RESULTS AND DISCUSSION

Different parameters affecting the adsorption process were examined to optimize the removal of the dyes from aqueous solutions. These parameters include pH of the dye solution, ionic strength, contact time, dye concentrations, adsorbent dose, stirring rate and temperature.

3.1. Determination of pH_{pzc} of the activated carbon samples

The surface functional groups and pH_{pzc} are important characteristics for any activated carbon as they indicate: the acidity/basicity of the adsorbent, type of activated carbon (either H- or L-type), and the net surface charge of the carbon in solution. The activated carbon has both basic and acidic properties. The acid functional groups are carboxylic, lactonic, and phenolic [85]. The basic functional groups include oxygen-containing species such as ketonic, pyronic, chromenic, and p-electron system of carbon basal planes [86]. The density of surface functional groups depends on the activated carbon preparation conditions and on the nature of the precursor [87]. Many chemical treatment procedures have been employed to increase the density of surface functional groups of activated carbon, highlighting the importance of functional group interaction with polar solutes from solution [88]. The combined influence of all the functional groups of activated carbon determines pHpzc, i.e., the pH at which the net surface charge on carbon was zero. The carbon surface charge is mainly determined by the pH of the adsorbate solution. It is known that [89] the net charge on carbon surface is positive at a solution pH lower than that corresponding to the point of zero charge (pH_{PZC}) of the surface and is negative at a solution pH higher than pH_{PZC}. Therefore, it is very important to determine the pH_{PZC} for the carbon material.

Batch equilibrium method was applied for the determination of pH_{PZC} of the two types of activated carbon (AC1 and AC2) used in the present study. pH_{final} readings for the determination of pH_{PZC} were plotted as a function of $pH_{initial}$ in **Fig. (3-1)**. The pH_{final} value of the plateau observed in **Fig. (3-1)** corresponds to the pH at which there is no net OH^- or H^+ adsorption [90]. At this pH, the difference between the initial and the final $[H^+]$ or $[OH^-]$ is zero. This pH was determined to be 4.8 and 2.7 which were taken as the pH_{PZC} of AC1 and AC2, respectively. The presence of strong acidic groups is suggested by the value of the pH_{ZPC} obtained for the two activated carbon samples [91].

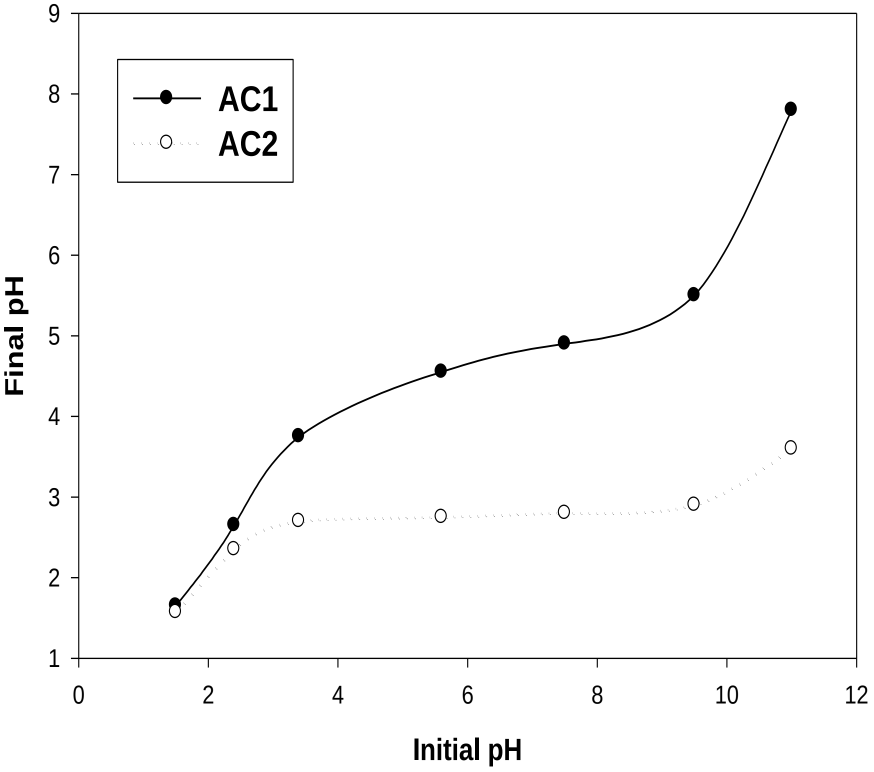

Fig. (3-1): Plot of final pH vs. initial pH for AC1 and AC2

3.2. Effect of contact time

Equilibrium time is an important parameter for an economical wastewater treatment system. For a given substance to be effective as an adsorbent of organic dyes, its adsorption rate must be fast and quantitative. The effect of contact time on the amount of dye adsorbed on the AC was investigated at 25 ml of dye solution of initial concentration of 50 mg/L. The system was subjected to an agitation speed of 100 rpm for 90 min. **Fig. (3-2)** shows a rapid adsorption of all dyes on AC1 at the initial stages of the adsorption and equilibrium was attained within about 60 min. Such uptake indicates a high degree of affinity towards dye molecules via chemisorptions [92]. After the rapid uptake, the capacity of the adsorbent became exhausted and the adsorption would be replaced by the transportation of dye from the external sites to the internal sites of the adsorbent particles. Therefore, the uptake rate began to drop down, which can be explained by intra-particle diffusion model [93]. The equilibrium was attained, the removal percent was evaluated as: Dye I (87%) > Dye IV (52%) > Dye II (40%) > Dye III (33%).

By a similar way, the dye solutions treated with AC2 at the same conditions. The removal of dye was followed as a function of contact time. For all the four dyes, the rate of dye removal gradually increased rapidly in the beginning till the equilibrium was attained after about 60 min with the exception of blue 5G, the equilibrium was reached after about 120 min. The dye removal percent at equilibrium times was 99.8%, 98.8%, 99.3% and 90.6% . **Fig. (3-3)** shows the relation between the contact time and the dye removal percent for the different dyes on the AC2. The equilibrium was attained in about an hour and the removal percent was evaluated as: Dye I (88.2%) > Dye IV (53.2%) > Dye II (41.0%) > Dye III (33.6%).

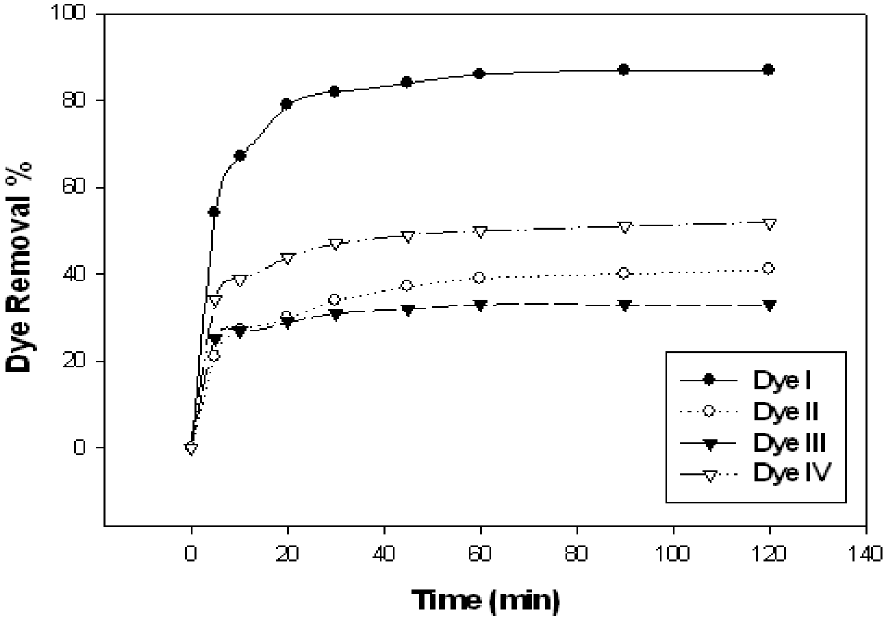

Fig. (3-2): Effect of contact time on percent of dye removal on AC1

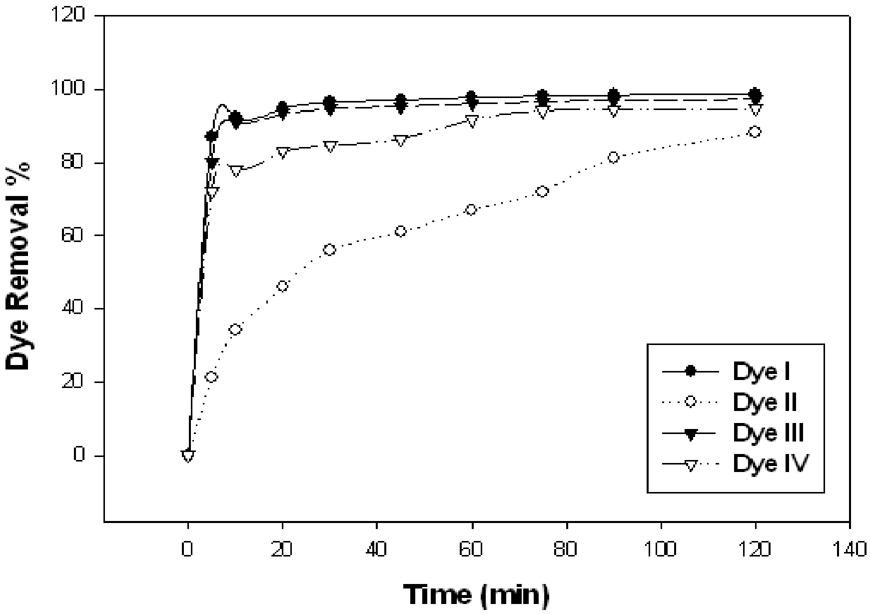

Fig. (3-3): Effect of contact time on percent of dye removal on AC2

3.3. Effect of pH on efficiency of dye removal

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The variation in adsorption capacity in the studied pH range was largely due to the influence of pH on the surface adsorption characteristics of the AC.

