Thermodynamic and Kinetic Study to the Adsorption of Fluorescien Dye over Activated Carbon

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***Abstract*— The study involves using of activated carbon to the removal of Fluorescien dye from aqueous solution. The study involved the adsorption isotherm of the dye over the activated carbon. The study assumes that the adsorption of dye over activated carbon is pseudo first order investigation of the effect of concentration, temperature, time and pH of the media was studied in detail to choose the suitable condition for the kinetic and thermodynamic studies.**

***Index Terms*— Adsorption of Dyes, Study of adsorption kinetic and thermodynamic for Dyes.**

I. INTRODUCTION

Dyes are chemical compounds have been used in many industries for coloration purposes such as, in food processing, textiles, papers, cosmetics and other industries. Therefore, the removal of such compounds from water [1]. Activated carbons have long been used as adsorbents in industry due to their superior adsorption capacities. Major contaminants found in wastewater include biodegradable, volatile, and recalcitrant organic compounds; toxic metals; microbial pathogens; and parasites causing deterioration of the surrounding medium that can present a great danger to the environment and human health [2]. Adsorption techniques have proven successful in removing colored organic species, with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials [3]. Several studies have been undertaken on the toxicity of dyes and their impact on ecosystems. Their properties depend on the pore structure, which in turn depends on the preparation conditions as well as the chemical nature of the carbon surface [4]. Many research groups have investigated the feasibility of using various low cost substances adsorbents for the removal of dyes from waste water. Identification of a potential dye sorbent must be in good agreement with its dye binding capacity, regeneration properties, requirement and limitations with respect to environmental conditions. Activated carbon remains the most effective and widely used adsorbent for the removal of dyes from aqueous solutions [5]. The term adsorption kinetic represents the rate of molecular uptake from the adsorbate solution to the adsorbent surface after overcoming all of the internal intermolecular forces that trying to preclude the adsorption process (6). Kinetic data are valuable for determining the period required to reach equilibrium and assessing the adsorbent performance for effluent species adsorption [7], [8]. These data also help to understand the mechanism of adsorption which is essential for improving the efficiency of such process. For this reason, a great attention has been paid recently toward the development of such studies [9].

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II. EXPERIMENTAL

CHEMICAL AND INSTRUMENTS

Activated carbon (99%) (BDH), Fluorescien dye (99.99%) (Fluka), Distillation water, Hydrochloric acid [Sp.gr.36.5] (36%) (Fluka), NaOH (BDH), NaNO2 (BDH) and Ethanol (99.99%) (BDH).

UV-Visible spectrophotometer made by (Thermo Spectronic-Heλ10Sα) the range (900-200nm). pH-meter made by (WTW) (Calomel and Glass Electrodes) and Shaker made by (Certomat IS Sartorius).

DRYING OF THE ACTIVATED CARBON

20 g of industrial activated carbon BDH grade of a powdered form was dried in an oven at 110°C for 3hrs. The sample was kept closed for use in the next step.

OPTIMUM ACTIVATED CARBON AMOUNT AND DYE CONCENTRATION TO REACH THE EQUILIBRIUM

The kinetic and thermodynamic study require to find out t he best amount of the adsorbant and adsorbet in order to foll ow the colour changes from the beginning of the adsorption t o require time a certain. The amount of activated carbon requ ired was 0.2 g, on the other hand the amount of Fluorescien was 70 ppm to follow the adsorption [10].

STUDY OF THE EQUILIBRIUM REQUIRED TIME

The study involved preparation of nine samples of the same concentration (70 ppm) from Fluorescien. The amount of car bon added to each sample is 0.2 g and sample was shaked for (10-90) min, the best time for the adsorption and equilibrium was found to be 60 min [10].

EFFECT OF DYES CONCENTRATION

Seven samples of the Fluorescien dye were prepared by di lution to 40-100 ppm. The amount of carbon added was 0.2 g The mixture was shaked for 60 min and filtered directly. The spectra in the visible region for filtrates. The absorbance of each sample were used to calculate the percentage absorbed dye [10].

EFFECT OF TEMPERATURE

The effect of temperature variation on the adsorption abil ity of carbon was studied using seven samples (70 ppm), to which 0.2 g of carbon was added. The mixture was shaked fo

r 60 min at 15-45°C, using 5°C increment, After filtration, absorbance was measured and the percentage of adsorption was calculated [10].

EFFECT OF pH

The effect of pH after determining the ideal conditions (Conc., Temp., and Time), was studied in which five samples having the same concentration were mixed separately with 0.2 g of carbon. The mixture was shaked for the same time and at each pH. After adsorption was finished, the absorbance measured and the percentage of adsorption was calculated [10].

$$\% \text{ Adsorption} = (X / a) \times 100 \ldots . (1)$$

Where (X) is the concentration of the adsorbed dye which represents the difference between the initial concentration (a) and the dye concentration in the solution after treatment (a – X).

