Studying thermodynamic and kinetic as for the adsorption of a number of dyes from their aqueous solutions on a new kind of activated carbon prepared by the residues vacuum distillation of air oxidation for Beji asphalt by chemical treatment

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ABSTRACT

This research included the preparation of many samples of the activated carbon by using the residues of vacuum distillation for Beji asphalt as a result of air oxidation, the suitable ratios of the spent lubricant oil added were determined as well as determining the suitable ratios of the anhydrous ferric chloride used as catalyst, in the existence of a fixed ratio of sulfur at one time, and the non-existing of it in other time. And then the oxidized asphalt was treated with different ratios of resinous novolak. Then, an atmospheric and vacuum distillation was done and later on, the distillation residues of the oxidized asphalt were treated as for the samples which gave a higher content of asphalten with different ratios of potassium hydroxide, and thus different kinds of activated carbon prepared. The activity of the prepared carbon-samples activated were determined by measuring its features like (density, content of ash, humidity and measuring its activity towards the adsorption iodine from its aqueous solution as well as using a number of dyes in order to determining the efficiency of adsorption). The efficiency of the prepared carbon samples was tested by making a thermodynamic and kinetic study through using a prepared adsorbent material. This study was done at initial concentrations for the dyes: 2×10^{-4} M, the time of contact was at (5-70 min) and the temperatures were at (15-55 C^0) . The thermodynamic functions were calculated by depending on the results of temperatures effects (ΔG^0, ΔH and ΔS^0), results indicate that the adsorption of dyes under study gets spontaneously and which is exothermic process and has a physical nature. Furthermore, the research contained the application of Freundlich and Langmuir and Tempkin isotherms as for the experimental data for adsorption, and found that the isotherm Freundlich is more applicable. And in a kinetic study that the pseudo first order models, the pseudo second order, Elovich equation and the Intra partical diffusion were also applied on the experimental data for adsorption, the results showed that the adsorption system is subject to the equation pseudo second order.

INTRODUCTION

The activated carbon can be defined as a porosity-solid material which has a large space in its inside and a porosity developing structure, having these features, the activated carbon is regarded as a stuff having high capacity of adsorption for many chemical-gas materials as well as the liquids ones[1].

In the past, the activated carbon was preparing from the coconut shells, definitely, at the beginning of 20th century. But there was increasing demand to have this stuff and due to the insufficient number of coconut shells , it was prepared by other organic materials like stone coal, tar of coal, different kinds of wood, polymers, asphalt materials, and other different stuffs[2].

There is increasing demand for the activated carbon due to the environmental problems, especially in the purification of air and water. The dyes are regarded one of the most important organic compounds that causes water pollution because of their large use in industry, they are used in fabric products, printing, added to oil products, and many other fields. Moreover, looking for cheap adsorbent- materials and to be less poisonous on the environment, this led to using simple and agricultural residues, oil remains, carbonic remanants from the industrial works and the various coefficients to prepare the activated carbon[3].

When review the literatures find many of method and materials that used to prepared activated carbon and the following some of them:

Murakawa[4] and his companions prepared an activated carbon from the residues of vacuum distillation of petroleum and by using sulfur, as it is a carbonizing material, the first carbonization was at the degree 165 C^o for twenty minute, then the carbonization process finished with higher temperature, the sample was activating at 950C^0 ,till the equilibrium of weight and the adsorption features for the carbon resulted were studied.

Hamdoon [5] prepared the activated carbon from the residues of vacuum distillation to Al-Gayyara raw petroleum by chemical treatment using the factors(NaOH, KOH, LiOH, Na$_3$PO$_4$, CH3COONa, Na$_2$CO$_3$) and at the temperatures (550±25)C^o.

Also, Hamdoon[6] prepared an activated carbon from Beji asphalt by using Condensation-oxidation process through passing a current of air, in the finding of different ratios of ortho phosphoric acid between the weight (5-20)%. Then, the activated carbon was prepared through chemical activation by increasing potassium hydroxide at (550±50) C^0 for 3 hours, this sort of activated carbon gave good adsorption characteristics.

Al-Dubooni[7] and his groups tackled the preparation of an activated carbon from Al-Gayyaara asphalt where the asphalt was modified by many ways contained other catalystion treatments with many polymers to change its own chemical structure, after that, this asphalt was carbonized by two ways, first by heating treatments of sulfur and second by heating treatment of H$_2$SO$_4$ where the difference in adsorptive features of carbon was in relation to the difference of the chemical structure of the primary material which it was prepared by. Also it was noticed difference in these features due to the differentiation-way of the followed carbonization which used in the course of fixing the kind of material under treatment.

In addition, in a kinetic and thermodynamic study, Sutue[8] and his groups studied the adsorption of one of the dyes which is di-azo ,so called Brilliant Red HE-3B from its aqueous solutions, specifically on one of the commercial activated carbon. So, he studied the effect of the pH, initial concentration, temperature degree, as well as the effect of the time contact. Furthermore, he applied Freundlich and Langmuir models on the experimental data for adsorption at the equilibrium and the equation of the pseudo first order and pseudo second order. The kinetic analysis of data got showed experimentally that the pseudo second order model was more suitable for the system under study.

Acar[9] and his groups handled the possibility of choosing the activated carbon powder and the flying ash of the fly Turkey's remainders to the adsorption of the dye(Reactive Blacks), which is a di-azo dye from its aqueous solution and he studied the effect of the initial concentration and the quantity of adsorbent material on the efficiency of adsorption , he used Langmuir and Freundlich isotherm to the experimental data of the adsorption system at the equilibrium, later on, the data were analyzed kinetic by using two models of the pseudo first order- equation and the pseudo second order; the findings showed that the efficiency and capacity of adsorption differentiate much between the activated carbon and the flying ash as for the fly Turkey, the first one was(58.823mg/g) that was more efficient and capacity than the second which was (7.936mg/g), also it was found that the pseudo second order equation was more suitable for the adsorption system.

Kandah [10] and his team could prepare an activated carbon from changing the cheap and very available asphalt by chemical treatment with H$_2$SO$_4$ and HNO$_3$ acids at 450 C^o. The final product had a good capacity-adsorption 191..2 meq/100g and the activated carbon prepared was used as a positive ion- exchanging.

Othman[11] enabled to prepare a granulose activated carbon having good quality from Beji asphalt by mixing 15% weight of the concentrated H$_2$SO$_4$. The ratio of the total production was 80% of the raw material used. The carbon got had a superficial space and by a penetrability of air, totally was 4605m^2/g , the iodine number: 960mg/g, the content of ash was up to a maximum of 5.3%, the solidity No. 99%, the density: 0.604g/cm^3, and a voluminous activity 582.9mg/L, these features make this prepared activated carbon appropriate for process-treatments of the residues and other uses.

Furthermore, Hata[12] and his group prepared an activated carbon from resinous phenol by activating potassium hydroxide and the heating by using the microwave, thus, an activated carbon was got, having a large superficial area (1700m^2/g).

Al-Ra'hoo[13] made use of the polymers residues in increasing the asphalt content of the spent Lubricant Oils by using two catalyst treatments and air oxidation and then, preparing an activated carbon by means of chemical treatment; later on, he measured the activity of the prepared samples and studying their efficiency in returning the raw material in which it was prepared; the results were excellent in this regard.

Ambursa[14] and his companions made an activated carbon from asphalt and made attempts to compare the efficiency of the carbon adsorption prepared with the commercial one(Calgon carbonF-300) as for the adsorption Zn^{+2}, Cr^{+6}, Pb^{+2} of adsorption related to the human excrements waters(health drainage) and he applied Freundlich and Langmuir isotherm so as to analyzing the adsorption efficiency. The findings showed that the activated carbon was more efficient than the commercial carbon. Thus, there has been possibility of using the asphalt(remains of refinement) to remove Zn^{+2}, Cr^{+6}, Pb^{+2} as for drainage of human excrements waters.

Jayaraj[15] and his group prepared an activated carbon from marine algae which are treated with the concentrated H_2SO_4 and used in removal the dye: Congo Red from its aqueous solution. It was studied thermodynamically to see the effect of the adsorbent- material dosage, the pH and the time of contact). The results showed that the adsorption reached the equilibrium in 180 minutes for both concentrations 5 up to 25 mg/L for dye and Freundlich and Langmuir isotherms were applied; the results indicated that Freundlich ones were more applicable where the correlation coefficient was about (R^2=0.6992-0.8460) at the concentration 60 mg/L for the dye, the efficiency of adsorption was 97.77% and it increased during the increasing of the acid function i.e. pH= 1-5.

Dim[16] studied the adsorption of the two dyes (methyl red, methyl orange) by using tree bark powder(LBP), Mongo tree bark powder (MBP), Neem bean tree bark powder (NBP), locust bean. He studied the effect of dosage and the level of acidity, it appeared that the efficiency of adsorption dyes were increasing when the dosage was increasing. He experimented Langmuir isotherm and applied on the data got, moreover, these materials can be used to clean the wastes of textiles and spin.

Okeola[17] and his group enabled to remove the dye (Congo Red) from the waters of industrial drainage by the activated carbon- adsorption, specifically from that carbon prepared from the seeds Thevetia Peruvianna. Also he studied the effect of the pH, dosage, and the concentration of dye. He used the batch way in a constant temperature $30C^o$ by using an electric shaker 100rpm. The results showed that the dye adsorption was increasing when the quantity of the adsorbent-material increased; the ideal acidity degree was pH= 7. The kinetic study conducted that the pseudo second order equation was the best. He tested Freundlich and Langmuir isotherm and he found out Freundlich isotherm was the best.

Fuma[18] and his team studied the adsorption dye of Methyl Orange (MO) from its water compound by using the Kaolinite (KAO), the activated Methakaolinite (MK), activated geopolymer(GEO-7) and he studied the effect of the dosage, time contact,pH, and the initial concentration of the dye. He found out that the time contact reaches the equilibrium condition in 15 minutes as to (GEO-7 and KAO) and 10 minutes to (MK); the best adsorption was at pH=2.5, he applied Freundlich and Langmuir model and found out the latter was more applicable in to Langmuir and pseudo second order equation where R^2= 0.999, two model Elovich and the Intra particle diffusion.

Jalilov[19] and his companions enabled to prepare an activated carbon by asphalt carbonization through potassium hydroxide (KOH), the temperature was at(>600 C^o) the superficial area for this prepared activated carbon was $2780m^2$/g, it pumps Co_2 of 21%wt at $25C^o$, adding the nitrogen 9.3% and the superficial area increases when CO_2 increases as well.

EXPERIMENTAL PART

1.1: Air Oxidation of Beji Asphalt

The device used in the air oxidation process consists of round flask having threefold heads that the air passes through one of the heads, fixing the thermometer on the other, whereas the condenser is on the last head. A specific weight of raw Beji asphalt was taken and put in the flask mentioned, many activated materials were added to it, i.e. anhydrous $FeCl_3$, fixed ratios of sulfur, different ratios of the spent lubricant oil, and heated in hot ranges (150,200,300)C^o, the air was passed in the speed $120cm^3$/min and the time at (1,2,3) hours. The purpose of the process was to fix the typical conditions for air oxidation operation.

1.1.1: De-Asphalting

All oxidized samples were isolated from Asphalten when 1g of different asphalt samples was put in a glass flask in addition to 40ml of the normal hexane with the ratio (1:40)(weight: volume), shake the solution by using an electric shaking appliance for 3 hours at the temperature (0)C^o, after that, separating the Asphalten through filtering the mixture mentioned, the Asphalten represents the non-melted part (precipitate). After the filtering process, the precipitate is washed of a sufficient quantity of hexane till the washing drops have become colourless, The precipitate was dried at the temperature of room and then the Asphalten percentage was calculated in the oxidized sample[20].

1.1.2: Treatment of Oxidized Asphalt

The oxidized asphalt in the item(1.1) was under the treatments to get the biggest possible carbonized mass to be used in preparing the activated carbon.

1.1.2.1: Treatment of Oxidized with Spent Lubricant Oil

The optimal ratio of spent lubricant oil was determined via changing this oil, the weight of the spent lubricant oil used was (5- 25)% and under the same oxidized conditions showed in the item(1.1). The optimal ratio of the catalyst anhydrous ferric chloride was determined via changing the ratios of this catalyst to have the best samples that were got as to their Asphalten content which used (0.5 - 3%) weight of catalyst.

1.1.2.2: Treatment of Oxidized Asphalt with Novolak Resin
The best samples were tackled according to their asphalten content which resulted from the asphalt oxidation process, the item(2.3.2) with different weighty relations were about (1-4%) weight of resinous novolak at (200)C^o, for (1,2,3) hours and under the same oxidized conditions explained previously.

1.2: Preparation of Activated Carbon
The best samples were taken in terms of Asphalten content and the following distillation processes were done:

1- Atmospheric Distillation
Sample drops(100)g were for the best oxidized sample by using a distillation flask (250)ml, under normal air pressure to remove the biggest number of light particles such as the gases H_2S, RSH and the light oils.

2- Vacuum Distillation
After the procedure of distillation process under the atmospheric pressure, the residues production were distilled under low pressure 20 mm. of mercury, then the residue of the stuff from the distillation process was used in preparing the activated carbon.

1.2.1: The Primary Carbonization
The vacuum distillation residue was put in a steel container resisting the rust and coated by nickel and was mixed with potassium hydroxide of ratios were about[(1:0.5) - (1:3)] [the vacuum distillation residue: KOH] and through increase reached 0.5% weight of the basic per reaction at 350 C^o for 3 hours.

1.2.2: Activation:
The mixture was heated up $(550\pm25)C^o$ for two hours to achieve the activation process. After that, the samples were left to be cold up to the room temperature.