The observed relatively low adsorption rate of different dyes on AC at acidic pH values may be because the surface charge became positively charged, thus making (H^+) ions compete effectively with dye molecules causing a decrease in the amount of dye adsorbed. As the pH of the adsorption solution was increased, the negative charges on the surface increased. This would attract the positively charged functional groups located on the dye [94]. The effect of pH on the dye removal onto AC1 and AC2 are shown in **Fig. (3-4)** and **Fig.(3- 5)**, respectively. As shown in

Fig. (3-4), the removal percent on AC1 increases from about 56% to 91% (dye I), from 18% to 68% (dye II), 27% to 74% (dye III) and from 33% to 92% (dye), when pH increases from 1.5 to 10.5. **Fig.(3- 5)** shows the relationship between the removal efficiency expressed as removal % and the pH change of the dye solution, the color removal percent on AC2 changed as following: from 86.4% to 96.2% (dye I), 74.5% to 82.1% (dye II), 93.8% to 98% (dye III) and 94.5% to 96.4% (dye IV). Similar observations were reported for adsorption of dyes indicating that the adsorbent has a net positive charge on its surface [95].

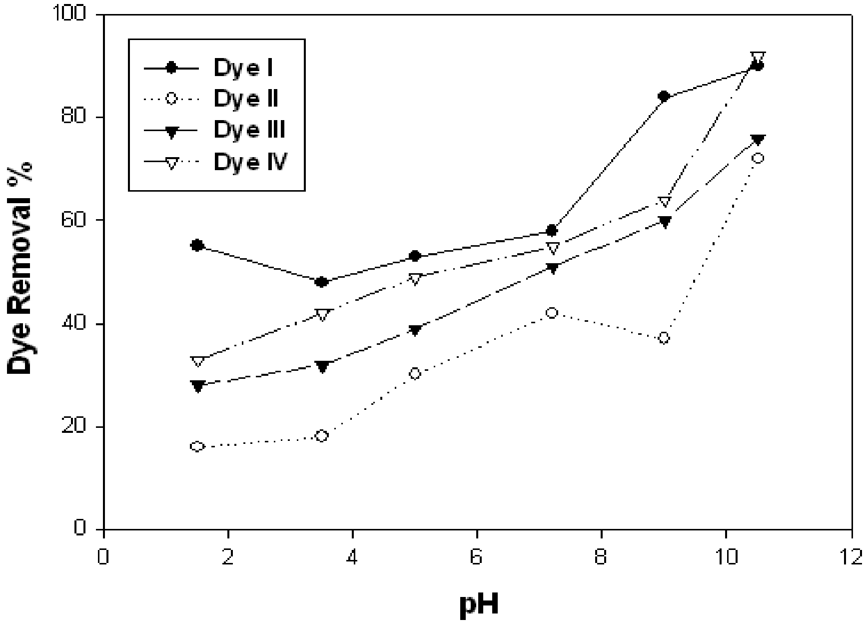

Fig. (3-4): Effect of pH on percent of dye removal on AC1

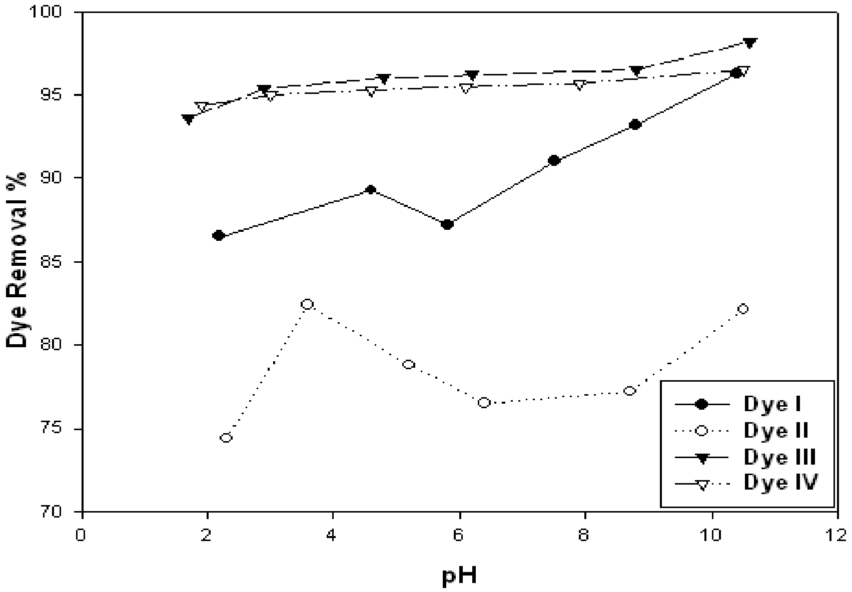

Fig. (3-5): Effect of pH on percent of dye removal on AC2

3.4. Effect of ionic strength on efficiency of dye removal

Generally, various salts and metal ions exist in dye containing wastewater. The salts lead to high ionic strength, which may affect the dye adsorption onto adsorbents. The influence of salinity on dye sorption by different AC was investigated to determine solution chemistry effects. Different values of KCl (4, 12, 20 and 28 g/L) were added to dye solutions with a constant dye concentrations. The effect may be varied for different dyes and adsorbents. Generally, with increasing the salinity, there is usually a little decrease in dye removal percent which can be attributed to presence of sorption sites of different affinities.

As shown in the **Fig. (3-6)**, the ionic strength is an important factor influencing aqueous phase equilibrium. Generally, there was a slight decrease in dye adsorption with increasing the salinity by adding KCl to the aqueous solution of different dyes at equilibrium for adsorption on AC1. This could be attributed to the competitive effect between dye ions and cations from the salt for the sites available for the biosorption process. And, with the ionic strength increasing, the activity of dye species and the active sites decreases, so the adsorption amount of the dye decreases [96]. The data obtained from the investigated solutions with AC1 are listed below in **Table (3-1)**.

Fig. (3-7) . shows the effect of the ionic strength (expressed as g/L of KCl) on the percentage of dye removal. The removal % of dye I and dye III decreased slightly with increasing of KCl concentration, but for dye IV, the removal % increased slightly by increasing KCl concentration. The removal % increased remarkably for dye II by increasing KCl concentration from 4 to 28 g/L KCl, **Table (3-2)**.

It has been stated that increase in the ionic strength of the solution increases adsorption at pH values below the isoelectrical point and decreases adsorption at pH values above the isoelectrical point [97]. A cause of increase of adsorption with increasing ionic strength is that increase in the ionic strength increases the positive charge of the surface below the isoelectrical point, resulting in greater attraction of anions, and increases the negative charge of the surface above the isoelectrical point, resulting in greater repulsion of anions [98]. Such behavior was detected in the literature [99].

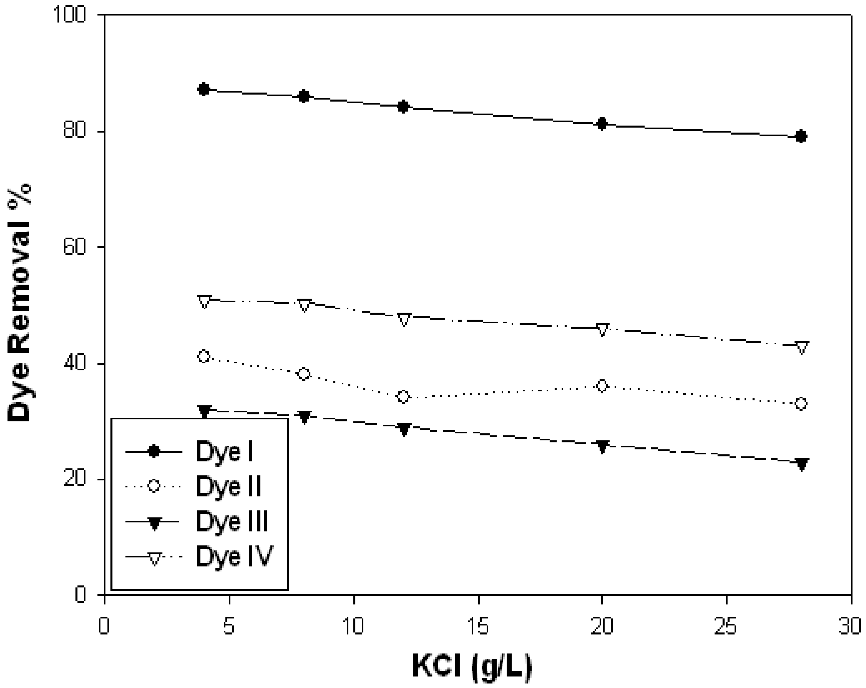

Fig. (3-6): Effect of ionic strength on percent of dye removal on AC1

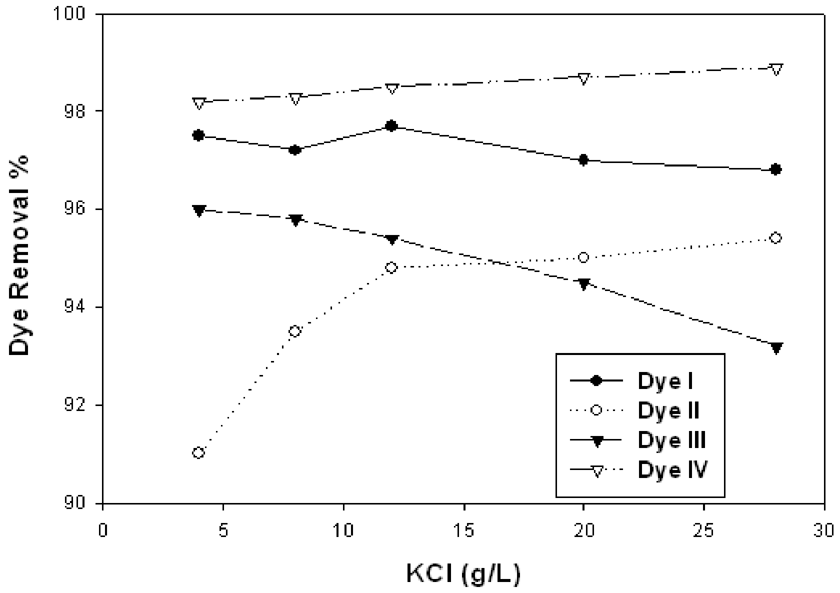

Fig. (3-7): Effect of ionic strength on percent of dye removal on AC2

Table (3-1): Effect of addition of KCl on dye removal by AC1.