THERMODYNAMIC STUDY

Value of enthalpy of adsorption helps to determine the nature and the kind of forces those control the process of attachment with the solid surface. The adsorption equilibrium constants are calculated at various temperatures from the ratio between the adsorbed and free dye concentrations. The value of ΔH is calculated from the slope of the straight line (ΔH/R) that resulted from plotting lnK versus (1/T) when applying the Van't Hoff' s equation which can be expressed as [10].

$$\ln K = \ln K_0 - \Delta H / RT \ldots . (2)$$

Where (R) is the gas constant (8.314 J. mol^{-1}. K^{-1}), (T) is the absolute temperature (273 + ^{0}C), (K) is equilibrium constant, (K_0) is the intercept and (ΔH) is enthalpy of the reaction.

In addition to the ΔH calculation ΔG was also calculated using following equation.

$$\Delta G° = - R T \ln K \ldots . (3)$$

On the hand, ΔS was calculated using the following equation.

$$\Delta G° = \Delta H° - T \Delta S°$$
$$\Delta S° = \Delta H° - \Delta G ° / T \ldots . (4)$$

KINETIC STUDY

In the kinetic study we recognize the adsorption of the dye is very fast and require to be adjusted in term of concentration, temperature and time. The study used the same concentration of dye amount to carbon at constant temperature, while the time is variant between (2-10) min. The mixture was shaked for the given time. The remaining dye was filtered in each case and its absorbance was determined. From the literature the adsorption of dyes on active carbon is considered as a pseudo first order reaction, k was calculated using the following equation [10].

$$\ln (a-x) = \ln a - k t \ldots . (5)$$

III. RESULTS AND DISCUSSION

The activated carbon was used in the kinetic and thermodynamic study of Fluorescien adsorption. Before studying the kinetic of dyes adsorption, the dyes used was recrystalised from ethanol. The suitable concentration used in the adsorption was 40-100 ppm at 25°C (water bath temperature). The result of the adsorption is calculated from standard curve of Fluorescien dye at 570 nm. The results are given in Table 1 and Figure 1.

Table (1): The absorbance of different concentration of Fluorescien

Conc. (ppm)	Absorbance
10	0.473
20	0.892
30	1.301
40	1.782
50	2.199
60	2.654
70	3.134
80	3.584
90	4.043
100	4.491

The data of the adsorption of Fluorescien dye at different concentration follow a linear first order equation that of the type **y=0.0447x + 0.0024**.

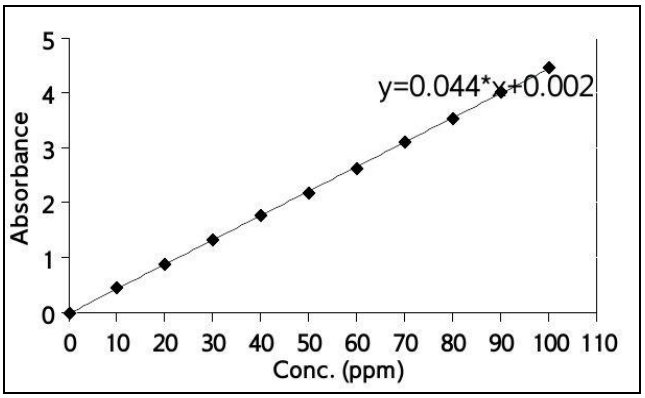


Figure (1): The standard calibration curve of the Fluorescien at different concentration at 570 nm

The results in the table indicate a fast adsorption of the dye between 10-30 ppm Table 2.

Table (2): The effect of concentration of Fluorescien over activated carbon at constant temperature (25°C) and time (60min)

Primary Conc. (ppm)	Finally conc. (ppm)
10	0
20	0
30	0
40	3.55
50	3.87
60	4.24
70	4.54
80	6.57
90	9.86
100	12.43

The result of dyes adsorption and the concentration is given in the Table 3.

Table (3): The variation of concentration of the Fluorescien treated with activated carbon and the percentage adsorbed

Conc. of dyes before adsorption (ppm)	Percentage of dye adsorbed (%)
40	91.12
50	92.26
60	92.93
70	**93.51**
80	91.78
90	89.04
100	87.57

The effect of the time on the adsorption of the dyes and the best time for equilibrium was studied as given in Table 4.

Table (4): The effect of time on the adsorption of Fluorescien

Time (min)	Percentage of dye adsorbed (%)
10	78.94
20	81.43
30	83.03
40	84.36
50	85.73
60	85.73
70	87.14
80	87.14
90	87.14

The results indicate that 50-60 min is the best time for e quilibrium of the dye adsorption moreover , the effect of incr easing temperature was investigated between 15-45°C with 5 °C increment , the best temperature for the dyes adsorption is 25°C to give 83.79%. The adsorbed dye below 25°C increas e which may be due to the formation of hydrogen bonding an d some electrostatic adsorption forces. These forces started t o decay after 25°C due to the exothermic nature of the adsor ption process and the energy added by increasing the temper ature. The results are given in Table 5 [11].