1.2.3: Purification of Activated Carbon
The activated carbon prepared was purified by washing it by distilled water many times, then reflex heat by using 10% of HCl for 2 hours to remove the biggest number of metals as possibly as possible. After that, the sample was filtered and washed by distilled water till the washing water became neutral, then, it was dried in the oven at 120 C^o for 24 hours and was kept in a closed container.

1.3: Conducting some Measuring on Prepared Activated Carbon Samples

1.3.1: Measuring o the Internal Surface Area of Activated Carbon by Adsorption Iodine in its Aqueous Solution
This way is considered one of the familiar and common ways used in calculating the inner superficial area of the activated carbon and it represents the number of iodine milligrams that are under adsorption through the solution by 1gram of the activated carbon. 1gram of the activated carbon was weighed and put in a conic flask has the capacity 250ml and 10ml of 5% HCl; later on, the contents of the flask were heated up to boiling for 30 seconds, then it was cooled up to the laboratory temperature, then, added (100)ml iodine solution, 0.1N. The mixture was shook for half hour, after that, it was filtered and 20ml left at the beginning of the filtering process, 50ml was collected to be standardized with 0.1 N solution of aqueous sodium thiosulfate and by using starch as proof and according to the quantity of sodium thiosulfate used through the burette. Later on, the weight of iodine adsorption from the activated carbon was calculated via applying the following equation[21] :

X=A-[2.2B X ml of Thiosulfate Used] ……..(1)

A=N_1 X 12693 ……..(2)   B=N_2 X 126.93 ……..(3)

X: represents the iodine weight by adsorption mg. via the activated carbon.
N_1: the standardization of iodine solution (0.1 N).
N_2: the standardization of sodium thiosulfate.

Whereas the iodine No. can be calculated by the following equation:

$$In = \frac{X}{M} D \;...........(4)$$

    M: the weight of the activated carbon sample that is used.
    D: correction factor.

1.3.2: Measuring the Density

A specific quantity of the activated carbon was put in a voluminous bottle, its capacity 5 ml. which the carbon activated occupying its volume taking into account some minutes in one level at the symbol boundary, then, the carbon found in that voluminous bottle by using a sensitive scales and the density was calculated as follows[22] :

$$Density(g/cm^3) = mass/volume$$

1.3.3: Measuring of Ash Content Percentage

1g of the activated carbon was weighed and put in a dish evaporating which was put in an electric oven at 1000 C^o for 3 hours, then it was left to be cooled, after that it was weighed by a sensitive scales to calculate the ash residues for every sample of the activated carbon prepared; later on, the percentage rate of the ash was calculated in every sample.[23]

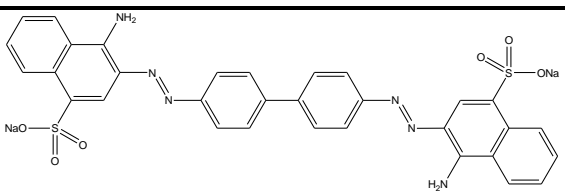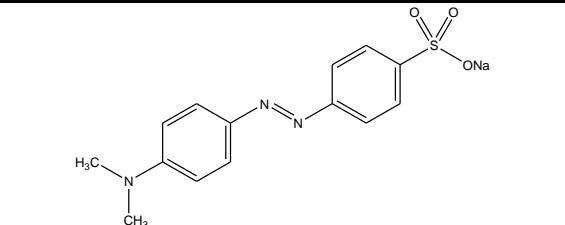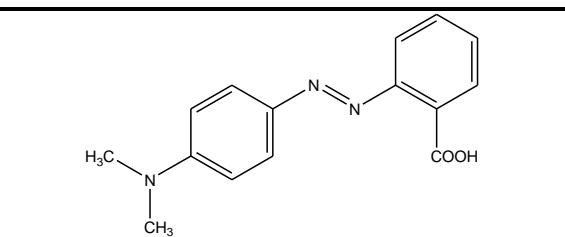### 1.3.4: Measuring of Humidity Percentage

1g of the sample was weighed accurately and put in an oven whose temperature was 150C^o for 3 hours, then, it was cooled and weighed accurately and quickly; making differentiations between weights, the humidity content was measured in the form of percentage rate.

1.4: Study of Optimum Conditions for Adsorption

This part consisted of studying the favorable conditions for adsorption of the dyes as for the concentrations range used in the material which was under adsorption, the quantity of the adsorption-material, the effect of time contact in reaching the adsorption of the equilibrium condition, and the effect both of the concentration and temperature on the adsorption dyes.

The Used Dyes

Table (1): represents the names of the used dyes and some of their physical characteristics as well as the values λ_{max} of it

Dye name	Structural form	Color	Malting point (C^o)	λ_{max} (nm)
Congo Red (CR)		Red	360>	497
Methyl Orange (MO)		Orange	>300	507
Methyl Red (MR)		Dark Red	179-182	410

1.4.1: Preparing the Standard Solutions

A standard solution for all dyes was prepared by the concentrations (10^{-3} M) within a mixture of ethanol-water 50% by solubility a specific weight of dye in a limited quantity of ethanol (50ml), it was diluanted by distilled water up to (100ml). The wavelength was measured of maximum absorption (λ_{max}) for the dyes by means of using the same ratio of ethanol and distilled water as reference solution(Blank).

1.4.2: Effect of Dose on Adsorption Capacity

A specific weights of the activated carbon prepared were taken and they were about (0.01-0.04g) in the volume(20ml), and the concentration was(2×10^{-4}M). It was found that the best quantity used was 0.01g (the dose: 0.5g/L), it is worth mentioning that this quantity of the activated carbon was used in the later study.

1.4.3: Limiting the Equilibrium Time for Adsorption System

Nine solutions having equal volumes and concentrations(2×10^{-4}M) were prepared, also these solutions had the same quantity of the activated carbon prepared and at constant temperature; after the continuous shaking, the nine solutions were filtered and by different times (5, 10, 15, 20, 30, 40, 50, 60, 70) minutes respectively; the adsorption quantities were estimated by means of using the spectrum way. A calibration curve was executed on each material, at maximum wavelength(λ_{max}) and within the range of concentrations. The adsorption on the special wavelength for each material was followed up. The results showed that getting adsorption time up to the equilibrium condition in all conditions was about(60-70) minutes.

1.4.4: Effect of Concentration

The effect of concentration on the adsorption was investigated according to the following steps:

1- Four solutions having equal volumes were prepared of each dye, by different concentrations, and by the range (1×10^{-4} - 5×10^{-4})M. Also, the same quantity of the activated carbon (0.01g) was added to each solution.
2- The solutions were shaken for (70) minutes by the shaker and then, they were filtered.
3- The percentage rate of adsorption was estimated by using the spectrum way and by the calibration curve for each material. The percentage rate of adsorption was calculated by the following equation:

$$\%ads = \frac{C_{ads}}{C_i} \times 100 \quad \dots (5)$$

C_{ads} : the concentration of the adsorbate-material(mg/L)

C_i : The initial concentration(mg/L)

1.4.5: Effect of Temperature

The effect of temperature was studied on the adsorption by applying the following steps:

1- After specifying the concentration which has triggered at higher adsorption rate, it was selected to prepare five solutions consisting of the same concentrations of the solutions dyes and the same quantity of the activated carbon.
2- The solutions were shaken separately for(70) minutes and at temperatures (15, 25, 35, 45, 55) C° respectively, by using the shaker which has water bath inside(programmed) that its temperature was run exactly.
3- The solutions were filtered, The absorption values were recorded , and the capacity of spectrum adsorption was estimated by using the following equation:

$$q_e = \frac{C_i - C_e}{m} \times V \quad \dots (6)$$

q_e : represents the adsorption capacity at the equilibrium (mg/L)

C_i : represents the initial concentration of the dye(mg/L)

C_e : represents the concentration of the dye's rest in the solution at the equilibrium

m: the weight of the adsorbent material(activated carbon) (gm)

V: the volume solution used in estimating the adsorption(L)

1.4.6: Calculating the Thermodynamic Functions

The values of the equilibrium constant for adsorption (K) at different temperatures in the equilibrium condition were calculated as for the ratio between the adsorbate concentration and the residues of the concentration for the dye solution, whereas the values of the thermodynamic functions of the equilibrium (ΔG^o, ΔH, ΔS^o) were calculated by using equations. The adsorption enthalpy can be calculated by applying Vant Hoff equation which represents the relation between the equilibrium constant and temperature.

$$K = K_0 e^{-\Delta H / RT} \quad \dots(7)$$

Where (ΔH) represents the adsorption temperature (adsorption enthalpy), (K) is the adsorption-equilibrium constant, whereas (k_o) represents a constant value. By taking the ln for both sides, we can get on the following form of the equation:

$$\ln K = \ln K_0 - \frac{\Delta H}{RT} \quad \ldots\ldots\ldots(8)$$

The value (ΔH) can be calculated by drawing the relation between ($\ln K$) in opposite to the reversed temperature (l/T) which gives a straight line whose slop is equal to $-\Delta H/R$. The other thermodynamic functions (ΔG^o, ΔS^o) can be calculated by the following equations:

$$\Delta G^0 = -RT \ln K \ldots\ldots(9)$$
$$\Delta G^0 = \Delta H - T\Delta S^0 \ldots\ldots\ldots(10)$$
$$\Delta S^0 = (\Delta H - \Delta G^0)/T \ldots\ldots\ldots(11)$$

1.4.7: Applying Freundlich, Langmuir & Tempkin Isotherms on the Adsorption of Dyes with the Activated Carbon

The values of Freundlich constants(K_f , n) were calculated from drawing the relation between the value $\log q_e$, $\log C_e$ according to the following equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad \ldots\ldots\ldots(12)$$

q_e represents the adsorption capacity at the equilibrium(mg/g), C_e is the concentration of the dye remainder in the solution during the equilibrium (mg/L), K_f , n are Freundlich constants, The value of n has a relation to the adsorption intensity and its value indicating to the favorable adsorption when it becomes within the range (1-10), but it refers to the chemical adsorption when its value is less than 1. Whereas the value of K_f has a relation to the adsorption capacity[25].

By the same way, Langmuir constants(b) were calculated as well as the maximum capacity of adsorption from drawing the relation between C_e/q_e in opposite to C_e and according to the following equation[26]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad \ldots\ldots\ldots(13)$$

Q_{max} represents the value of maximum theoretical adsorption capacity for the adsorbent(mg/L), whereas b represent a constant having a relation to the correlation strength of the dye through the adsorption surface.

Similarly, Tempkin constants (K_T, B_T) were calculated from drawing the relation between the value q_e in opposite to $\ln C_e$ according to the following equation:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad \ldots\ldots\ldots(14)$$

B_T is referring to a constant having a relation to the differential capacity surface as to adsorption capacity for each power unit of link, whereas K_T (L/mg) represents a linkage constant of equilibrium and it indicates to the maximum linkage energy.[27]

1.4.8: Kinetic Study Adsorption
1.4.8.1: The Application of Pseudo First Order Equation and the Pseudo Second Order Equation

Pseudo first order equation[28,29]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \ldots\ldots\ldots(15)$$

Pseudo-second order equation[30,31]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots\ldots\ldots(16)$$

1.4.8.2: The Application of Elovich Equation and the Equation of Intra Particle Diffusion

The sample of the kinetic Elovich equation was experimented on the process data for dyes adsorption on the activated carbon prepared and under the conditions mentioned previously through drawing the relation between the adsorption capacity at specific times(q_t) in opposite to $\ln t$ and in terms of the following equation[32]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad \ldots\ldots\ldots(17)$$

α represents the rate of the initially adsorption speed (mg. g^{-1}, min^{-1}) and β represents the adsorption constant (g. mg^{-1}) through any one test. Similarly, the equation of intra particle diffusion was applied on the process data, by drawing the relation between the adsorption capacity at different times (q_t mg/g) in opposite to($t^{1/2}$), and from the linear relation

that was got is possible to calculate C(mg. g^{-1}) of the straight line section which has a relation to the layer thickness-limit of the liquid which is next to the solid surface (mg/g), has **k$_{diff}$** (mg/g.min$^{1/2}$) in, which represents the velocity of the intra particle diffusion and according to the following equation.[33]