Dye Removal %				**KCl (g/L)**
Dye IV	**Dye III**	**Dye II**	**Dye I**	
51.3	32.0	41.0	87.2	4
50.4	31.0	38.1	86.0	8
48.0	29.0	34.2	84.1	12
46.0	26.2	36.0	81.2	20
43.2	23.0	33.0	79.0	28

Table (3-2): Effect of addition of KCl on dye removal by AC2

.

Dye Removal %				**KCL (g/L)**
Dye IV	**Dye III**	**Dye II**	**Dye I**	
98.2	96.0	91.0	97.5	4
98.3	95.8	93.5	97.2	8
98.5	95.4	94.8	97.7	12
98.7	94.5	95.0	97.0	20
98.9	93.2	95.8	96.8	28

3.5. Effect of stirring rate on efficiency of dye removal

The effect of the stirring rate on the dye removal is shown in **Fig. (3- 8)** and **Fig. (3-9)**, respectively. The stirring speed was varied up from 0 to 400 rpm, keeping other parameters constant. The results clearly show that there was a definite improvement in the dye removal efficiency with the increase in the stirring rate from 0 to 200 rpm. However, on further increasing the stirring rate from 200 to 400 rpm the uptake of dye is not much affected and the equilibrium time remains unaltered in case of AC2. Depending upon the degree of agitation of the fluid particle system, the rate of adsorption is controlled either by film diffusion or pore diffusion. At lower agitation speeds, the fluid film around the particle is thicker and the film diffusion seems to be rate limiting step. The adsorption kinetics is influenced by low mass transfer of adsorbate to the internal surface of particle. It is likely that at higher agitation speeds, the film diffusion increases to a maximum value and pore diffusion thus becomes the rate controlling step [25]. This behavior is observed in other works dealing with the dye removal by adsorption [100].

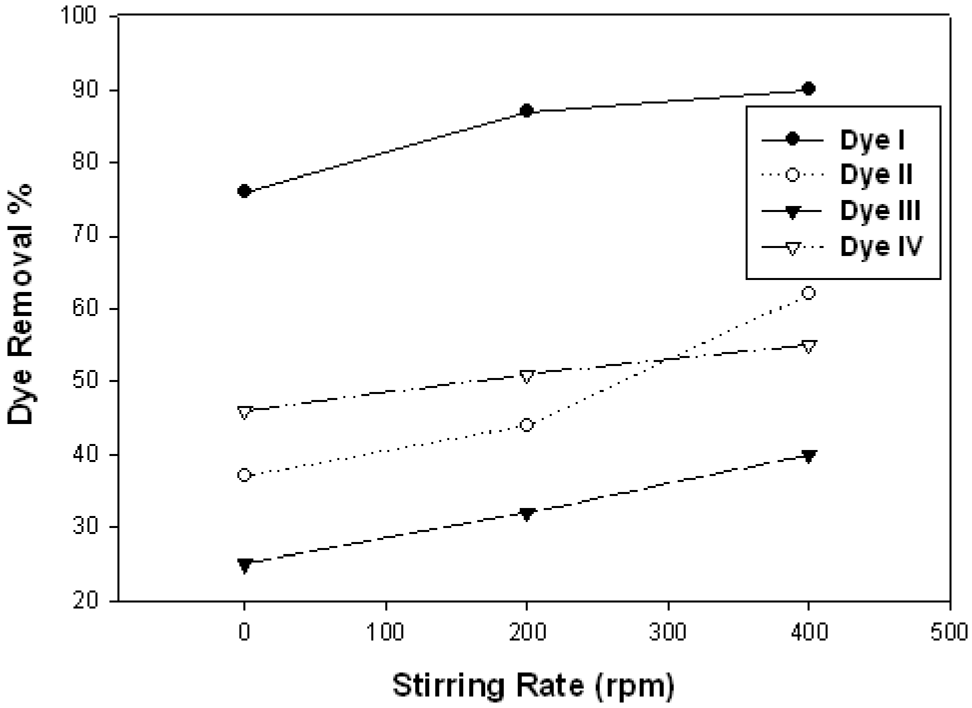

Fig. (3-8): Effect of stirring rate on percent of dye removal on AC1

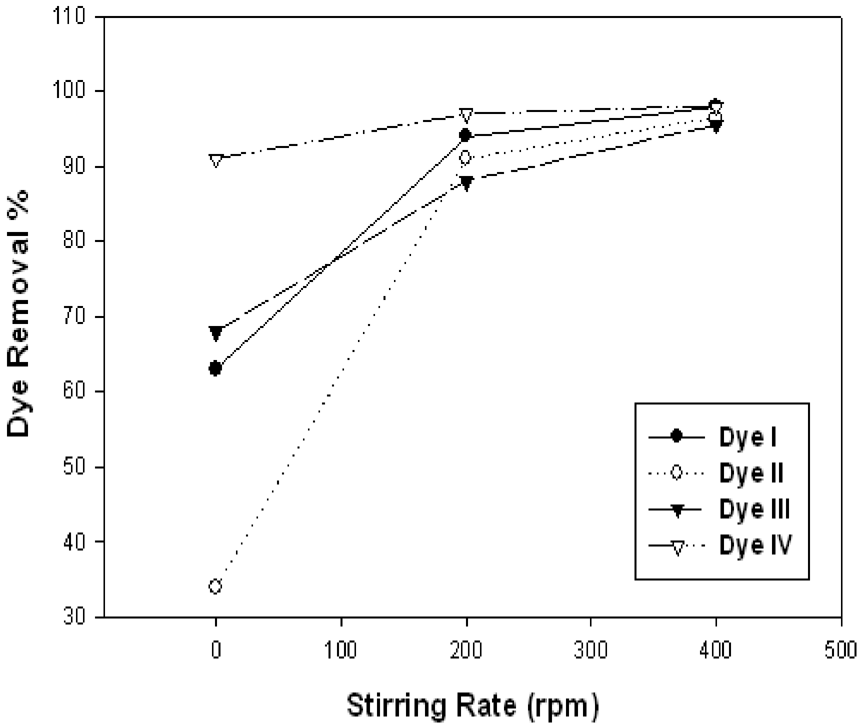

Fig. (3-9): Effect of stirring rate on percent of dye removal on AC2

3.6. Effect of adsorbent dose on efficiency of dye removal

The effect of sorbent dosages on the percentage removal of different dyes has been shown in **Fig. (3-10) and Fig. (3-11)** for AC1 and AC2, respectively. It followed the predicted pattern of increasing percentage sorption as the dosage was increased and reaches a saturation level at high doses. This is probably because of the resistance to mass transfer of dye from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading in which the experiment was conducted. The removal of all dyes increased when the dosage was changed from 2 to 10 g/L. The increase in removal efficiency is quite obvious, as the doses of adsorbent increases, the surface area available is more to adsorb dye. As expected, at constant initial concentration of dye, increasing the sample dose provides a greater surface area and larger number of sorption sites and hence enhancement of dye uptake [101]. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [102].

The solid/solution ratio is an important factor determining the capacity of a sorbent in a batch sorption study. It can be clearly seen that the removal of all dyes increased with increasing the amount of AC. However, the amounts of dye sorbed per unit weight of the AC decreased with increasing the solid/solution ratio. The values of removal % of different dyes on different doses of AC1 and AC2 are shown in **Tables (3-3) and (3-4)**, respectively.

