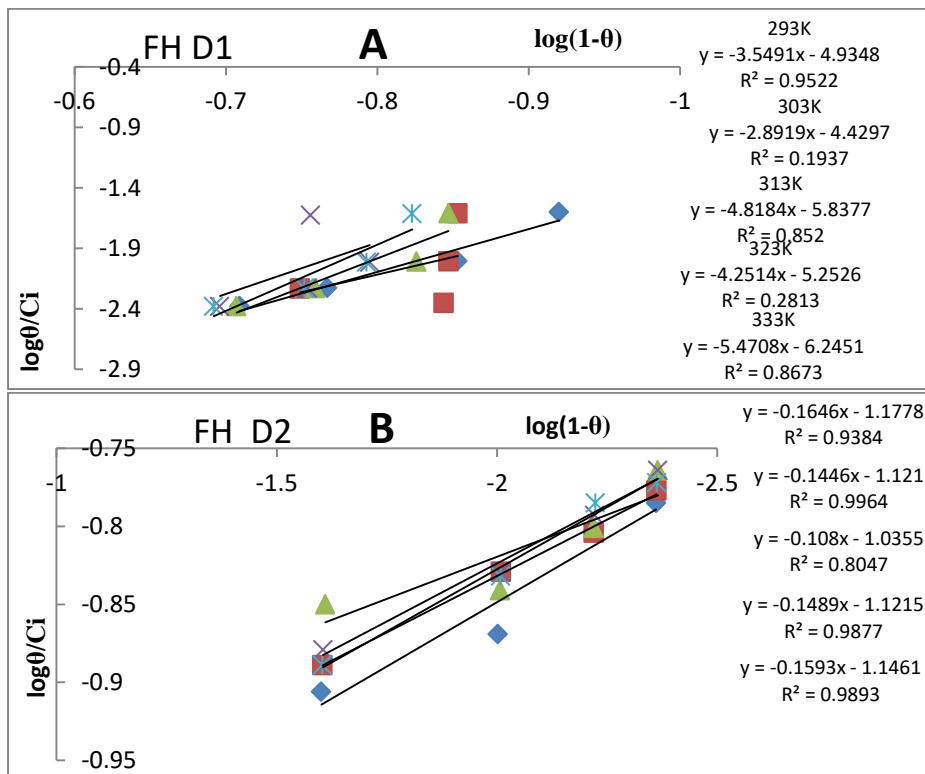R² = 0.9877
y = -0.1593x - 1.1461
R² = 0.9893

Figure (7):Plots of FH isotherm at different concentrations and each time with a various temperature. A : for D1 and B: D2

Table (9): Application of the FH isotherm on experimental data of D2

T K°	Ci mg/l	Ce mg/l	C_{ads} mg/l	%	θ	Log θ/ci	Log $(1-\theta)$	K_{FH}	n_{FH}	R^2	ΔG° kJ.mole^{-1}
293	35	4.311	30.689	87.682	0.876	–1.601	–0.906	6.840	5.700	0.9384	–4.682
	87	11.690	75.310	86.563	0.865	–2.002	–0.869				
	140	21.955	118.045	84.317	0.843	–2.22	–0.804				
	192	31.399	160.601	83.646	0.836	–2.361	–0.785				
303	35	4.491	30.509	87.168	0.871	–1.604	–0.889	7.732	6.891	0.9964	–5.151
	87	12.841	74.159	85.240	0.852	–2.009	–0.829				
	140	21.873	118.127	84.376	0.843	–2.220	–0.804				
	192	31.939	160.061	83.365	0.833	–2.362	–0.777				
313	35	4.926	30.074	85.925	0.859	–1.610	–0.850	8.113	7.448	0.8047	–5.446
	87	12.523	74.477	85.605	0.856	–2.007	–0.841				
	140	21.994	118.006	84.290	0.842	–2.220	–0.801				
	192	32.953	159.047	82.836	0.828	–2.365	–0.764				
323	35	4.608	30.392	86.834	0.868	–1.605	–0.879	7.466	6.634	0.9877	–5.397
	87	12.855	74.145	85.224	0.852	–2.009	–0.829				
	140	22.511	117.489	83.920	0.839	–2.222	–0.793				
	192	32.855	159.145	82.888	0.828	–2.365	–0.764				
333	35	4.499	30.501	87.145	0.871	–1.604	–0.889	7.137	6.208	0.9893	–5.446
	87	12.746	74.254	85.349	0.853	–2.008	–0.832				
	140	22.821	117.179	83.699	0.836	–2.223	–0.785				
	192	32.27	159.73	83.192	0.831	–2.363	–0.772				