$$q_t = K_{diff} \ t^{1/2} + C \quad \text{........(18)}$$

RESULTS AND DISCUSSION

The following schedule was put to illustrate the main and branch points that were dependent to fulfill the study so as to showing the work steps by an explanatory style and related results got to make harmonizing and obvious discussion. The beginning was from the materials used and the end was about studying the activated carbon prepared (its features) and comparing it to the commercial activated carbon as follows:
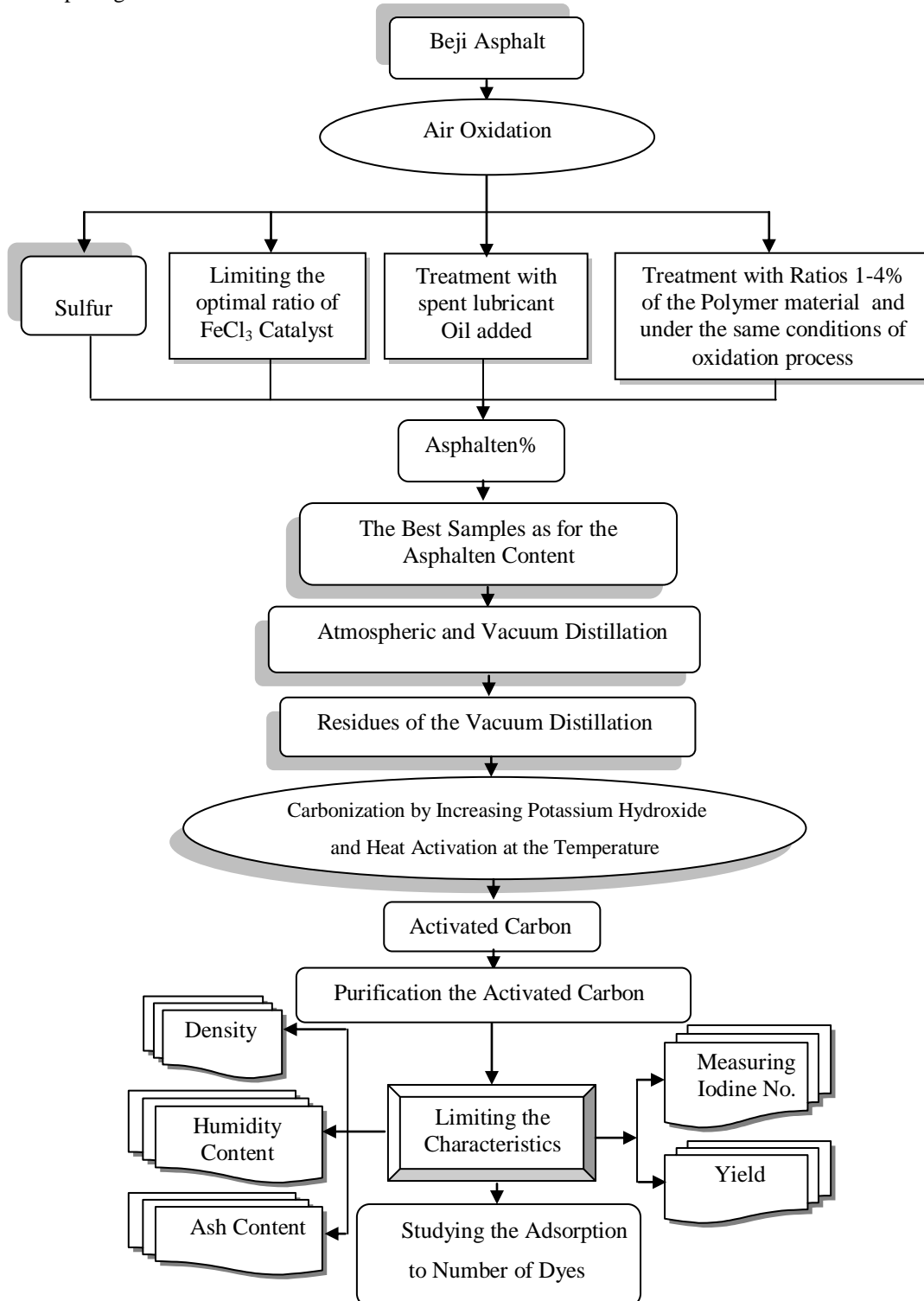

Fig. (1): A schedule for the Main and Branch operations that contents in this study

1: Treatment of Oxidized with Spent Lubricant Oil

To increase the Asphalten content for Beji asphalt, different ratios of the spent lubricant oil were added and were about (5-25)% weight as the spent lubricant oil is changing to Asphalten in the course of its air oxidation, furthermore, the typical ratios of the spent lubricant oil added were determined as well as the typical ratio of the anhydrous ferric chloride catalyst was determined, by the existence of sulfur in one time and the non existence in other, as in the following table:

Table (2): The percentage rate of the Asphalten, that is produced by the air oxidation of Beji asphalt at different temperatures, times, in addition to different ratios of the spent lubricant oil, catalyst, and sulfur

Sample	Time hr.	Spent lubricant oil %	sulfur %	Fecl₃ %	Temp. C⁰	Asphalten %
A	-	-	-	-	-	21.00
1	1hr	5	-	1	150	21.72
2	2hr	5	-	1	150	21.93
3	3hr	5	-	1	150	23.05
4	1hr	5	-	1	200	25.83
5	2hr	5	-	1	200	29.06
6	3hr	5	-	1	200	28.22
7	1hr	10	-	1	200	29.31
8	2hr	10	-	1	200	31.74
9	3hr	10	-	1	200	30.26
10	1hr	15	-	1	200	32.55
11	2hr	15	-	1	200	33.4
12	3hr	15	-	1	200	34.14
13	1hr	20	-	0.5	200	33.92
14	2hr	20	-	0.5	200	34.16
15	3hr	20	-	0.5	200	34.07
16	1hr	20	-	1	200	33.06
17	2hr	20	-	1	200	32.49
18	3hr	20	-	1	200	34.78
19	1hr	20	-	2	200	31.79
20	2hr	20	-	2	200	36.81
21	3hr	20	-	2	200	40.92
22	1hr	20	-	3	200	31.22
23	2hr	20	-	3	200	32.17
24	3hr	20	-	3	200	30.80
25	1hr	25	-	1	200	33.75
26	2hr	25	-	1	200	34.08
27	3hr	25	-	1	200	34.27
28	1hr	5	-	1	300	26.53
29	2hr	5	-	1	300	29.97
30	3hr	5	-	1	300	28.62
31	1hr	5	1	1	150	22.14
32	2hr	5	1	1	150	24.73
33	3hr	5	1	1	150	27.01
34	1hr	10	1	1	150	29.02
35	2hr	10	1	1	150	33.14
36	3hr	10	1	1	150	34.21

37	1hr	5	1	1	200	29.33
38	2hr	5	1	1	200	29.94
39	3hr	5	1	1	200	30.12
40	1hr	10	1	1	200	30.88
41	2hr	10	1	1	200	33.06
42	3hr	10	1	1	200	33.24
43	1hr	15	1	1	200	31.66
44	2hr	15	1	1	200	34.37
45	3hr	15	1	1	200	38.67
46	1hr	20	1	1	200	41.13
47	2hr	20	1	1	200	46.96
48	3hr	20	1	1	200	45.71
49	1hr	25	1	0.5	200	47.21
50	2hr	25	1	0.5	200	41.93
51	3hr	25	1	0.5	200	42.80
52	1hr	25	1	1	200	44.97
53	2hr	25	1	1	200	45.57
54	3hr	25	1	1	200	45.22
55	1hr	25	1	2	200	45.43
56	2hr	25	1	2	200	46.57
57	3hr	25	1	2	200	47.31
58	1hr	25	1	3	200	38.52
59	2hr	25	1	3	200	39.95
60	3hr	25	1	3	200	45.79
61	1hr	5	1	1	300	30.27
62	2hr	5	1	1	300	32.14
63	3hr	5	1	1	300	31.98

A: percentage of Asphalten from original Asphalt

The aim of executing the heat catalyzing and oxidizing treatments as in the table above is to have a primary material of high Asphalten content to got a primary material to suitable a prepare activated carbon, as how know increasing Asphalten content leading to increasing of the yield activated carbon prepared , so, this is a positive side with regard to the commercial and industrial sectors. The sample No. (21) and No. (53) were selected to prepare the activated carbon to be reinforced of high rate of Asphalten. We could notice of the table that the sample having the sulfur in, gave higher rate of Asphalten due to the hydrogen removal-process as well as the other reactions as a result of ferric chloride use.

2: Preparing The Activated Carbon
The residues of the vacuum distillation were under carbonization by using potassium hydroxide with ratios were about [(1:0.5)-(1:3)] weight. The two tables (3) and (4) are showing the features of activated carbon prepared.

Table (3) : The features of activated carbon prepared by the residues of vacuum distillation of air oxidation for Beji asphalt at 200C°, there was 20% spent lubricant oil and (2%) weight FeCl₃, the time: 3 hours

Samples	Vacuum Residues : KOH	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
C_n	1:0	465.070	0.397	1.07	1.10	29.790
1	1:0.5	501.374	0.348	1.42	1.17	27.901
2	1:1	615.864	0.307	1.79	3.28	24.735
3	1:1.5	825.299	0.298	2.40	3.75	23.560
4	1:2	920.240	0.288	3.12	4.25	21.083

5	1:2.5	811.337	0.302	3.37	3.51	18.712
6	1:3	797.375	0.308	4.15	3.27	16.475
B.D.H[*]	-	908	0.345	3.200	0.80	-

C_n : Activated Carbon prepared from Residues vacuum distillation without treatment with base.

B.D.H[*] : Commercial activated carbon. We can notice from the table above that increasing the basic added leads to the increasing in the values of iodine adsorption from its solution up to the ratio (1:2), then, it begins at lowering because of the hydroxide increasing leads to breaking part of the gaps and the forming pores at the rate (1:3). Also, we can notice of the table that the ash content increases in course of the increase in the basic, this indicates that there was a simple corrosion in the reactions which have no rust. As for the values of humidity content, there were about (1.10-4.25)% and it was a relative measurement. It shows the possibility of using the prepared samples in the adsorption vapour water process.

As far as the values yield , they were about (16.475- 29.790)%, those values were calculated from the oxidized asphalt before fulfilling the distillation processes, both of their types. We can notice that the yield decreases when the potassium hydroxide added increases, this is self-evident as the increase of the basic added leading to the increase in the rate of loss as for the carbon content for the primary material, thus, the yield decreases. Whereas the density values were about (0.308 - 0.397)g/cm^3, they were low values and it was proved that the density values decreases in the course of the increase in the iodine No.

Table (4): The features of the activated carbon prepared by the residues of the vacuum distillation of air oxidation for Beji asphalt at 200C^o, the existence 25% of the spent lubricant oil, (1%) weight FeCl$_3$, 1% Sulfur and the time:2hours.

Samples	Vacuum Residues : KOH	Iodine number (mg/g)	Density (g/cm^3)	Ash content %	Humidity content %	Yield %
C_n	1:0	632.60	0.342	2.58	1.67	48.512
7	1:0.5	682.884	0.324	2.03	2.34	45.301
8	1:1	839.262	0.307	2.17	3.91	39.829
9	1:1.5	976.092	0.254	3.25	5.31	38.057
10	1:2	1029.149	0.248	3.59	8.72	36.951
11	1:2.5	1004.017	0.278	2.95	7.91	30.731
12	1:3	990.054	0.280	3.72	6.21	25.182
B.D.H[*]	-	908	0.345	3.200	0.80	-

The two tables show that the best activation rate is (1:2) as it gives the highest iodine No.

Using the potassium hydroxide is regarded as a significant factor in the activation process which is working on developing the minute pore structure for the primary material used in the activated carbon production. The process of using H_2SO_4 and even the sulfur in the activated carbon production needs an activation process after the carbonization procedure ,because H_2SO_4 is a dried stuff draws water gradually, or the tar stuff is going by and leaving the carbon, while the sulfur works on removing the hydrogen out of the stuff, in form of H_2S as opposed to the alkaline hydroxide which works on causing a shortcoming in the crystal pavement and forming pores in the activation carbon. The following reactions happen in the case of the primary material used in preparing the activation carbon contains the sulfur in its structure:[34]

$$2Na^+ + N_2 + 3O_2 \rightarrow 2NaNO_3 \xrightarrow{300C^o} Na_2O + NO_2$$
$$\downarrow S$$
$$Na_2SO_4 \leftarrow NaS + SO_2 + O_2$$
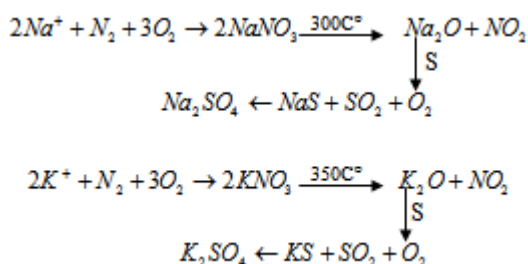
In this research when used KOH, the following reactions happened of the primary material.

$$2K^+ + N_2 + 3O_2 \rightarrow 2KNO_3 \xrightarrow{350C^o} K_2O + NO_2$$
$$\downarrow S$$
$$K_2SO_4 \leftarrow KS + SO_2 + O_2$$

3: Treating the Oxidized Asphalt with the Resinous Novolak

The best samples were treated through its Asphalten content with different weighty ratios were about (1-4)% of resinous novolak as it is showing in the table[5].

Table (5): The percentage rates of Asphalten after treating the asphalt with different ratios of resinous novolak by the air oxidation process.

Sample	Time hr.	Spent lubricant oil %	Sulfur %	Fecl₃ %	Novolak resin wt%	Temp. C⁰	Asphalten %
64	1hr	20	-	2	1	200	31.82
65	2hr	20	-	2	1	200	37.04
66	3hr	20	-	2	1	200	41.25
67	1hr	20	-	2	2	200	32.08
68	2hr	20	-	2	2	200	38.16
69	3hr	20	-	2	2	200	43.72
70	1hr	20	-	2	3	200	34.29
71	2hr	20	-	2	3	200	39.50
72	3hr	20	-	2	3	200	53.26
73	1hr	20	-	2	4	200	36.18
74	2hr	20	-	2	4	200	44.27
75	3hr	20	-	2	4	200	68.35
76	1hr	25	1	1	1	200	45.23
77	2hr	25	1	1	1	200	54.12
78	3hr	25	1	1	1	200	50.75
79	1hr	25	1	1	2	200	47.01
80	2hr	25	1	1	2	200	60.24
81	3hr	25	1	1	2	200	52.06
82	1hr	25	1	1	3	200	53.37
83	2hr	25	1	1	3	200	78.05
84	3hr	25	1	1	3	200	54.98
85	1hr	25	1	1	4	200	54.18
86	2hr	25	1	1	4	200	66.31
87	3hr	25	1	1	4	200	48.03

We notice from the table above that the increase in resinous novolak quantity from 1 to 4 %, fixing the temperature and increasing the time lead to increasing the Asphalten formed, the highest ratios were at (4)% of resinous novolak and the reaction time was 3 hours which reached (68.35)% as it was seen in the sample No.(75), i.e. the created functional groups have become of the reaction and growth till the time was over at highest rate, Also, it was noticed of the table above that the highest rate was at (3)% of resinous novolak , the time of reaction was (2) hours which reached (78.05)% as it was shown in the sample No.(83), where the created functional groups have reacted for a period of time and the structured formula starting with degeneration in the course of the increasing of the polymer compound added, this indicates that the formed Asphalten compounds were unstable. The samples No.(75) and No.(83) were selected to prepare the activated carbon, they can be carbonation by potassium hydroxide of the ratio(1:2) -which is the best- as it was illustrated previously and according to the following table:

Table (6): The characteristics of the activated carbon prepared.