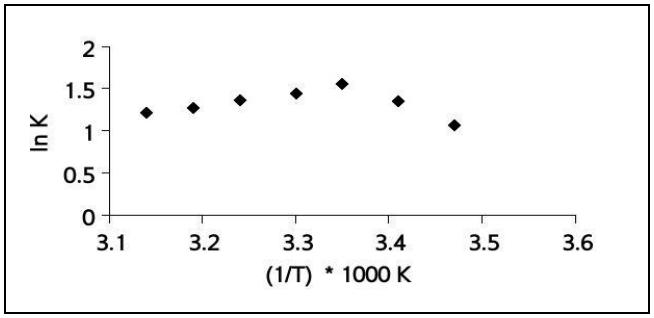
Table (5): The effect of temperature variation on the adsorption of Fluorescien

Temperature (0 C)	Percentage of dye adsorbed (%)
15	79.67
20	80.81
25	**83.79**
30	82.35
35	81.39
40	81.00
45	80.25

The thermodynamic parameters are calculated by using equations 2, 3 and 4. Its values are explained in Table 6, and the enthalpy of reaction is calculated from equilibrium constant as shown in Figure 2.

Table (6): The values of thermodynamic parameters for adsorption of Fluorescien adsorption

T (Kelvin)	K	ΔG° (J. mol^{-1})	ΔH° (J. mol^{-1})	ΔS° (J. mol^{-1}. k^{-1})
288	2.95	-2585.9	-12848.9	-10263.0
293	3.67	-3312.9	-12848.9	-9536.0
298	**4.83**	**3865.0**	-12848.9	**-8983.9**
303	4.34	-3677.9	-12848.9	-9171.0
308	4.12	-3610.6	-12848.9	-9238.3
313	3.65	-3356.9	-12848.9	-9492.0
318	3.44	-3251.9	-12848.9	-9597.0



Figure(2): The relationship between ln equilibrium constant and reciprocal of temperature in Kelvin

Study of the pH effect of media on the adsorption of Fluorescien indicates that increasing the acidity from 6.5 to 2 improves the adsorption of the dye. However increasing the basisty from 6.5 to 11 shows great reduction in the adsorption of the dye which may be due to the formation of COO-Na+, O-Na+ and could be reached to the solution that may prevent adsorption. Therefore, adsorbent amount of Fluorescien decreased with increased pH, as shown in Table 7 [10], [12].

Table (7) effect of pH on the adsorption of Fluorescien

pH	Percentage of dye adsorbed (%)
2	94.11
4	86.68
6.5	**81.07**
9	79.16
11	30.66

After variation of temperature, concentration and pH of t he dye for the purpose of thermodynamic study we started st udying the kinetic of the adsorption of dye over activated car bon and noted that the adsorption of over the activated carbo n is very fast at the interval of 1-10 min and the amount adsor bed after that start to slow down which may be due to the for mation of second layer or multilayer [10]. The results for the study is give in Table 8.

By employing largergreen equation (5) and plotting the r emained concentration of the dyes with time as given in the F igure 3. From the Figure 3, the value of the rate constant (k) is calculated, k = 2.25 x 10^{-1} sec^{-1} [13], [14].

Table (8) The effect of time variation on the amount of Fluorescien adsorbed to study the kinetic

Time (min)	Percentage of dye adsorbed (%)
2	50.00
4	62.85
6	74.28
8	75.71
10	78.57

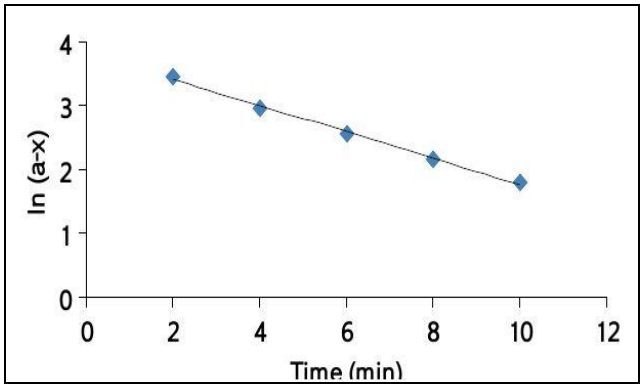


Figure (3): The relationship between ln (a-x) and time

IV. CONCLUSION

Generally, the best temperature for the dyes adsorption is 25°C to give 83.79%. The adsorbed dye below 25°C increase which may be due to the formation of hydrogen bonding and some electrostatic adsorption forces. A fast adsorption of the dye between 10-30 ppm. The dyes adsorption and the conce ntration is 70 ppm to give 93.51%. The thermodynamic para meters are calculated by using equations (2-4). The enthalpy of reaction is calculated from equilibrium constant as shown in Figure 2. The adsorbent amount of Fluorescien decreased with increased pH, as shown in Table 7.

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