9. Thermodynamic Study

As it is well known, adsorption isotherms are studied in a range of concentrations, at a constant temperature, at equilibrium conditions. In this study, these isotherms were applied on a certain range of concentrations and at different temperatures each time at a certain temperature. In contrast to thermodynamics, which is studied at a fixed concentration and in a range of temperatures at equilibrium as well, the results obtained from the application of the FH isotherm on the practical data of the adsorption of dyes D1 and D2 indicated the following: The application of the F-H isotherm on the experimental data of the D1 dye showed non-linear relations with a weak correlation coefficient, as shown in table (8). Thus, the adsorption system of the D1 dye cannot be interpreted based on this result. The FH isotherm is better applied to the practical results of D2. Accordingly, the results obtained

were consistent with values of free energy which indicate to spontaneous adsorption process. The spontaneity was found to increase with increasing temperature, connection between the dye molecules and the active sites on the carbon surface are physical in nature. and the adsorption process leads to more ordered system at a concentration of 35 mg/L, while at higher concentrations the results were more random order for both dyes (D1 and D2). This can be attributed to the fact that increasing the concentration increases the number of remaining molecules in the dye solutions, thus increasing the randomness of the system, especially after equilibrium.

Table(10): The values of the equilibrium constants Calculation of thermodynamic functions at equilibrium for dye D1

Ci (mg/l)	Temp K º	K	H Δ (KJ.mol^{-1})	GºΔ (KJ.mol^{-1})	ΔSº (J.mol^{-1}.K^{-1})
35	293	3.763	-4.370	-3.201	-3.724
	303	3.406		-3.162	-3.879
	313	3.208		-3.019	-3.848
	323	3.114		-3.047	-3.851
	333	3.040		-3.054	-3.798
87	293	3.163	-1.375	-2.874	4.781
	303	3.008		-2.843	4.847
	313	3.208		-2.838	4.867
	323	2.695		-2.199	4.853
	333	2.399		-2.948	4.878
140	293	2.714	-0.785	-2.475	5.979
	303	2.731		-2.541	5.739
	313	2.698		-2.537	5.789
	323	2.656		-2.613	5.789
	333	2.624		-2.868	5.749
192	293	2.520	-0.504	-2.323	5.787
	303	2.428		-2.298	5.727
	313	2.476		-2.394	5.797
	323	2.405		-2.460	5.757
	333	2.453		-2.446	5.757

Table(11) : The values of the equilibrium constants Calculation of thermodynamic functions at equilibrium for adsorption of dye (D2)

Ci (mg/l)	Temp K°	K	ΔH (KJ.mol^{-1})	ΔG^o (KJ.mol^{-1})	ΔS^o (J.mol^{-1}.K^{-1})
35	293	3.793	-5.085	-3.231	-6.929
	303	3.438		-3.413	-6.302
	313	3.390		-3.141	-6.121
	323	3.026		-3.400	-6.395
	333	2.914		-2.926	-6.269
87	293	2.947	-1.654	-2.565	3.464
	303	2.942		-2.730	3.409
	313	2.825		-2.772	3.545
	323	2.739		-2.775	3.440
	333	2.784		-2.979	3.446
140	293	2.402	-0.826	-2.105	4.379
	303	2.359		-2.190	4.410
	313	2.360		-2.204	4.402
	323	2.354		-2.278	4.431
	333	2.361		-2.352	4.339
192	293	2.056	-0.660	-1.706	4.995
	303	2.404		-1.810	3.940
	313	2.300		-1.824	3.955
	323	3.081		-1.858	3.906
	333	2.020		-1.912	3.905

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