Samples	Novolak resin %	Iodine number (mg/g)	Density (g/cm³)	Ash content %	Humidity content %	Yield %
13	4	1031.941	0.231	3.60	8.43	27.034
14	3	1059.866	0.224	4.76	9.24	40.720
B.D.H*	-	908	0.345	3.200	0.80	-

It can be observed from the table above that using the resinous novolak has improved the activated carbon susceptibility for adsorption. The following table appears the activated carbon prepared samples which have been chosen to act the adsorption of the dyes under study.

Table (7): Samples of the activated carbon prepared chosen for the study, depending on giving them the highest iodine number

Sample	Type Active carbon prepared	Code briefly	Iodine number (mg/g)	pH V:V Ethanol : Distillation Water %50
4	activated carbon prepared by the residues of vacuum distillation for oxidation asphalt with 20% spent lubricant oil and 2% $FeCl_3$ by using (1:2) (Vacuum Resides:KOH)	ACRO20	920.240	5.51
10	activated carbon prepared by the residues of vacuum distillation for oxidation asphalt with 25% spent lubricant oil and 1% $FeCl_3$ 1% S by using (1:2) (Vacuum Resides:KOH)	ACRO25	1029.149	5.93
13	activated carbon prepared by the residues of vacuum distillation for oxidation asphalt with 20% spent lubricant oil and 2% $FeCl_3$ 4% novolak resin by using (1:2) (Vacuum Resides:KOH)	ACRN4	1031.941	6.82
14	activated carbon prepared by the residues of vacuum distillation for oxidation asphalt with 25% spent lubricant oil and 1% $FeCl_3$ 1% S 3% novolak resin by using (1:2) (Vacuum Resides:KOH)	ACRN3	1059.866	7.35

To follow up this study at spectrum way, it is necessary to find the values(λ_{max}) for these dyes, then making a calibration curve for each dye and within the range of concentration which is compatible to the colour intensity of these dyes. The calibration curves were achieved by depending on Lambert Beer's law which can be expressed by the following equation:

........(19) $A = \varepsilon LC$

A: represents the absorption of the dye, ε : the factor of the absorbance molar (Liter.mol^{-1}.cm^{-1}), L: the length of the light line for the visible rays (L=1 cm), and C: the molar concentration (mol.Liter^{-1}). The selected dyes in this study showed that they were suitable to Lambert Beer's law represented by linear relations which were got by drawing the absorbance relation (A) in front of the concentration.

1: Effect of adsorbent dose

Studying the Effect of the adsorbent on Adsorption the dyes (CR, MO, MR) and at different initial concentrations at 139.332, 65.466 and 53.86 mg/L respectively, with changing the adsorbent dose within the range 0.5-2.0 g/L. These experiments were achieved at 25 C^{o} and the results which were got, were listed in the following table:

Table (8): The effect of the activated carbon quantity on the adsorption capacity at 25 C^{o} and an initial concentration (2×10^{-4} M)

Type Active carbon prepared	Dye	Dose (gm/L)	C_i mg/L	C_e mg/L	q_e mg/g	%ads.
ACRO20	CR	0.5	139.332	23.686	231.292	83.00
		1.0		21.596	117.736	84.50
		1.5		13.933	83.599	90.00
		2.0		5.573	66.879	96.00
	MO	0.5	65.466	12.438	106.056	81.00
		1.0		9.492	55.974	85.50
		1.5		6.873	39.062	89.50
		2.0		4.582	30.442	93.00
	MR	0.5	53.86	12.926	81.868	76.00
		1.0		10.502	43.358	80.50
		1.5		7.809	30.700	85.50
		2.0		5.655	24.102	89.50

ACRO25	CR	0.5	139.332	15.326	248.012	89.00
		1.0		13.933	125.399	90.00
		1.5		11.843	84.992	91.50
		2.0		5.573	66.879	96.00
	MO	0.5	65.466	11.456	108.02	82.50
		1.0		9.819	55.647	85.00
		1.5		5.891	39.716	91.00
		2.0		4.909	30.278	92.50
	MR	0.5	53.86	11.849	84.022	78.00
		1.0		8.617	45.243	84.00
		1.5		7.001	31.239	87.00
		2.0		4.847	24.506	91.00
ACRN4	CR	0.5	139.332	14.629	249.406	89.50
		1.0		8.359	130.973	94.00
		1.5		7.663	87.779	94.50
		2.0		5.573	66.879	96.00
	MO	0.5	65.466	8.510	113.912	87.00
		1.0		7.855	57.611	88.00
		1.5		6.546	39.28	90.00
		2.0		5.564	29.951	91.50
	MR	0.5	53.86	9.964	87.792	81.50
		1.0		7.271	46.589	86.50
		1.5		4.847	32.675	91.00
		2.0		4.308	24.778	92.00
ACRN3	CR	0.5	139.332	11.146	256.372	92.00
		1.0		10.449	128.883	92.50
		1.5		5.573	89.172	96.00
		2.0		4.179	67.576	97.00
	MO	0.5	65.466	6.219	118.494	90.50
		1.0		5.891	59.575	91.00
		1.5		4.255	40.807	93.50
		2.0		3.927	30.769	94.00
	MR	0.5	53.86	8.079	91.562	85
		1.0		7.540	46.32	86.00
		1.5		6.463	31.598	88.00
		2.0		5.924	23.968	89.00

Noticing the table above, we find that the adsorption capacity, its value decreases when the used quantity of the adsorbent dose increases; this differentiation in the adsorption capacity relation and its efficiency with changing of the adsorbent quantity can be explained by the following: It is obvious that as soon as the quantity of the adsorbent increases, the number of qualified locations of the adsorption is going to increase, this increase reinforces the efficiency of adsorbent to remove the dyes from the aqueous solution. But this causes deficiency as for the adsorption capacity in the course of calculating it mathematically, where the adsorbate material is expressed for each mass unit of the adsorbent material(mg/g), the increasing of the adsorbent material quantity will leave active locations for adsorption, empty when there is a constant concentration of the absorbate material. The results got are compatible to other ones observed in alike studies in the literature, when they were explained by two different view points; the first is that the lack of the adsorption capacity with the increasing of absorbent material quantity was due to the slowness and non-saturation of the activated locations for adsorption in the course of the adsorption process.[35, 33]

In the second view, the researchers argued that the reason behind this change is possibly to create intra particle intersections between the molecules of the adsorbent material. Because of these intersections, the increase in the adsorbent material quantity leading to collapsing it, thus, the whole superficial area of the adsorbent material decreases and this leading to the increase of the spreading paths length of the adsorbate molecules through it.[36]

2: Effect of contact time

The time contact is regarded one of the most important variables which can be used to assess the information as for the experimental application for the adsorption process, particularly in the kinetic study. This study was achieved by fixing

all the variables which react on the adsorption process except the time. The time effect was calculated at an initial concentration 2×10^{-4}M for the dyes, and by shaking a specific volume of dye solution (20 ml) and by using a constant quantity of the activated carbon (0.01g) at temperature 25 C^{o}. The results got were listed in the following table:

Table (9): The effect of the time contact on the capacity adsorption at 25 C^{o}, initial concentration 2×10^{-4}M, the speed of shaking: 100 circle/min and the volume of dye solution: 20ml.

Type Active carbon prepared	Dye	Time (min)	C_i mg/L	C_t mg/L	q_t mg/g	%ads.
ACRO20	CR	5	139.332	69.666	139.332	50
		10		65.486	147.692	53.00
		15		60.609	157.446	56.50
		20		50.159	178.346	64.00
		30		36.922	204.820	73.50
		40		35.529	207.606	74.50
		50		24.383	229.898	82.50
		60		23.686	231.292	83.00
		70		23.686	231.292	83.00
	MO	5	65.466	39.279	52.374	40.00
		10		36.006	58.92	45.00
		15		32.733	65.466	50
		20		31.096	68.74	52.50
		30		23.240	84.452	64.50
		40		16.366	98.200	75.00
		50		14.025	102.882	78.57
		60		12.438	106.056	81.00
		70		12.438	106.056	81.00
	MR	5	53.86	37.702	32.316	30
		10		29.623	48.474	45
		15		26.93	53.86	50
		20		20.466	66.788	62.00
		30		16.965	73.79	68.50
		40		14.542	78.636	73.00
		50		13.734	80.252	74.50
		60		12.926	81.868	76.00
		70		12.657	82.406	76.50
ACRO25	CR	5	139.332	67.576	143.512	51.50
		10		65.486	147.692	53.00
		15		52.946	172.772	62.00
		20		49.462	179.74	64.50
		30		31.349	215.966	77.50
		40		30.653	217.358	78.00
		50		16.719	245.226	88.00
		60		15.326	248.012	89.00
		70		14.629	249.406	89.50
	MO	5	65.466	36.006	58.92	45.00
		10		32.733	65.466	50
		15		31.423	68.086	52.00
		20		27.495	75.942	58.00
		30		22.913	85.106	65.00
		40		14.729	101.474	77.50
		50		12.111	106.71	81.50
		60		11.783	107.366	82.00
		70		11.456	108.02	82.50
	MR	5	53.86	29.623	48.474	45
		10		26.93	53.86	50
		15		24.237	59.246	55
		20		18.851	70.018	65
		30		14.542	78.636	73.00

		40		12.926	81.868	76.00
		50		12.657	82.406	76.50
		60		11.849	84.022	78.00
		70		11.849	84.022	78.00
ACRN4	CR	5	139.332	65.486	147.692	53.00
		10		61.306	156.052	56.00
		15		49.462	179.74	64.50
		20		42.496	193.672	69.50
		30		35.529	207.606	74.50
		40		17.416	243.832	87.50
		50		15.326	248.012	89.00
		60		14.629	249.406	89.50
		70		13.236	252.192	90.50
	MO	5	65.466	26.841	77.25	59.00
		10		19.312	92.308	70.50
		15		18.985	92.962	71.00
		20		17.021	96.89	74.00
		30		14.402	102.128	78.00
		40		13.093	104.746	80.00
		50		9.492	111.948	85.50
		60		8.510	113.912	87.00
		70		8.510	113.912	87.00
	MR	5	53.86	25.852	56.016	52.00
		10		21.813	64.094	59.50
		15		18.581	70.558	65.50
		20		16.965	73.79	68.50
		30		12.387	82.946	77.00
		40		10.502	86.716	80.50
		50		10.502	86.716	80.50
		60		9.964	87.792	81.50
		70		9.694	88.332	82.00
ACRN3	CR	5	139.332	25.776	227.112	81.50
		10		22.989	232.686	83.50
		15		20.899	236.866	85.00
		20		19.506	239.652	86.00
		30		15.326	248.012	89.00
		40		12.539	253.586	91.00
		50		11.146	256.372	92.00
		60		11.146	256.372	92.00
		70		10.449	257.766	92.50
	MO	5	65.466	20.294	90.344	69.00
		10		16.693	97.546	74.50
		15		15.711	99.51	76.00
		20		15.384	100.164	76.50
		30		10.474	109.984	84.00
		40		9.492	111.948	85.50
		50		6.873	117.186	89.50
		60		6.219	118.494	90.50
		70		6.219	118.494	90.50
	MR	5	53.86	16.696	74.328	69.00
		10		16.427	74.866	69.50
		15		15.080	77.56	72.00
		20		14.003	79.714	74.00
		30		11.310	85.1	79.00
		40		9.694	88.332	82.00
		50		9.694	88.332	82.00
		60		8.079	91.562	85
		70		8.079	91.562	85

Noticing the results got listed in the table(9), we find that the efficiency of the activated carbon prepared for the dye adsorption CR is bigger than its efficiency for adsorption the other two dyes MO, MR and for all carbon kinds. The adsorption efficiency was about 50% in the first dye within the first 5 minutes, the efficiency of the second dye adsorption was 40%, whereas the third was 30%; the percentage rate of the adsorbate material increases through the time, but this ratio is gradually slowing down till the adsorption reaches to the equilibrium condition. It was noticed that the adsorption process remains approximately stable after the adsorption process is achieved, also it was noticed that all dyes under investigation reach the equilibrium condition in a time about (60-70)minutes. The time chosen was 70 minutes to achieve the next studies for all dyes.

3: Effect of initial concentration

The initial concentration is regarded as an important factor in studying the mass transform in the solutions and forming one of the significant powers which is controlling the adsorption process and necessary to overcoming the resistance appeared by molecules for movement that is necessary between two phases: liquid and solid. So, it was seen that there was no study without tackling the effect of concentration in order to determining the excellent conditions for adsorption system. In this study, the effect of concentration of the dyes under discussion was studied around the range (1×10^{-4} - 5×10^{-4}) M at the temperature 15C^{o}, the solution(20ml) of each dye was shaken in constant speed 100 cycle/min and by using the same quantity of the adsorbent material 0.01g for 70 minutes. The results which have been got from this study listed in the following table:

Table (10): The concentration effect on the adsorption capacity at 15C^{o}, the time of shaking: 70 min, the activated carbon weight: 0.01g, the velocity of shaking: 100 cycle/min and the solution volume of the dye: 20ml.