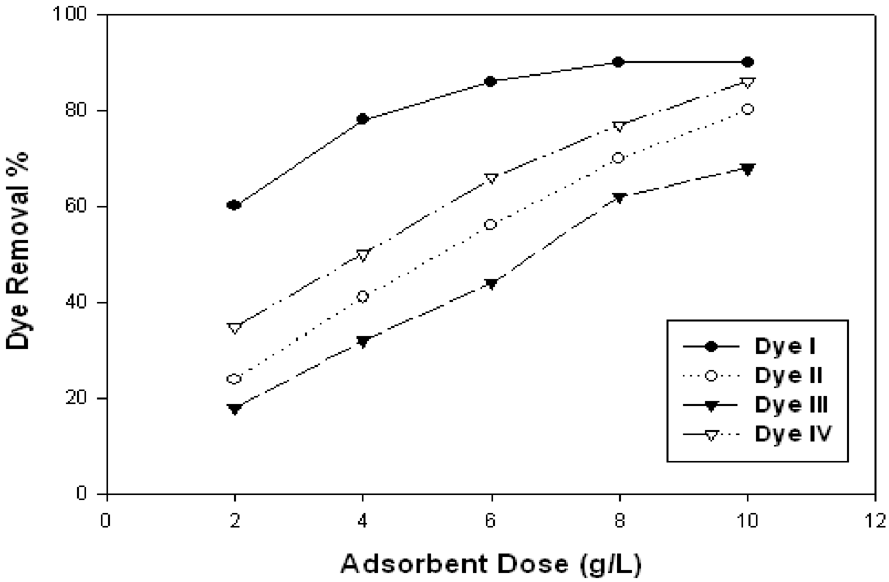

Fig. (3-10): Effect of adsorbent dose on percent of dye removal on AC1

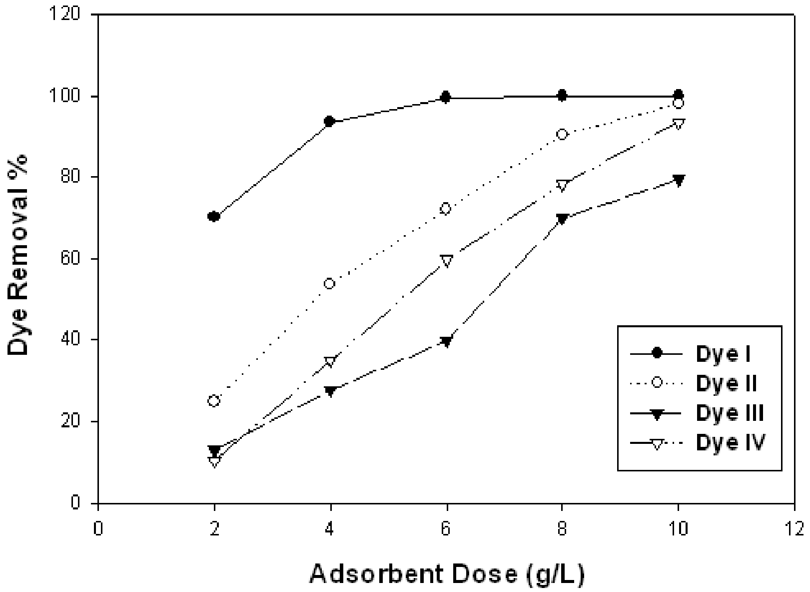

Fig. (3-11): Effect of adsorbent dose on percent of dye removal on AC2.

Table (3-3): Effect of initial AC1 dose on removal % of different dyes.

Dye Removal %				**Adsorbing Dose (g/L)**
Dye IV	**Dye III**	**Dye II**	**Dye I**	
36.0	18.7	23.5	60.2	2
50.0	31.1	40.6	78.4	4
66.2	43.3	56.6	86.0	6
77.3	61.7	71.0	91.2	8
86.0	70.5	80.0	91.2	10

Table (3-4): Effect of initial AC2 dose on removal % of different dyes .

Dye Removal %				**Adsorbing Dose (g/L)**
Dye IV	**Dye III**	**Dye II**	**Dye I**	
10.4	13.0	24.8	70.2	2
34.9	27.7	53.6	93.6	4
59.7	39.8	72.1	99.5	6
78.3	70.0	90.4	99.9	8
93.4	79.5	98.0	99.9	10

3.7. Effect of initial dye concentration on efficiency of dye removal

The effect of the initial dye concentration on the dye adsorption rate was investigated in the range (5–50 mg/L) without changing the initial pH of the medium. The results presented in **Fig. (3-12)** and **Fig. (3-13)** show that the percentage of removal decreased with increasing initial dye concentration for AC1 and AC2, respectively. The lower uptake at higher concentration resulted from an increased ratio of initial number of moles of dye to the available surface area; hence fractional adsorption becomes dependent on initial concentration. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration (saturation of the adsorbent). Similar results were also reported by other researchers [103,104].

Fig. (3-12) and **Fig. (3-13)** represent the removal % of the different dyes versus the initial concentration of the dye (5, 10, 20, 30, 40 and 50 mg/L) using AC1 and AC2, respectively at an optimum pH. As shown in these figures, an increase in the initial dye concentration leads to a decrease in the removal percent and an increase in the adsorption capacity of the dye on AC.

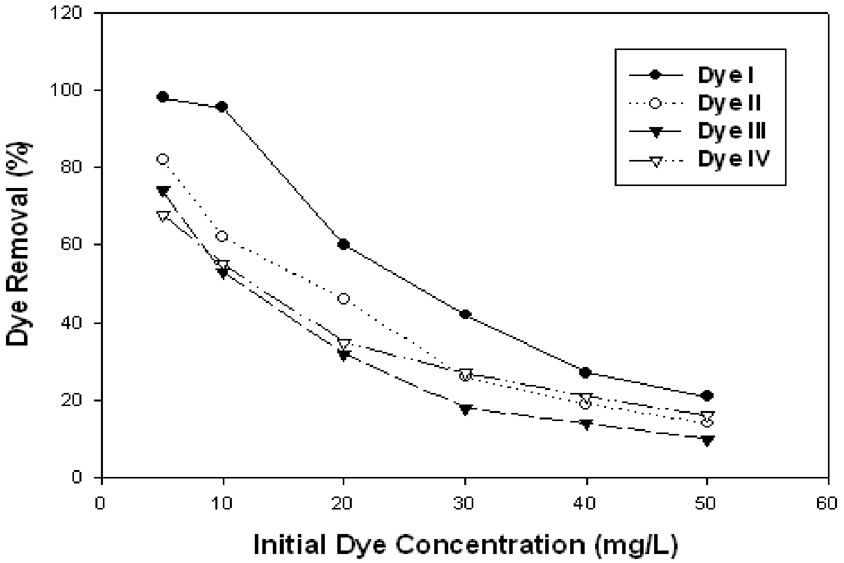

Fig. (3-12): Relation between initial dye concentration on percent removal for different dyes on AC1

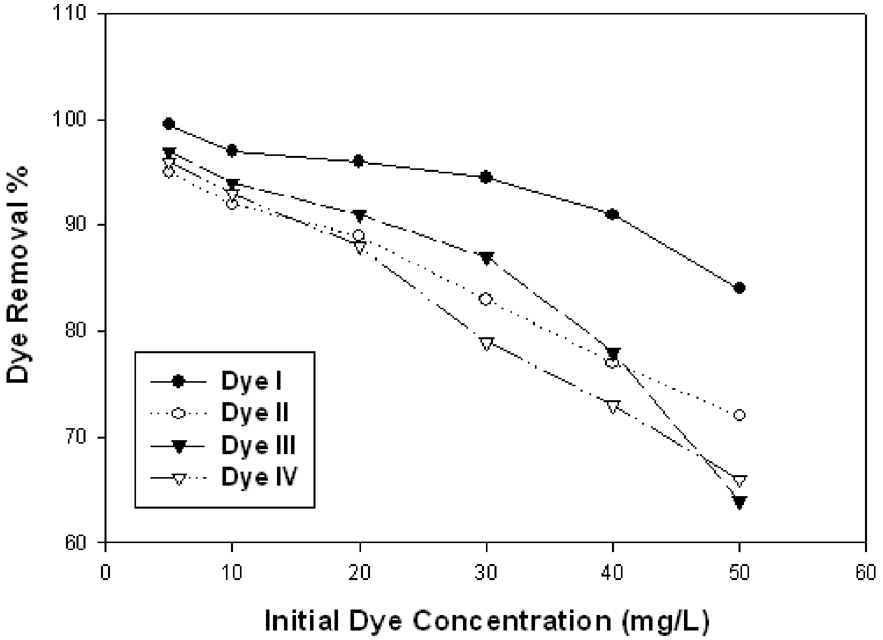

Fig. (3-13): Relation between initial dye concentration on percent removal for different dyes on AC2.

3.8. Isotherm data analysis

Adsorption is the accumulation of a mass transfer process that can generally be defined as the material at the interface between solid and liquid phases. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbet and that remaining in the solution at a fixed temperature at equilibrium. The adsorption isotherm is important from both a theoretical and a practical point of view. Isotherm data should accurately fit into different isotherm models to find a suitable model that can be used for the design process [105]. The parameters obtained from the different models provide important information on the sorption mechanisms, the surface properties and affinities of the sorbent. There are several isotherm equations available for analyzing experimental sorption equilibrium data, the most famous adsorption models for single-solute systems are the Langmuir and Freundlich models.

In order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system, three common isotherm models were tested: Langmuir, Freundlich and Tempkin. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients (R^2). The data required for applying different isotherms are shown in **Tables (3-5)** and **(3-6)**, these data are C_o, C_e, q_e, ln C_e, ln q_e and C_e/q_e for the different dyes on AC1 & AC2 respectively . The applicability of the isotherm equations was compared by judging the correlation coefficients, R^2.

Table (3-5): Data required for applying different isotherm models of adsorption of dyes (I-IV) on AC1.

C_e/q_e	ln q_e	q_e (mg/g)	ln C_e	C_e (mg/L)	C_o (mg/L)	Dye
0.041	0.896	2.45	-2.302	0.10	5	**Dye I**
0.105	1.558	4.75	-0.693	0.50	10	
1.330	1.791	6.00	2.079	8.00	20	
2.000	1.840	6.30	2.533	12.60	30	
4.250	1.856	6.40	3.303	27.20	40	
5.518	1.894	6.65	3.603	36.70	50	
0.475	0.703	2.02	-0.041	0.96	5	**Dye II**
1.225	1.131	3.10	1.335	3.80	10	
2.347	1.280	3.60	2.549	12.80	20	
5.142	1.435	4.20	3.044	21.60	30	
6.880	1.504	4.50	3.443	31.00	40	
9.148	1.547	4.70	3.761	43.00	50	
0.70	0.615	1.85	0.262	1.30	5	**Dye III**
1.77	0.974	2.65	1.547	4.70	10	
3.05	1.163	3.20	2.278	9.76	20	
6.95	1.208	3.35	3.135	23.30	30	
9.11	1.281	3.60	3.490	32.80	40	
11.15	1.335	3.80	3.747	42.40	50	
0.94	0.530	1.70	0.475	1.60	5	**Dye IV**
1.63	1.011	2.75	1.504	4.50	10	
3.71	1.252	3.50	2.562	13.00	20	
5.22	1.423	4.15	3.077	21.70	30	
8.11	1.470	4.35	3.563	35.30	40	
9.11	1.504	4.50	3.713	41.00	50	

Table (3-6): Data required for applying different isotherm models of adsorption of dyes (I-IV) on AC2.