Type Active carbon prepared	Dye	C_i mg/L	C_e mg/L	C_{ads}	q_e mg/g	%ads.
ACRO20	CR	69.666	4.876	64.79	129.58	93.00
		139.332	18.809	120.523	241.046	86.50
		208.998	32.743	176.255	352.51	84.33
		278.664	68.969	209.695	419.39	75.25
		348.33	104.499	243.831	487.662	70.00
	MO	32.733	4.909	27.824	55.648	85.00
		65.466	10.801	54.665	109.33	83.50
		98.199	24.549	73.65	147.3	75.00
		130.932	36.006	94.926	189.852	72.50
		163.665	45.826	117.839	235.678	72.00
	MR	26.93	4.039	22.891	45.782	85.00
		53.86	12.387	41.473	82.946	77.00
		80.79	19.658	61.132	122.264	75.66
		107.72	29.623	78.097	156.194	72.5
		134.65	40.395	94.255	188.51	70
ACRO25	CR	69.666	3.483	66.183	132.366	94.30
		139.332	10.449	128.883	257.766	92.50
		208.998	42.496	166.502	333.004	79.66
		278.664	69.666	208.998	417.996	75.00
		348.330	97.532	250.798	501.596	72.00
	MO	32.733	4.909	27.824	55.648	85.00
		65.466	10.147	55.319	110.638	84.50
		98.199	28.150	70.049	140.098	71.33
		130.932	49.099	81.833	163.666	62.50
		163.665	72.012	91.653	183.306	56.00
	MR	26.93	4.308	22.622	45.244	84.00
		53.86	9.694	44.166	88.332	82.00
		80.79	19.658	61.132	122.264	75.66
		107.72	26.391	81.329	162.658	75.50
		134.65	43.088	91.562	183.124	68
	CR	69.666	3.483	66.183	132.366	95.00
		139,332	9.753	129.579	259.158	93.00
		208.998	21.596	187.402	374.804	89.66

		278.664	36.922	241.742	483.484	86.75
		348.330	59.216	289.114	578.228	83.00
ACRN4	MO	32.733	3.600	29.133	58.266	89.00
		65.466	7.855	57.611	115.222	88.00
		98.199	12.765	85.434	170.868	87.00
		130.932	18.657	112.275	224.55	85.75
		163.665	27.168	136.497	272.994	83.40
	MR	26.93	4.308	22.622	45.244	84.00
		53.86	9.156	44.704	89.408	83.00
		80.79	19.120	61.67	123.34	76.33
		107.72	26.930	80.79	161.58	75
		134.65	35.009	99.641	199.282	74
ACRN3	CR	69.666	1.393	68.273	136.546	98.00
		139.332	9.753	129.579	259.158	93.00
		208.998	27.169	181.829	363.658	87.00
		278.664	43.889	234.775	469.55	84.25
		348.330	69.666	278.664	557.328	80.00
	MO	32.733	2.291	30.442	60.884	93.00
		65.466	5.237	60.229	120.458	92.00
		98.199	8.837	89.362	178.724	91.00
		130.932	12.111	118.821	237.642	90.75
		163.665	16.366	147.299	294.598	90.00
	MR	26.93	2.693	24.237	48.474	90
		53.86	6.463	47.397	94.794	88.00
		80.79	11.041	69.749	139.498	86.33
		107.72	17.773	89.947	179.894	83.50
		134.65	26.122	108.528	217.056	80.60

The mentioned results in the above table showed that the adsorption capacity increases when the concentration increases, but the adsorption efficiency (percentage adsorption) decreases when concentration increases, this is due to the increasing in concentration at the beginning of the adsorption increases the number of the available molecules for adsorption; this is when the qualified locations of adsorption on the solid surface are available, by the time passing, the competition between dye molecules increases to have the rest active locations on the surface of constant quantity to the activated carbon used in increasing the concentrations. In addition, the increase in concentrations leads to staying behind larger quantity of the dye in solution after the equilibrium process and this reduces the adsorption efficiency when it is calculated mathematically from the ratio between the quantity of the adsorbate material to the rest of quantity in the solution.

4: Effect of temperature

The study of temperatures influencing on the adsorption process is considered of the very significant studies, this can give the researchers much of information related to the studied system; it makes the calculation and assessment of the thermodynamic functions(ΔG^o, ΔH and ΔS^o) easier, they explain the kind of powers which connects the adsorbent surface with polluted material and assessing the kind and nature of the adsorption process; as well as; the possibility of giving the researcher information which illustrating the direction of the process happening, the system needs or not to have external conditions for executing the process and arranging the system and nature of the powers running the adsorption operation, whether it is physical or chemical.

For these reasons, the effect of temperatures on the mentioned dyes at an initial concentration 2×10^{-4}M, in the range of temperatures 15-55C^o, by using a constant volume of dye solution (20ml) and a constant quality of the adsorbent material 0.01g. The solutions were shaken for 70 minutes and in fixed velocity was 100 cycle/min. The results got are shown in the following table:

Table (11): The effect of temperatures on the adsorption capacity at 15-55C^o , time shaking: 70 min, the carbon activated weight: 0.01g, the speed of shaking: 100cycle/min and the volume of dye solution: 20ml

Type Active carbon prepared	Dye	Temp. C^o	C_i mg/L	C_e mg/L	C_{ads}	q_e mg/g	% ads.
	CR	15	139.332	18.809	120.523	241.046	86.50
		25		23.686	115.646	231.292	83.00
		35		52.946	86.386	172.772	62.00

		45		68.969	70.363	140.726	50.50
		55		69.666	69.666	139.332	50
ACRO20	MO	15	65.466	10.801	54.665	109.33	83.50
		25		12.438	53.028	106.056	81.00
		35		17.675	47.491	94.982	73.00
		45		18.657	46.809	93.618	71.50
		55		19.639	45.827	91.654	70.00
	MR	15	53.86	12.387	41.473	82.946	77.00
		25		12.657	41.203	82.406	76.50
		35		15.619	38.241	76.482	71.00
		45		22.890	30.97	61.94	57.50
		55		26.93	26.93	53.86	50
ACRO25	CR	15	139.332	10.449	128.883	257.766	92.50
		25		14.629	124.703	249.406	89.50
		35		25.079	114.253	228.506	82.00
		45		30.653	108.679	217.358	78.00
		55		36.922	102.41	204.82	73.50
	MO	15	65.466	10.147	55.319	110.638	84.50
		25		11.456	54.01	108.02	82.50
		35		12.438	53.028	106.056	81.00
		45		19.312	46.154	92.308	70.50
		55		28.805	36.661	73.322	56.00
	MR	15	53.86	9.694	44.166	88.332	82.00
		25		11.849	42.011	84.022	78.00
		35		12.657	41.203	82.406	76.50
		45		15.619	38.241	76.482	71.00
		55		17.773	36.087	72.174	67.00
ACRN4	CR	15	139.332	9.753	129.579	259.158	93.00
		25		13.236	126.096	252.192	90.50
		35		21.596	117.736	235.472	84.50
		45		28.563	110.769	221.538	79.50
		55		35.520	103.812	207.624	74.50
	MO	15	65.466	7.855	57.611	115.222	88.00
		25		8.510	56.956	113.912	87.00
		35		9.819	55.647	111.294	85.00
		45		11.129	54.337	108.674	83.00
		55		15.384	50.082	100.164	76.50
	MR	15	53.86	9.156	44.704	89.408	83.00
		25		9.694	44.166	88.332	82.00
		35		10.233	43.627	87.254	81.00
		45		11.041	42.819	85.638	79.50
		55		12.657	41.203	82.406	76.50
ACRN3	CR	15	139.332	9.753	129.579	259.158	93.00
		25		10.449	128.883	257.766	92.50
		35		22.989	116.343	232.686	83.50
		45		27.866	111.466	222.932	80.00
		55		31.349	107.983	215.966	77.50
	MO	15	65.466	5.237	60.229	120.458	92.00
		25		6.219	59.247	118.494	90.50
		35		11.129	54.337	108.674	83.00
		45		12.111	53.355	106.71	81.50
		55		13.747	51.719	103.438	79.00
	MR	15	53.86	6.463	47.397	94.794	88.00
		25		8.079	45.781	91.562	85.00
		35		10.502	43.358	86.716	80.50
		45		11.310	42.55	85.1	79.00
		55		12.657	41.203	82.406	76.50

The results listed in table(11) indicate that the adsorption efficiency and capacity have been best at low temperatures and this is regarded of economic side in the course of designing the adsorption systems as well as it can give a sign that the powers running the adsorption process are of physical nature.

5: Calculation of thermodynamic functions

The thermodynamic functions are regarded important variables which give a considerable explanation during the study of adsorption process. They describe the nature of the investigated system, the kind of powers that controlling and driving the adsorption process, as well as they can give an idea about the sort of molecule intersections which might happen through the adsorption process and which might have an important role in determining its efficiency. The thermodynamic functions were calculated so as to reach these influences and having information explains the system nature (dye-activated carbon) by depending on the change happening during the study of temperature effect and with fixing all other conditions which influence on the adsorption efficiency. The values of the thermodynamic functions were calculated according to the mentioned equations in the item(1.4.6) and all the graphic drawings in this research were achieved by using the program(Excel). The calculated results in this study (K, ΔG^o, ΔH, and ΔS^o) were listed in the table(12), whereas the figures(2,3,4,5) detect the linear relations formed by drawing lnK in opposite to 1/T in the course of the application of Vant Hoff equation (8) used in calculating the values of change in the enthalpy.

(b) MO

$y = 2078x - 5.4848$
$R^2 = 0.8967$

(a) CR

$y = 5280x - 16.106$
$R^2 = 0.9052$

(c) MR

$y = 3295x - 9.8272$
$R^2 = 0.9246$
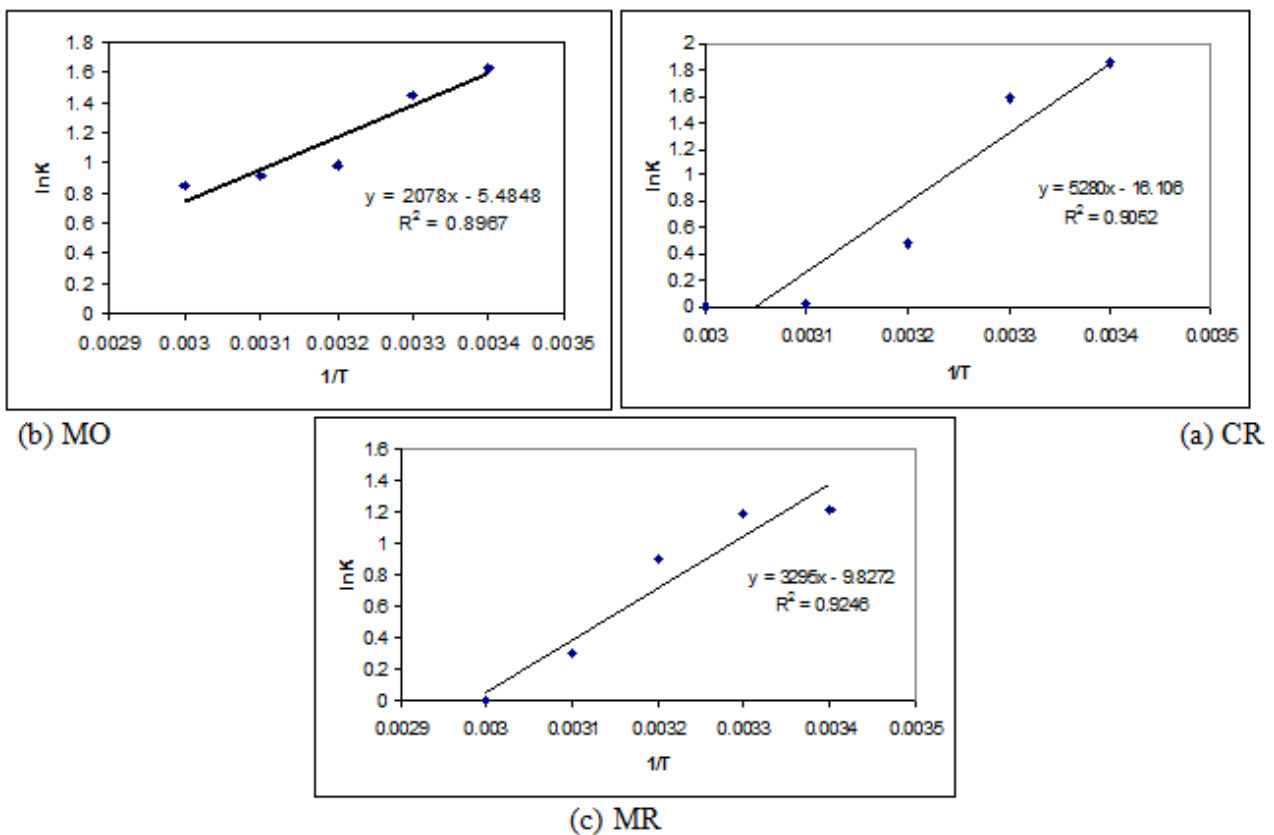
Figure (2): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for the activated carbon prepared ACRO20