C_e/q_e	ln q_e	q_e (mg/g)	ln C_e	C_e (mg/L)	C_o (mg/L)	Dye
0.010	0.908	2.48	-3.218	0.04	5	**Dye I**
0.062	1.578	4.85	-1.204	0.30	10	
0.083	2.261	9.60	-0.223	0.80	20	
0.116	2.651	14.17	0.500	1.65	30	
0.197	2.901	18.20	1.281	3.60	40	
0.381	3.044	21.00	2.079	8.00	50	
0.105	0.865	2.37	-1.386	0.25	5	**Dye II**
0.174	1.526	4.60	-0.223	0.80	10	
0.247	2.186	8.90	0.788	2.20	20	
0.316	2.561	12.95	1.410	4.10	30	
0.325	2.845	17.20	1.722	5.60	40	
0.381	3.044	21.00	2.079	8.00	50	
0.062	0.885	2.42	-1.89	0.15	5	**Dye III**
0.127	1.547	4.70	-0.512	0.60	10	
0.198	2.208	9.10	0.587	1.80	20	
0.298	2.568	13.05	1.361	3.90	30	
0.564	2.747	15.60	2.174	8.80	40	
1.125	2.772	16.00	2.890	18.00	50	
0.083	0.875	2.40	-1.609	0.20	5	**Dye IV**
0.150	1.536	4.65	-0.356	0.70	10	
0.272	2.174	8.80	0.875	2.40	20	
0.531	2.472	11.85	1.840	6.30	30	
0.739	2.681	14.60	2.379	10.80	40	
1.030	2.803	16.50	2.833	17.00	50	

3.8.1. Langmuir isotherm

The theoretical Langmuir sorption isotherm [106] is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. The model is based on several basic assumptions: (i) the sorption takes place at specific homogenous sites within the adsorbent; (ii) once a dye molecule occupies a site; (iii) the adsorbent has a finite capacity for the adsorbate (at equilibrium); (iv) all sites are identical and energetically equivalent. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The non-linear equation of Langmuir isotherm model can be written as followed:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (3)$$

where C_e is equilibrium liquid-phase concentration (mg/L), qe and q_m are the adsorption capacity at time t and the maximum adsorption capacity reflected a complete monolayer (mg/g), respectively. The adsorption equilibrium constant b represents enthalpy of sorption and should vary with temperature (L/mg) that is related to the apparent energy of sorption. The Langmuir isotherm (Eq. (3)) can be linearized into the form [107]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (4)$$

A plot C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(bq_m)$.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [108]:

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

where C_0 represents the initial concentration (mg/L) and b the Langmuir constant related to adsorption energy (L/mg). R_L value implies the shape of the isotherms to be either unfavorable (R_L), linear ($R_L = 1$), favorable (O< R_L < 1) or irreversible (R_L=0) [110]. As can be seen in **Tables (3-5)** and **(3-6)**, for the two sorption systems, R_L values at different concentrations are between 0 and 1, showing favorable adsorption (C_0 =5-50 mg/L) . The low values of R_L indicate high and favorable adsorption of all Dyes onto AC1 and AC2.

A linear plot is obtained when C_e /q_e is plotted against C_e over the entire concentration range of all dyes investigated. The Langmuir isotherm plots are shown in **Fig. (3-14)** and **Fig. (3-15)** for adsorption of dyes (I-IV) for AC1 and AC2, respectively. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in **Table (3-7)** and **Table (3-8)** for AC1 and AC2, respectively. As shown in the tables, the Langmuir model effectively described the sorption data with all R^2 values >0.99 in case of using AC1 as adsorbent. The adsorption isotherms of dyes (I-IV) exhibit Langmuir behavior, which indicates a monolayer adsorption. On the other hand, the R^2 values in case of AC2 are all >0.98 with the exception of dye II (R^2 = 0.9019) indicating that this model is not applicable for dye II when using AC2 as adsorbent.

According to q_m (mg/g) parameter obtained from Langmuir plot analysis, sorption of different dyes on AC1 is produced following the sequence:

Dye I (6.63 mg/L) > Dye IV (4.84 mg/L) ≈ Dye II (4.78 mg/L) > Dye II (3.89 mg/L). The sequence of sorption of dyes on AC2 is: Dye I (26.95 mg/L) > Dye III (13.35 mg/L) > Dye IV (8.23 mg/L) (after exclusion of dye II).

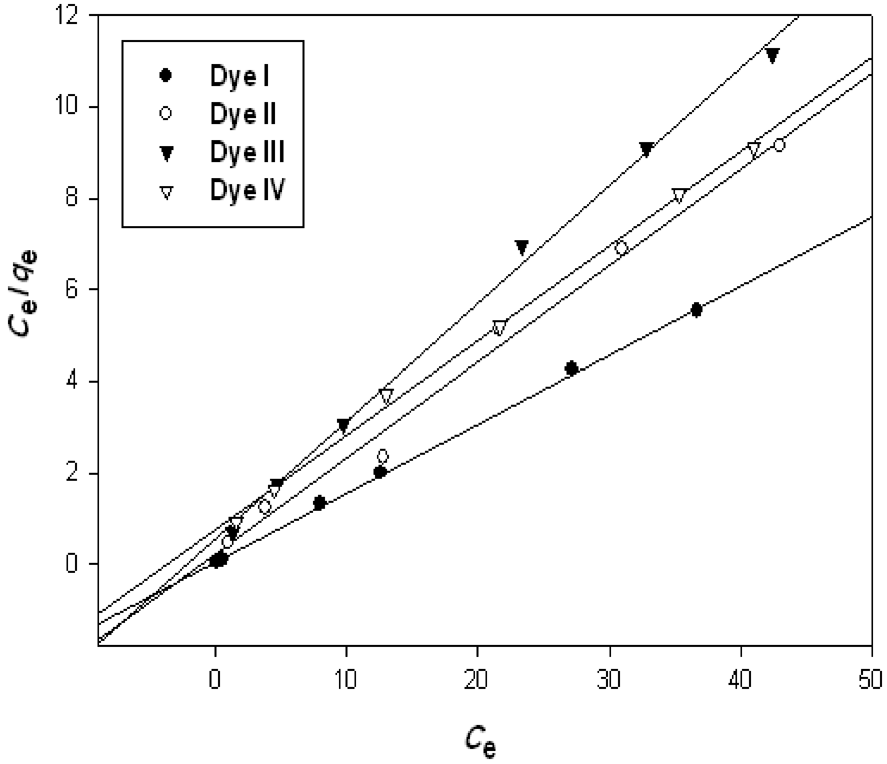

Fig. (3-14). Langmuir isotherm of dyes (I-IV) on AC1 at 25 ^{o}C.

Table (3-7): Parameters of Langmuir isotherm for adsorption of dyes (I-IV) on AC1.

Langmuir Isotherm						Dye
***R*²**	***R*L**	***b*** (L/mg)	***q*m** (mg/g)	**Intercept**	**Slope**	
0.9991	0.085-0.009	2.151	6.63	0.0701	0.1507	**Dye I**
0.9908	0.190-0.023	0.850	4.78	0.2459	0.2098	**Dye II**
0.9965	0.305-0.042	0.454	3.89	0.5652	0.2569	**Dye III**
0.9979	0.422-0.068	0.273	4.84	0.7564	0.2066	**Dye IV**

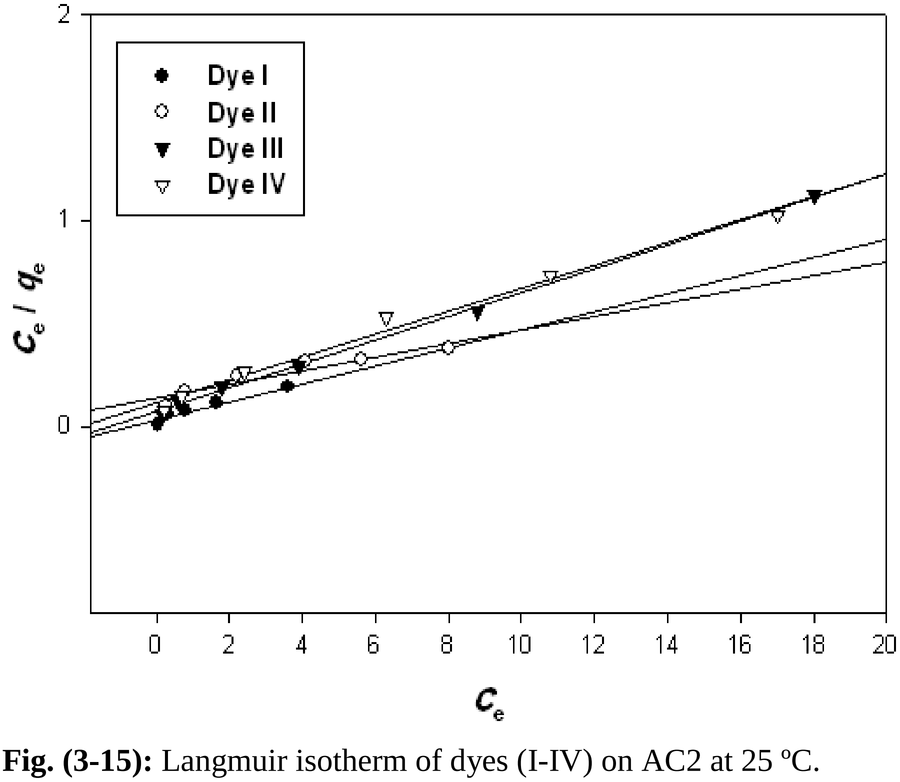

Fig. (3-15): Langmuir isotherm of dyes (I-IV) on AC2 at 25 ºC.