(b) MO

$y = 3590x - 10.327$
$R^2 = 0.8874$

a) CR

$y = 3863x - 10.671$
$R^2 = 0.9683$
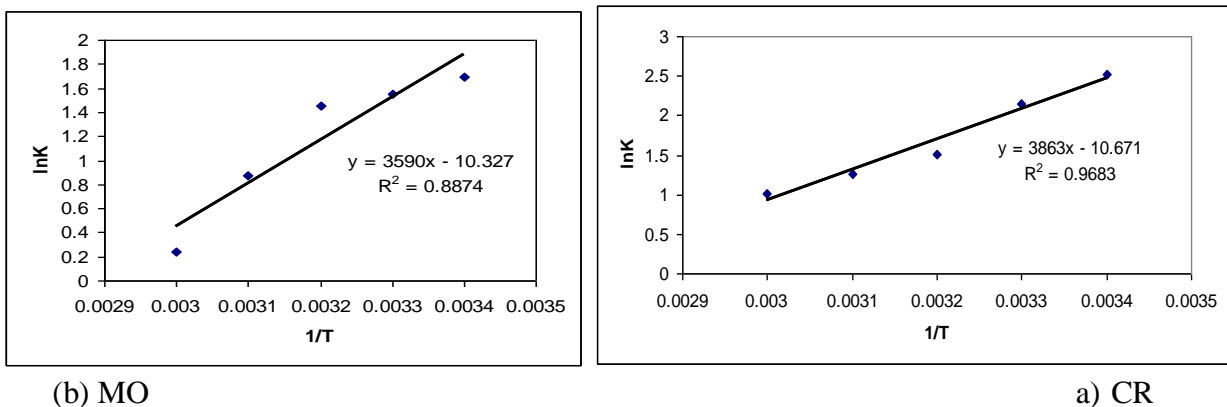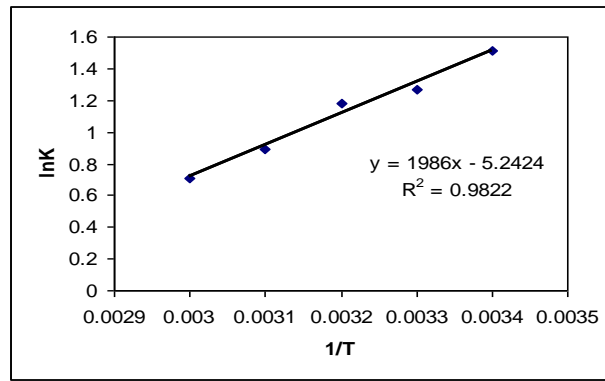
(c) MR

Figure (3): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for the activated carbon prepared ACRO25
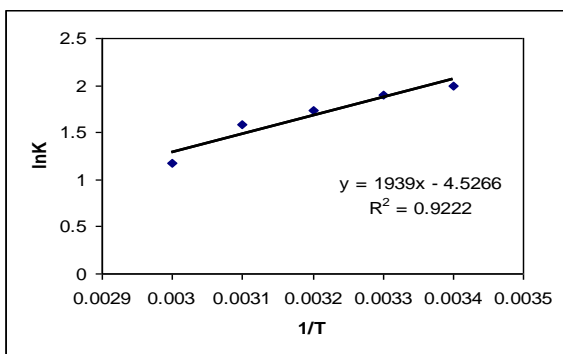
(b) MO
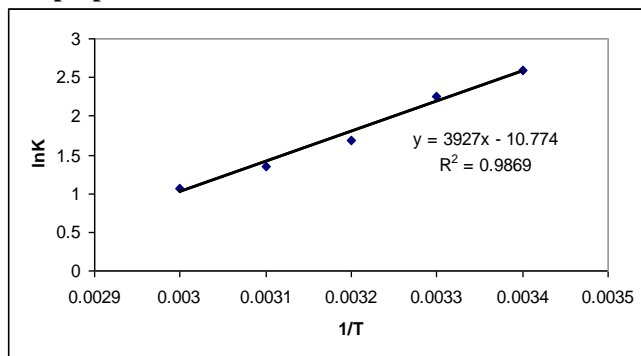
(a) CR
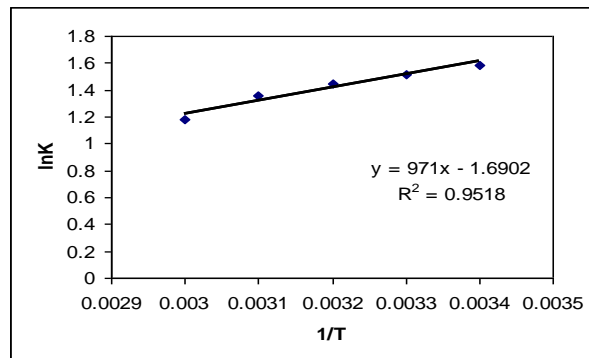
(c) MR

Figure (4): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for the activated carbon prepared ACRN4
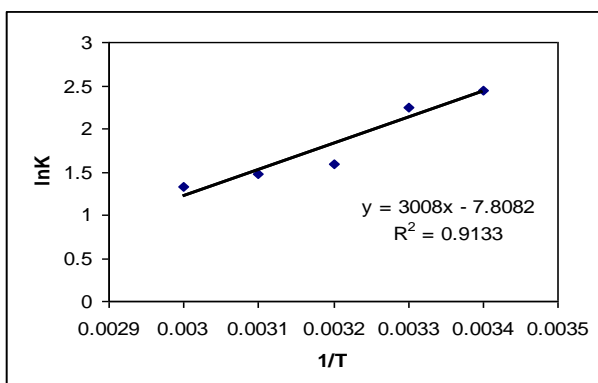
(b) MO
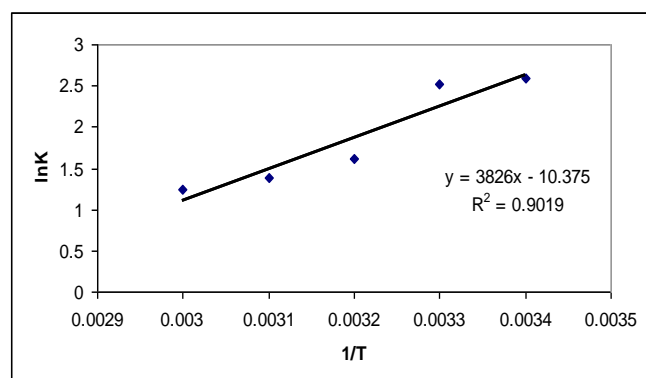
(a) CR
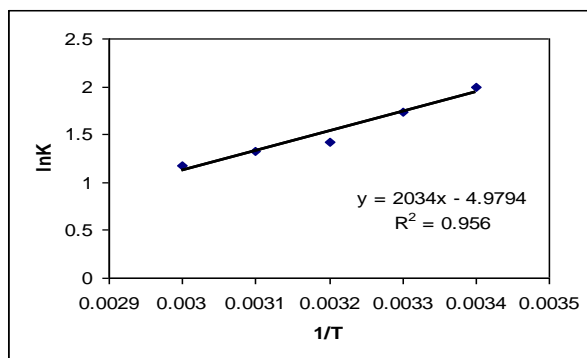
(c) MR

Figure (5): The relation between lnK in opposite to 1/T to calculate the value of Adsorption enthalpy for the activated carbon prepared ACRN3

Table (12): The values of the equilibrium constants and the thermodynamic functions during the equilibrium of adsorption dyes

Type Active carbon prepared	dye	Temp. K^o	K	ΔH (KJ.mol⁻¹)	ΔG^o (KJ.mol⁻¹)	ΔS^o (J.mol⁻¹.K⁻¹)
ACRO20	CR	288	6.407	-43.897	-4.446	-136.984
		298	4.882		-3.926	-134.130
		308	1.631		-1.252	-138.460
		318	1.020		-0.050	-137.885
		328	1		0	-133.835
	MO	288	5.061	-17.276	-3.881	-46.510
		298	4.263		-3.590	-45.927
		308	2.686		-2.529	-47.878
		318	2.508		-2.429	-46.688
		328	2.333		-2.309	-45.630
	MR	288	3.348	-27.394	-2.892	-85.076
		298	3.255		-2.923	-82.117
		308	2.448		-2.2918	-81.502
		318	1.352		-0.795	-83.644
		328	1		0	-83.520
ACRO25	CR	288	12.334	-32.116	-6.014	-90.632
		298	8.524		-5.306	-89.966
		308	4.555		-3.882	-91.671
		318	3.545		-3.344	-90.479
		328	2.773		-2.778	-89.445
	MO	288	5.451	-29.847	-4.058	-89.544
		298	4.714		-3.840	-87.271
		308	4.263		-3.710	-84.859
		318	2.389		-2.300	-86.626
		328	1.272		-0.654	-89.002
	MR	288	4.556	-16.511	-3.629	-44.727
		298	3.545		-3.134	-44.890
		308	3.255		-3.021	-43.798
		318	2.448		-2.366	-44.482
		328	2.030		-1.930	-44.453
	CR	288	13.286	-32.649	-6.192	-91.864
		298	9.526		-5.584	-90.820
		308	5.451		-4.340	-91.911
		318	3.878		-3.582	-91.404
		328	2.922		-2.923	-90.627
		288	7.334	-16.120	-4.769	-39.413
		298	6.692		-4.707	-38.300

		308	5.667		-4.440	-37.923
	MO	318	4.882		-4.190	-37.516
ACRN4		328	3.255		-3.217	-39.338
		288	4.882	-8.072	-3.795	-14.853
		298	4.556		-3.755	-14.486
	MR	308	4.263		-3.710	-14.163
		318	3.878		-3.582	-14.120
		328	3.255		-3.217	-14.801
		288	13.286		-6.192	-88.949
		298	12.334		-6.223	-85.858
	CR	308	5.060	-31.809	-4.150	-89.800
		318	4		-3.664	-88.506
		328	3.444		-3.370	-86.703
		288	11.500		-5.847	-66.532
		298	9.526		-5.584	-65.181
ACRN3	MO	308	4.555	-25.008	-4.058	-68.018
		318	4.405		-3.918	-66.321
		328	3.762		-3.610	-65.237
		288	7.333		-4.769	-42.156
		298	5.666		-4.296	-42.330
	MR	308	4.128	-16.910	-3.628	-43.123
		318	3.762		-3.500	-42.170
		328	3.255		-3.217	-41.746

The thermodynamic results of the study listed in the table (12) indicate that the adsorption system under discussion is a process exothermic and governed by physical powers (Vandervals' forces) represent the connecting forces between the dye and the adsorbent surface as well as the adsorption process in this system occurs simultaneously towards the formula relation with the surface, so this leads to reducing the randomness of the system.

6: Adsorption isotherm

6.1: Freundlich isotherm

Freundlich isotherm (equation 12) was applied on the experimental data for the dyes and the values of Freundlich constants (K_f , n) from the slop and section of the straight line formed from drawing the relation between $Logq_e$ in opposite to $LogC_e$ respectively. The results which were got, were listed in the table (13) and were graphically shown in the figures(6,7,8,9).


(b) MO

(a) CR

(c) MR
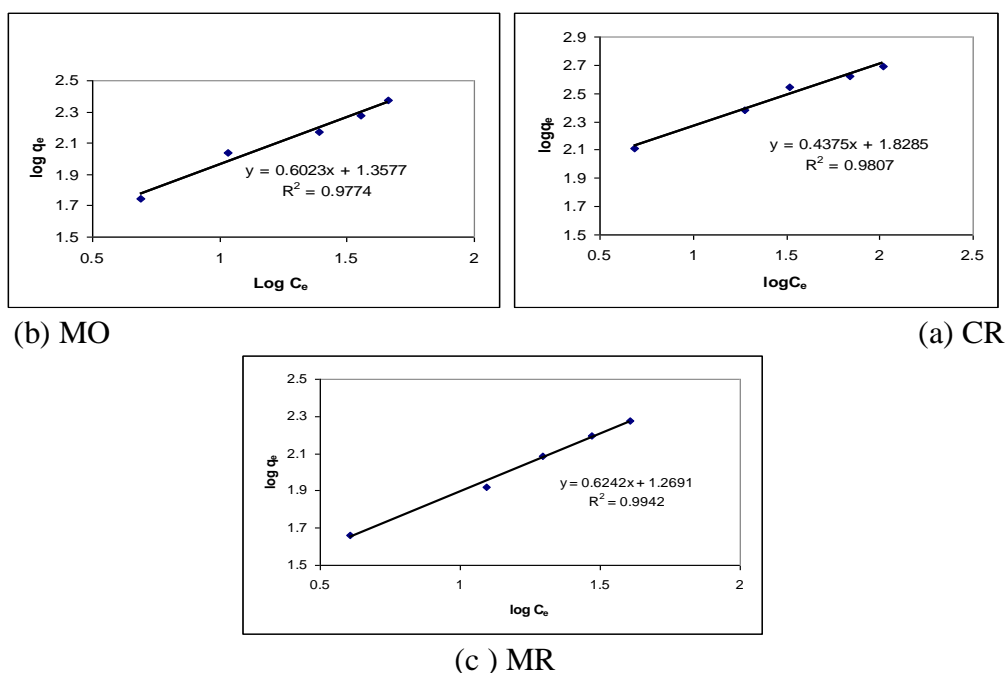
Figure (6): Freundlich isotherm for dyes adsorption by using the activated carbon prepared ACRO20

(b) MO

(a) CR

(c) MR
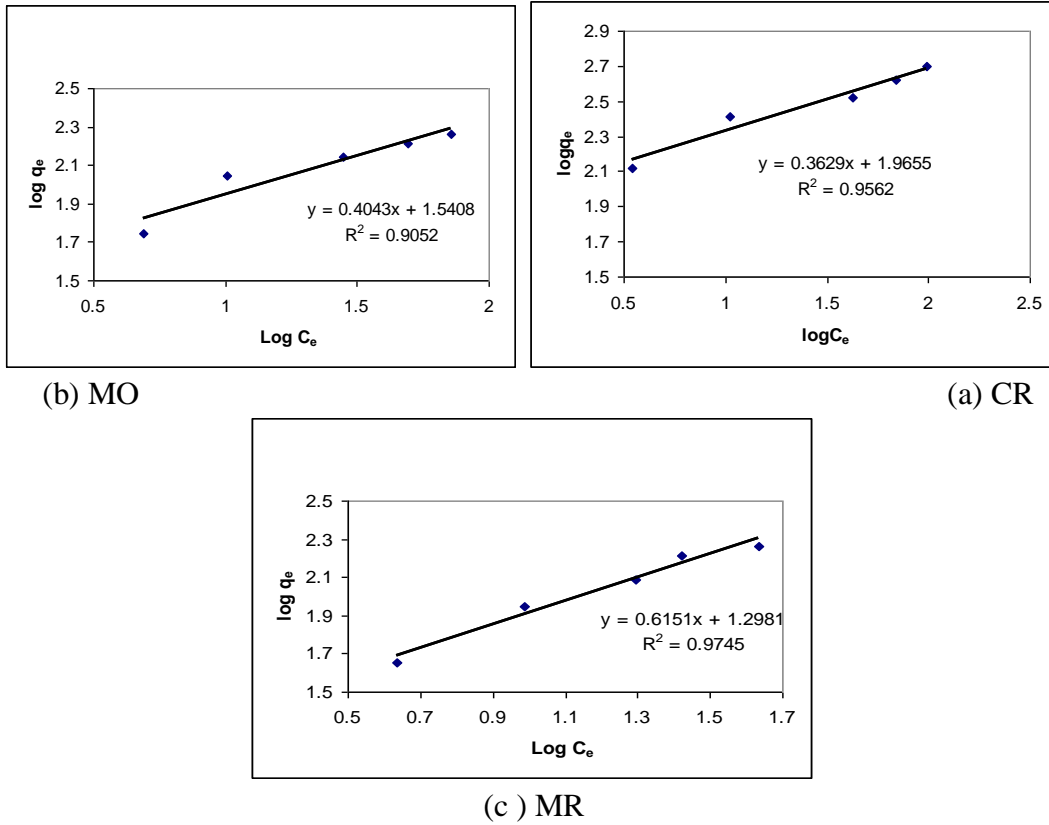
**Figure (7): Freundlich isotherm for dyes adsorption by using the activated carbon prepared ACRO25**

(b) MO

(a) CR

(c) MR
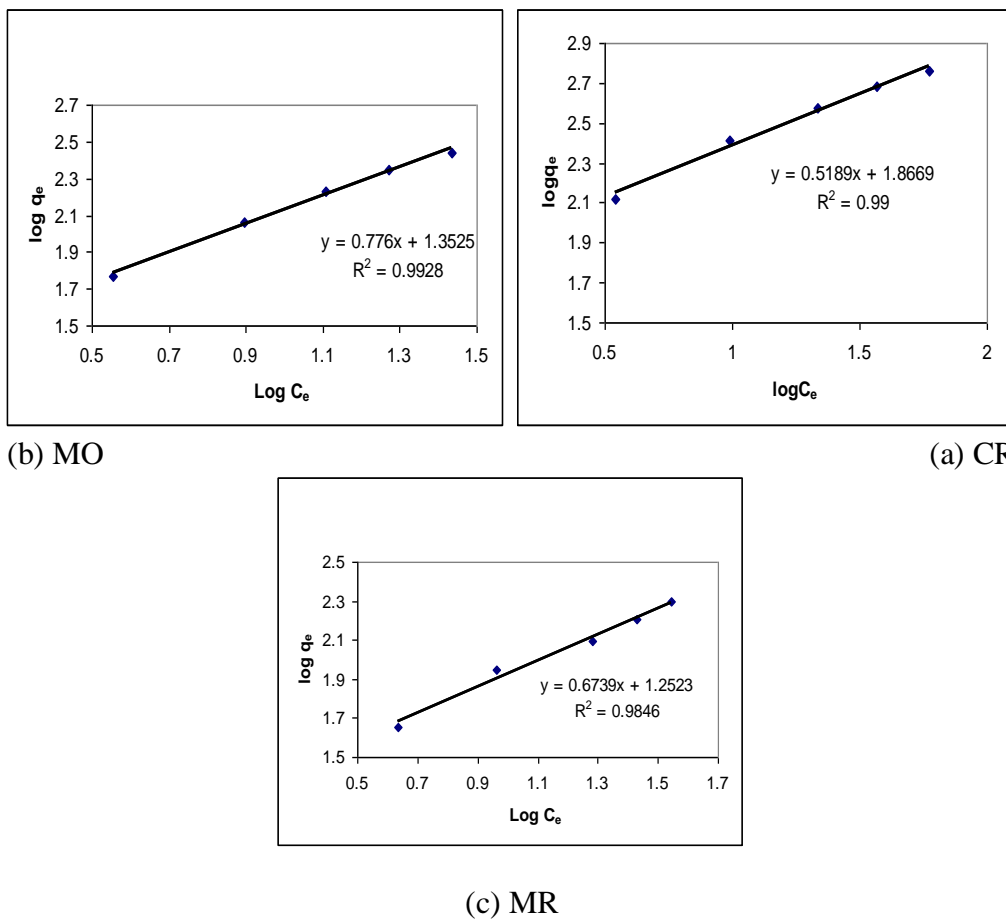
Figure (8): Freundlich isotherm for dyes adsorption by using the activated carbon prepared ACRN4

(b) MO

(a) CR

(c) MR
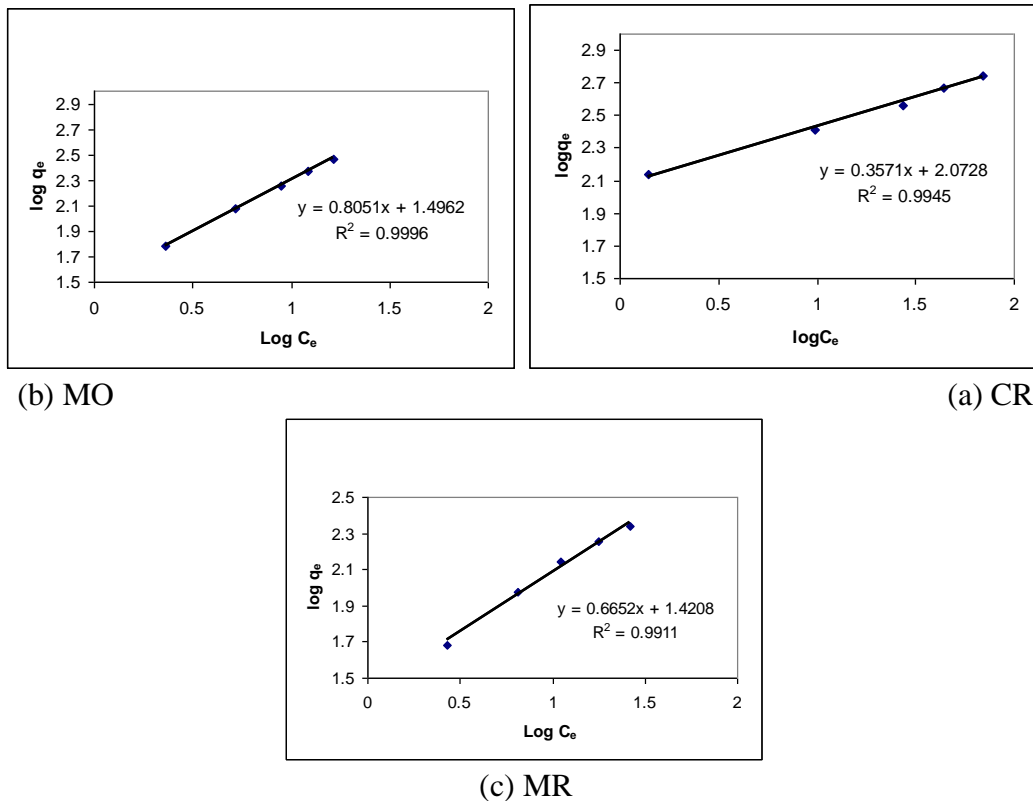
Figure (9): Freundlich isotherm for dyes adsorption by using the activated carbon prepared ACRN3

Table (13): The values of Freundlich constants(K_f , n) and the correlation coefficients which were got from the application on the experimental data for adsorption

Type Active carbon prepared	Dye	n	K_f	R^2
ACRO20	CR	2.2857	67.375	0.9807
	MO	1.6603	22.787	0.9774
	MR	1.6020	18.582	0.9942
ACRO25	CR	2.7555	92.363	0.9562
	MO	2.4734	34.737	0.9052
	MR	1.6257	19.865	0.9745
ACRN4	CR	1.9271	73.603	0.99
	MO	1.2886	22.516	0.9928
	MR	1.4838	17.877	0.9846
ACRN3	CR	2.8003	118.249	0.9945
	MO	1.2420	31.347	0.9996
	MR	1.5033	26.351	0.9911

The results in the table(13) indicate that Freundlich isotherm equation is applicable to the experimental data for the very well studied system, this indicates the values of coefficient correlate which are near to 1, whereas the value of n (from 1 to 10) indicates that the adsorption system is the favorable kind (governed by physical forces).

6.2: Langmuir isotherm

This sample of isotherms is important in describing and studying the mono-layer adsorption, it presupposes the homogeneity of energy on the surface of the adsorbent material at constant temperature. This gives the researcher information represents maximum capacity for adsorption (Q_{max}) for the adsorbent material as well as the strength of connection between the dye and adsorbent surface through the constant(b).

This sample was applied-as in the equation(13)- on the experimental data for dyes adsorption through drawing the relation between C_e/q_e in opposite to C_e. The constants Q_{max} and b were calculated through the slop and straight lines

section that were formed from the drawings respectively. The results got were listed in the table(14), they were represented graphically as in the following figures:

(b) MO

(a) CR

(c) MR
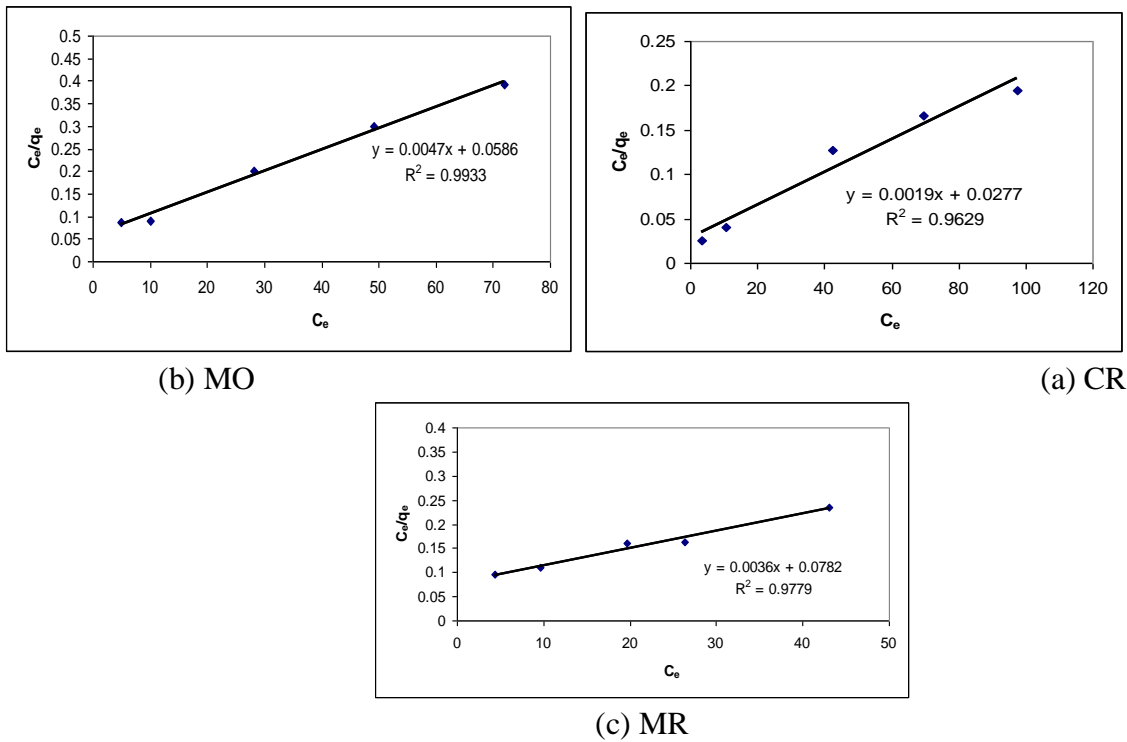
Figure (11): Langmuir isotherm for adsorption of dyes by using the activated carbon prepared ACRO25