Table (3-8): Parameters of Langmuir isotherm for adsorption of dyes (I-IV) on AC2.

Langmuir Isotherm						**Dye**
R^2	R_L	b (L/mg)	q_m (mg/g)	**Intercept**	**Slope**	
0.9866	0.166-0.019	1.000	26.95	0.0371	0.0435	**Dye I**
0.9019	0.166-0.019	1.000	6.99	0.1430	0.0329	**Dye II**
0.9979	0.167-0.019	0.996	13.35	0.0749	0.0578	**Dye III**
0.9882	0.166-0.019	1.000	8.23	0.1215	0.0555	**Dye IV**

3.8.2. Freundlich isotherm

The Freundlich isotherm model is the earliest known relationship describing the sorption process [110]. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation can be employed to describe heterogeneous systems and is expressed as follow:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

where K_F is the Freundlich constant (L/mg) related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above to unity adsorption is a favorable physical process [111]. Eq. (6) can be linearized in the logarithmic form (Eq. (7)) and the Freundlich constants can be determined:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_{\square} \tag{7}$$

The plot of ln q_e versus log C_e was employed to generate the intercept value of K_F and the slope of $1/n$ (**Tables 9** and **10**). The correlation coefficients $R^2 < 0.98$, obtained from Freundlich model indicate poor agreement of the Freundlich isotherm data with the experimental data, especially for Dye I ($R^2 = 0.8593$ and 0.6702) in case of AC1 and AC2, respectively. The correlation coefficient R^2 equals to 0.6172 and 0.7691 for Dyes II and III in case of adsorption on AC2, respectively.

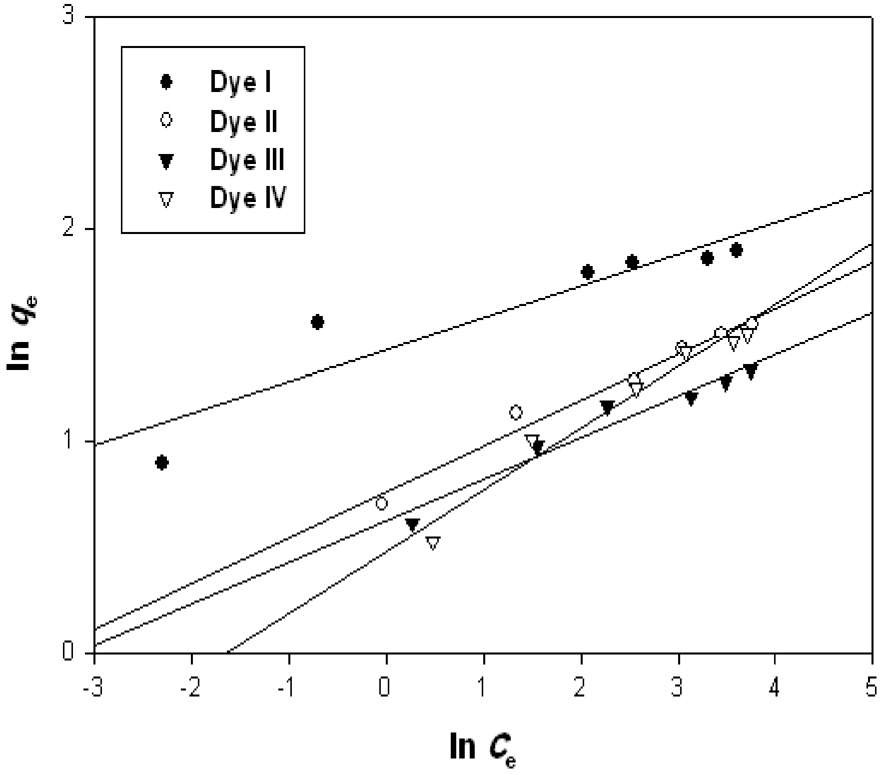

Fig. (3-16): Freundlich isotherm of dyes (I-IV) on AC1 at 25 ºC

Table (3-9): Parameters of Freundlich isotherm for adsorption of dyes (I-IV) on AC1.

Freundlich Isotherm					**Dye**
R^2	**n**	K_F (mg/g)(mg/L)$^{-1/n}$	**Intercept**	**Slope**	
0.8593	6.698	4.116	1.4270	0.1493	**Dye I**
0.9779	4.625	2.136	0.7592	0.2162	**Dye II**
0.9532	5.117	1.868	0.6252	0.1954	**Dye III**
0.9647	3.442	1.611	0.4772	0.2905	**Dye IV**

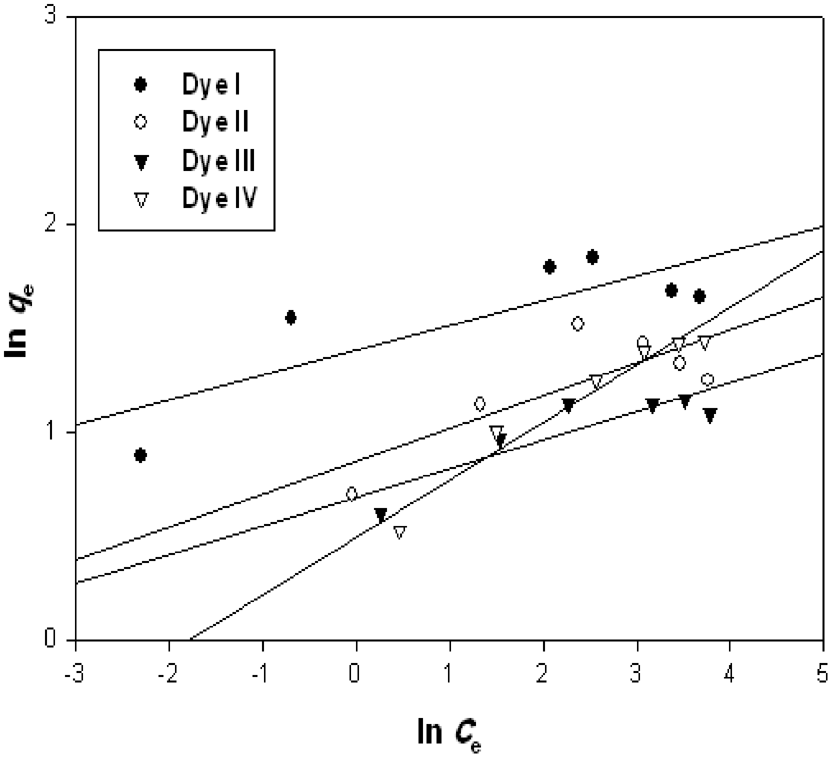

Fig. (3-17): Freundlich isotherm of dyes (I-IV) on AC2 at 25 ºC

Table (3-10): Parameters of Freundlich isotherm for adsorption of dyes (I-IV) on AC2.

Freundlich Isotherm					**Dye**
***R*²**	**n**	***K*F** (mg/g)(mg/L)$^{-1/n}$	**Intercept**	**Slope**	
0.6702	8.446	4.039	1.3960	0.1184	**Dye I**
0.6172	6.329	2.360	0.8587	0.1580	**Dye II**
0.7691	7.246	1.982	0.6845	0.1380	**Dye III**
0.9516	3.616	1.638	0.4938	0.2765	**Dye IV**

3.8.3. Tempkin isotherm

Temkin isotherm model contains a factor that explicitly takes into account adsorbing species–adsorbate interactions [112]. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Tempkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has commonly been applied in the following form (Eq. (8)) [113]:

$$q_e = \frac{RT}{b_T}\ln A_T + \frac{RT}{b_T} lnC_e \qquad (8)$$

where A_T (L/mg) and b_T (J/mol) are the Tempkin constants. T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 $Jmol^{-1}K^{-1}$. A_T and b_T constants are determined from the slope and intercepts of the plots obtained by plotting q_e versus time ln C_e. The plot of q_e values of different dyes versus ln C_e are shown in **Fig. (3-18)** and **Fig. (3-19)** for dyes adsorption on AC1 and AC2, respectively.

To study the applicability of the Tempkin isotherm models for the different dyes adsorption by the AC, all calculated parameters of these models are shown in **Table (3-11)** and **Table (3-12)**, for dyes adsorption on AC1 and AC2, respectively. From the linear regression correlation coefficient, R^2, it was found that Tempkin isotherm is not applicable to the adsorption of Dye I (when adsorbed on AC1), Dye I, II and III (when adsorbed on AC2). It shows that the equilibrium data could be well interpreted by the Tempkin isotherm only for Dyes II, III and IV (adsorbed by AC1) and Dye IV (adsorbed by AC2).

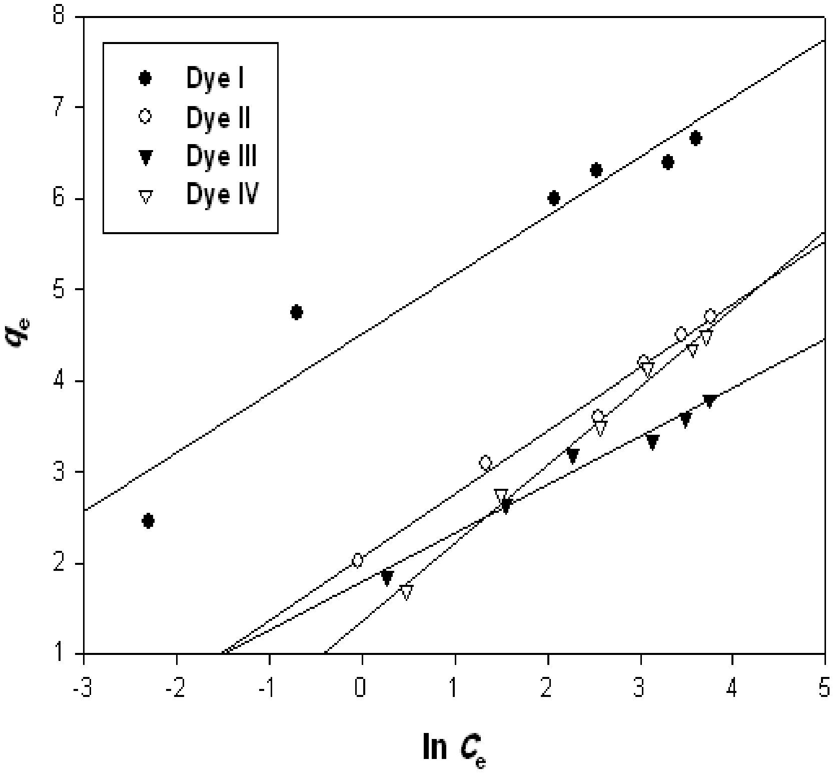

Fig. (3-18): Tempkin isotherm of dyes (I-IV) on AC1 at 25 ºC

Table (3-11): Parameters of Tempkin isotherm for adsorption of dyes (I-IV) on AC1.

Temkin Isotherm						**Dye**
R^2	***b_T*** (J/mol)	***A_T*** (L/mg)	**ln *A_T***	**Intercept**	**Slope**	
0.9268	3818.69	1032.77	6.940	4.5030	0.6488	**Dye I**
0.9863	3578.23	19.61	2.976	2.0610	0.6924	**Dye II**
0.9763	4650.97	28.84	3.362	1.7910	0.5327	**Dye III**
0.9921	2890.30	4.90	1.591	1.3640	0.8572	**Dye IV**

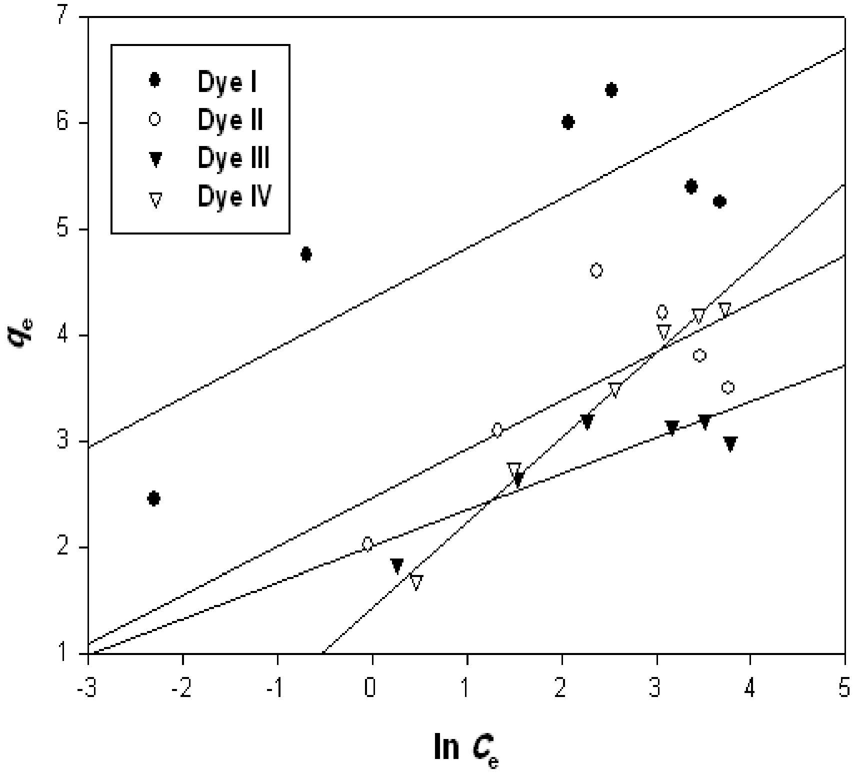

Fig. (3-19): Tempkin isotherm of dyes (I-IV) on AC2 at 25 ºC

Table (3-12): Parameters of Tempkin isotherm for adsorption of dyes (I-IV) on AC2.

Temkin Isotherm						**Dye**
R^2	b_T (J/mol)	A_T (L/mg)	**ln** A_T	**Intercept**	**Slope**	
0.6631	5306.43	11147.82	9.319	4.3510	0.4669	**Dye I**
0.5355	5400.11	216.80	5.379	2.4680	0.4588	**Dye II**
0.7558	7252.84	364.31	5.898	2.0150	0.3416	**Dye III**
0.9854	3093.09	5.99	1.791	1.4350	0.8010	**Dye IV**

3.9. Effect of temperature

The effect of temperature on the removal efficiency was investigated in the temperature range of 25–45 ºC. The experiments were carried out with AC dose of 2 g/L and initial dye concentration of 50 mg/L at pH 8.0. The uptake of different dyes by AC1 and AC2 increased from when increasing the temperature from 25 to 45 ºC, indicating that dye uptake was favored at higher temperatures (**Fig. (3-20)** and **Fig. (3-21**), for all dyes onto AC1 and AC2, respectively. The increase in temperature led to an increase in the dye adsorption rate this due to the great diffusion which increase the mass transfer of the dye molecules , which indicated a kinetically controlled endothermic process. The data of different dyes (I-IV) removal on the two types of activated carbon (AC1 and AC2) are shown in **Table (3-13)**.

Table (3-13): Effect of temperature on dye removal percent of dyes (I-IV) onto AC1 and AC2.

Temperature (^oC)			**Dye**	**Activated Carbon**
45	**35**	**25**		
99.5%	93.0%	88.2%	Dye I	**AC1**
71.0%	55.2%	45.0%	Dye II	
52.0%	45.5%	34.0%	Dye III	
76.2%	62.6%	52.3%	Dye IV	
99.5%	98.2%	94.0%	Dye I	**AC2**
99.7%	97.6%	90.0%	Dye II	
94.0%	91.2%	87.0%	Dye III	
99.4%	98.7%	96.1%	Dye IV	

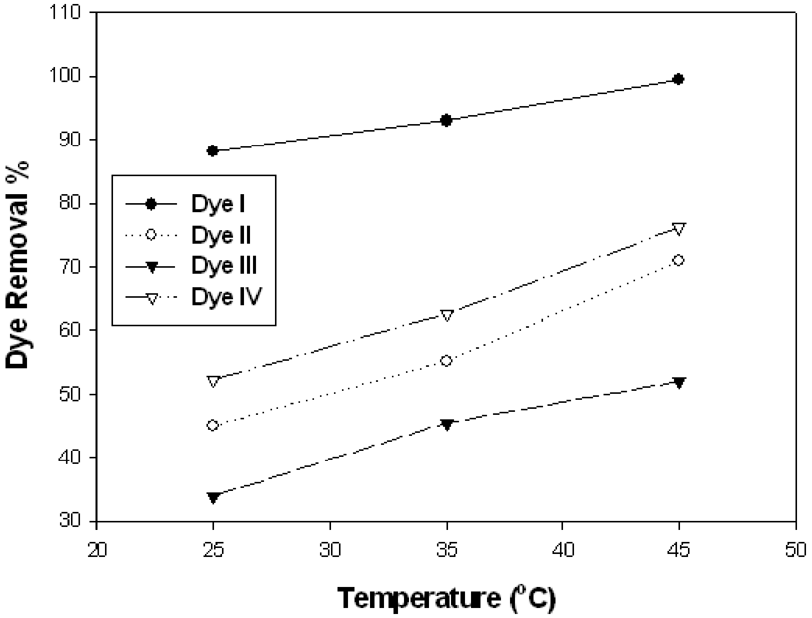

Fig. (3-20): Effect of temperature on dye removal percent on AC1

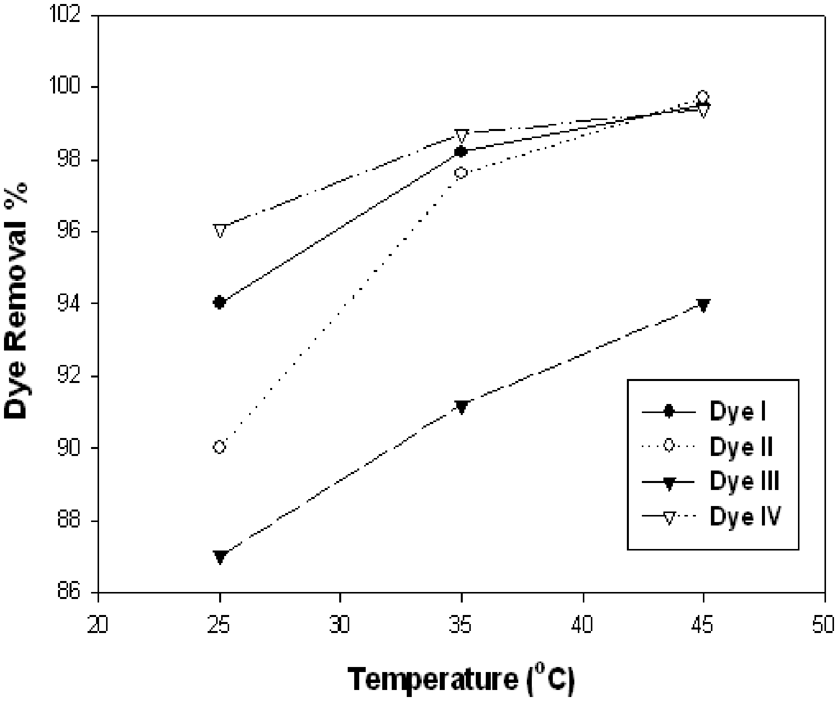

Fig. (3-21): Effect of temperature on dye removal percent on AC2

3.10. Thermodynamic Parameters

The feasibility of the adsorption process was evaluated by the thermodynamic parameters which including standard Gibbs free energy $\Delta G°$ (kJ mol^{-1}), the standard enthalpy ($\Delta H°$), and the standard entropy ($\Delta S°$) for adsorption of different dyes (I-IV) onto AC1 and AC2 were calculated using the following equations:

$$\Delta G^{\circ} = -RT \ln K_c \qquad (9)$$

The apparent equilibrium constant K_c (L/g) of the adsorption is defined as [114]:

$$K_c = C_{ad} / C_e \qquad (10)$$

where C_{ad}, C_e is the concentration of dye on the adsorbent (mg/g) and the concentration of dye in solution (mg/L) at equilibrium.

R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}) and T is the absolute temperature (K). The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) parameters were estimated from the equation:

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (11)$$

The change in Gibbs free energy ($\Delta G°$) for adsorption of different dyes (I-IV) onto activated carbon can be evaluated from the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (12)$$

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plots of $\ln K_c$ against $1/T$ (equation 11). The plot of $1/T$ versus $\ln K_c$ for dyes (I-IV) is shown in Figs. 24 and 25 for AC1 and AC2, respectively. The values of slopes and intercepts of different plots are shown in **Table (3-14)** for adsorption on AC1 and in **Table (3-15)** for adsorption on AC2.

For significant adsorption to occur, the free energy changes of adsorption, ΔG^{o}, must be negative. The thermodynamics relation between ΔG^{o}, ΔH^{o} and ΔS^{o} suggests that either (i) ΔH^{o} is positive and ΔS^{o} is positive and that the value of $T\Delta S$ is much larger than ΔH^{o}, or (ii) ΔH^{o} is negative and ΔS^{o} is positive or that the value of ΔH^{o} is more than $T\Delta S$. Dyes adsorption is endothermic in nature, giving a positive value of ΔH^{o}. Hence, ΔS^{o} has to be positive and that the positive value of $T\Delta S$ has to be larger than ΔH^{o}. The positive ΔH^{o} value confirms the endothermic nature of the overall-sorption process. The adsorption process in the solid-liquid system is a combination of two processes: (a) the desorption of the molecules of solvent (water) previously adsorbed, and (b) the adsorption of adsorbate species. The dye molecules have to displace more than one water molecule for their adsorption and these results in the endothermicity of the adsorption process. Therefore, the ΔH^{o} will be positive. The positive value of ΔS^{o} suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the dye towards AC. Also, positive ΔS^{o} value corresponds to an increase in the degree of freedom of the adsorbed species [115,116]. ΔG^{o} values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative ΔG^{o} indicates the feasibility and spontaneity of the adsorption process for the adsorption of dyes (I-IV) on AC1 and AC2.

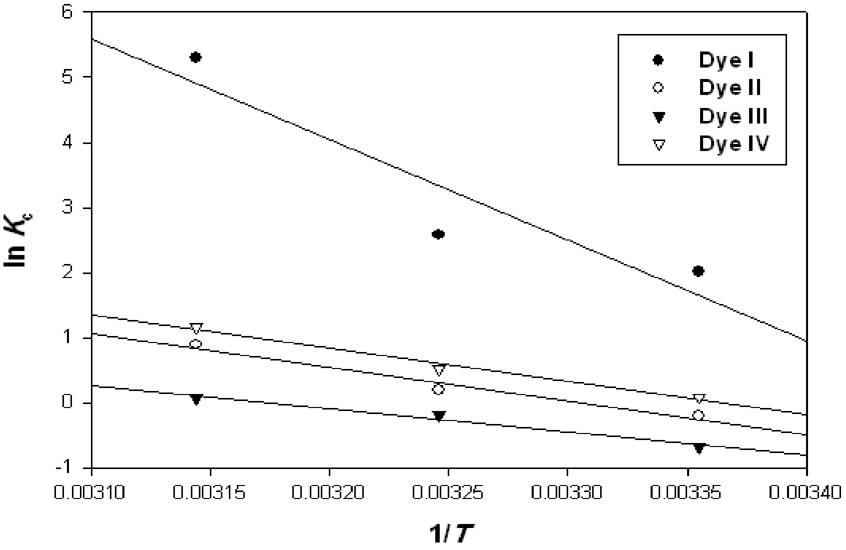

Fig. (3-22): Plot of ln K_c vs. 1/T for the estimation of thermodynamic parameters for adsorption of dyes (I-IV) onto AC1 to calculate thermodynamic parameters.

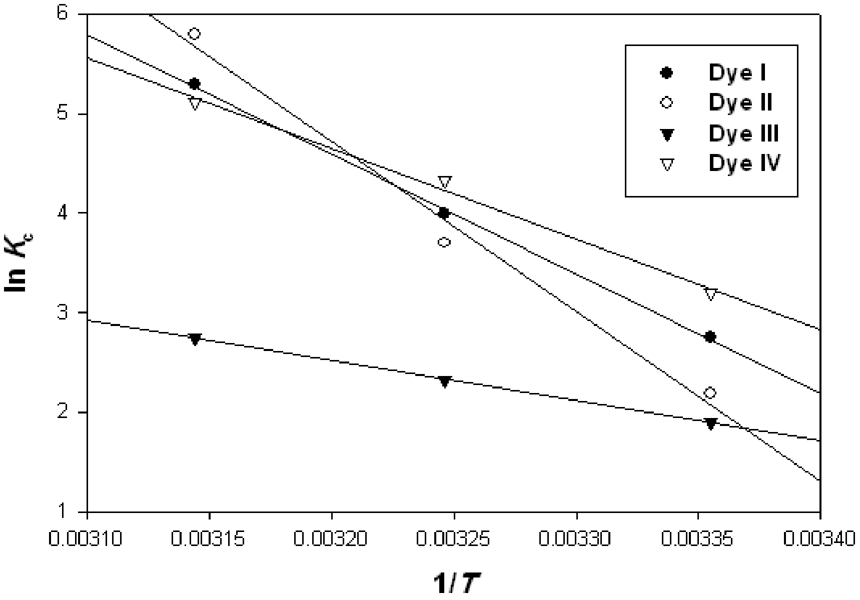

Fig. (3-23): Plot of ln K_c vs. 1/T for the estimation of thermodynamic parameters for adsorption of dyes (I-IV) onto AC2 to calculate thermodynamic parameters.

Table (3-14): Values of K_c, ln K_c and $1/T$ for adsorption of dyes (I-IV) onto AC1.

R^2	Intercept	Slope	1/*T*	ln K_c	K_c	Temp.	Dye
0.8638	53.44	-1544	3.355×10^{-3}	2.011	7.474	25	**Dye I**
			3.246×10^{-3}	2.586	13.285	35	
			3.144×10^{-3}	5.293	199.00	45	
0.9729	17.10	-5173	3.355×10^{-3}	-0.200	0.818	25	**Dye II**
			3.246×10^{-3}	0.208	1.232	35	
			3.144×10^{-3}	0.895	2.448	45	
0.9769	11.22	-3532	3.355×10^{-3}	-0.663	0.515	25	**Dye III**
			3.246×10^{-3}	-0.180	0.834	35	
			3.144×10^{-3}	0.080	1.083	45	
0.9833	17.04	-5063	3.355×10^{-3}	0.092	1.096	25	**Dye IV**
			3.246×10^{-3}	0.525	1.692	35	
			3.144×10^{-3}	1.163	3.201	45	

Table (3-15): Values of K_c, ln K_c and $1/T$ for adsorption of dyes (I-IV) onto AC2.

R^2	**Intercept**	**Slope**	**1/*T***	**ln K_c**	**K_c**	**Temp.**	**Dye**
0.9989	43.09	-12030	3.355×10^{-3}	2.75	15.66	25	**Dye I**
			3.246×10^{-3}	3.99	54.55	35	
			3.144×10^{-3}	5.29	199.00	45	
0.9872	59.35	-17070	3.355×10^{-3}	2.19	9.00	25	**Dye II**
			3.246×10^{-3}	3.70	40.66	35	
			3.144×10^{-3}	5.80	332.33	45	
0.9998	15.41	-4027	3.355×10^{-3}	1.90	6.69	25	**Dye III**
			3.246×10^{-3}	2.33	10.36	35	
			3.144×10^{-3}	2.75	15.66	45	
0.9925	33.67	-9067	3.355×10^{-3}	3.20	24.64	25	**Dye IV**
			3.246×10^{-3}	4.33	75.92	35	
			3.144×10^{-3}	5.11	165.66	45	

Table (3-16): Thermodynamic parameters for adsorption of dyes (I-IV) on AC1.

ΔS^o **(kJ/(mol K))**	**ΔH^o** **(kJ/mol)**	**ΔG^o** **(kJ/mol)**	**T** **(K)**	**Dye**
0.444	12.83	-4.98	298	**Dye I**
		-6.62	308	
		-13.99	318	
0.142	43.00	0.49	298	**Dye II**
		-0.53	308	
		-2.36	318	
0.093	29.36	1.64	298	**Dye III**
		0.46	308	
		-0.21	318	
0.141	42.09	-0.22	298	**Dye IV**
		-1.34	308	
		-3.07	318	

Table (3-17): Thermodynamic parameters for adsorption of dyes (I-IV) on AC2.

ΔS^o (kJ/(mol K))	**ΔH^o (kJ/mol)**	**ΔG^o (kJ/mol)**	**T (K)**	**Dye**
0.358	100.01	-6.74	298	**Dye I**
		-10.33	308	
		-13.91	318	
0.493	141.92	-5.12	298	**Dye II**
		-10.05	308	
		-14.99	318	
0.128	33.48	-4.69	298	**Dye III**
		-5.97	308	
		-7.25	318	
0.279	75.38	-8.04	298	**Dye IV**
		-10.83	308	
		-13.63	318	