(b) MO

(a) MR

(c) MR
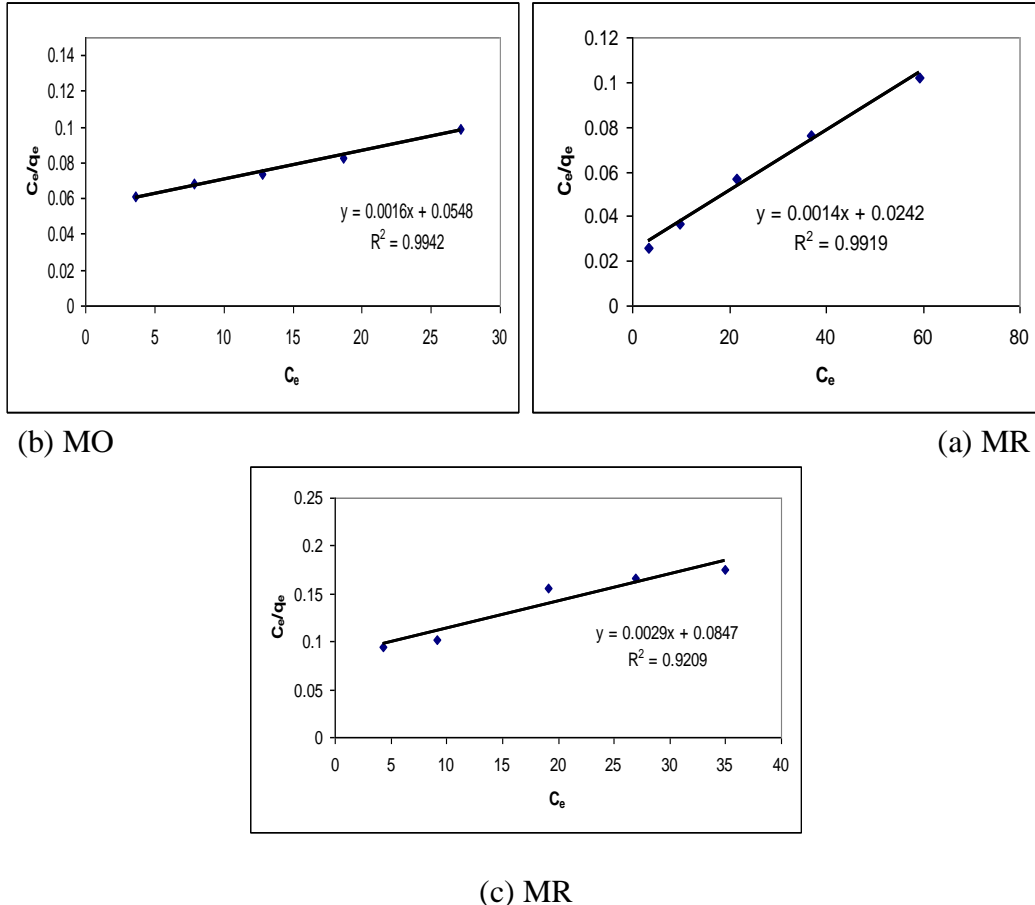
Figure (12): Langmuir isotherm for adsorption of dyes by using the activated carbon prepared ACRN4

(b) MO
(a) CR

(c) MR
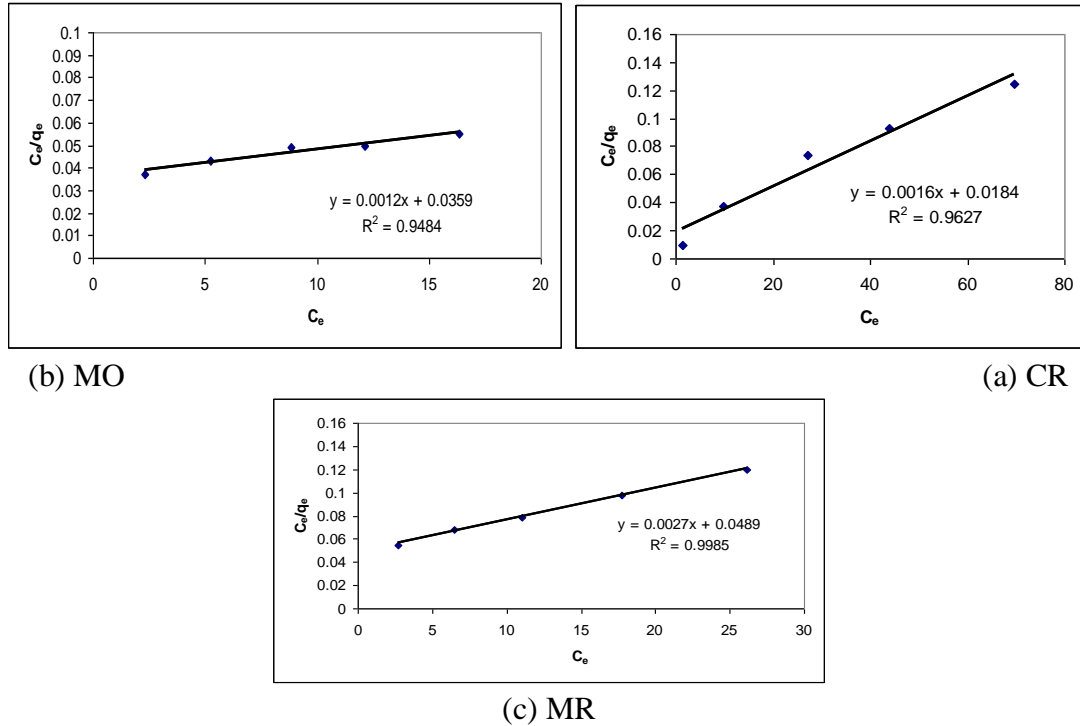
Figure (13): Langmuir isotherm for adsorption of dyes by using the activated carbon prepared ACRN3

Table (14): The values of Langmuir constants(Q_{max}, b) as well as the correlation coefficients which were got by applying them on the experimental data for adsorption

Type Active carbon prepared	dye	Q(mg/g)	b(L/mg)	R^2
ACRO20	CR	588.235	0.0461	0.9893
	MO	344.827	0.0383	0.9431
	MR	312.5	0.0348	0.9259
ACRO25	CR	526.315	0.0685	0.9629
	MO	212.765	0.0802	0.9933
	MR	277.777	0.0460	0.9779
ACRN4	CR	714.285	0.0578	0.9919
	MO	625	0.0291	0.9942
	MR	344.827	0.0342	0.9209
ACRN3	CR	625	0.0869	0.9627
	MO	833.333	0.0334	0.9484
	MR	370.370	0.0552	0.9985

Looking at the table(14), although the application of Langmuir sample showed a good linear relation as for all dyes under study,but it was less applicable on the experimental data than Freundlich isotherm; The values of correlation coefficient (R^2) indicated to that. We can notice that the values of the constant(b)-which is a powerful value- had a correlation force of the dye as to the carbon surface and its values were changing somehow with the adsorption efficiency; it changed from one hand by linear form of adsorption efficiency, in the existence of simple exceptions where the non-homogeneity of values with the adsorption efficiency could be accounted for many matters have relation to the molecule energy.

6.3: Tempkin isotherm

Tempkin isotherm was tested on the experimental data for adsorption system(dye-carbon) by using the (equation 14), through drawing the relation between q_e in opposite to lnC_e and the values of the constants B_T and K_T were calculated respectively from the slop and the straight lines section that were got. The results which were got, listed in the table(15), they were represented graphically as it is illustrated in the following figures:
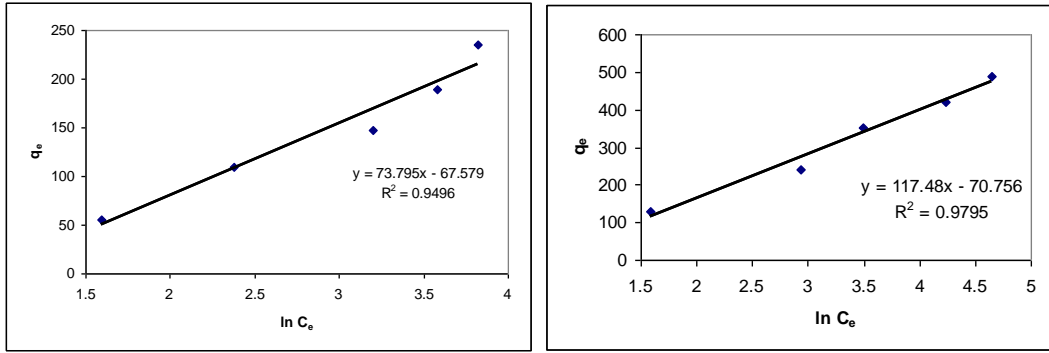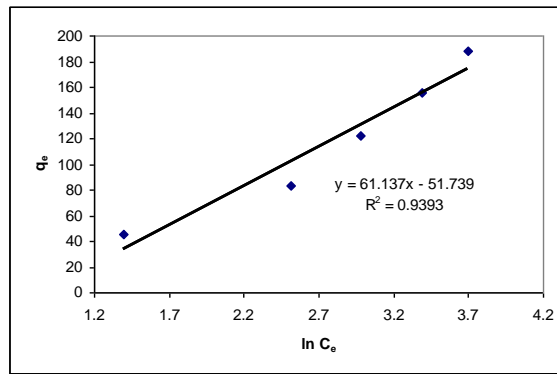
(b) MO   (a) CR

(c) MR

Figure (14): Tempkin isotherm for adsorption- dyes by using the activated carbon prepared ACRO20
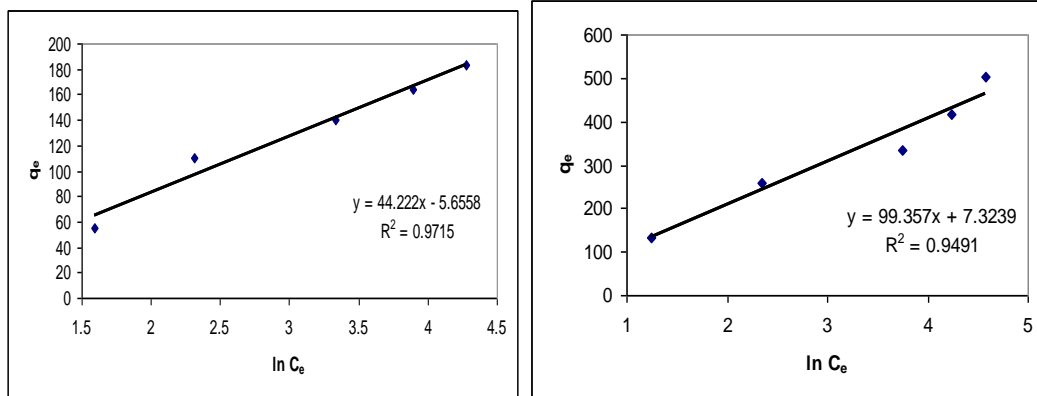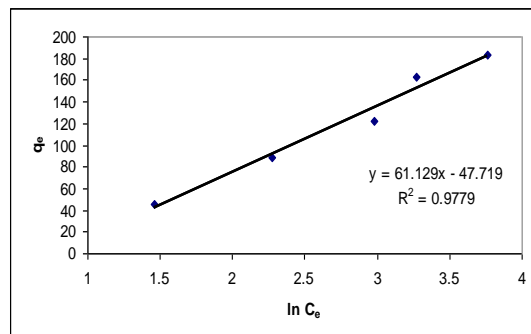
(b) MO   (a) CR

(c) MR

Figure (15): Tempkin isotherm for adsorption- dyes by using the activated carbon prepared ACRO25
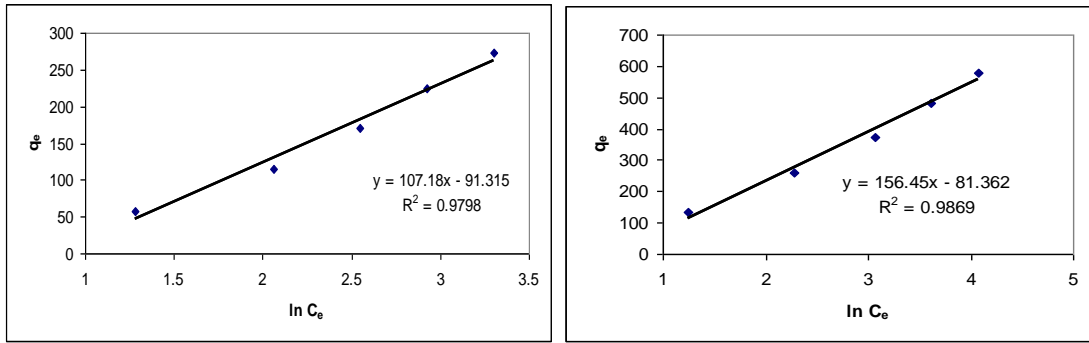
(b) MO

(a) CR
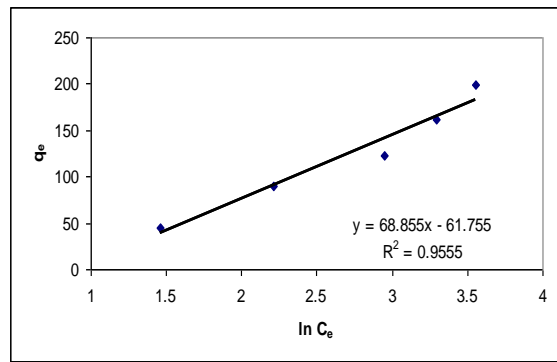
(c) MR

Figure (16): Tempkin isotherm for adsorption- dyes by using the activated carbon prepared ACRN4
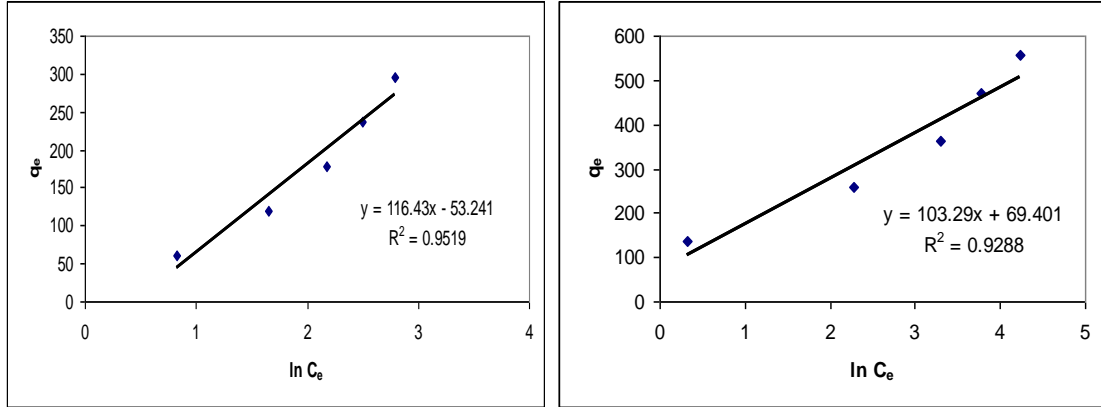
(b) MO

(a) CR
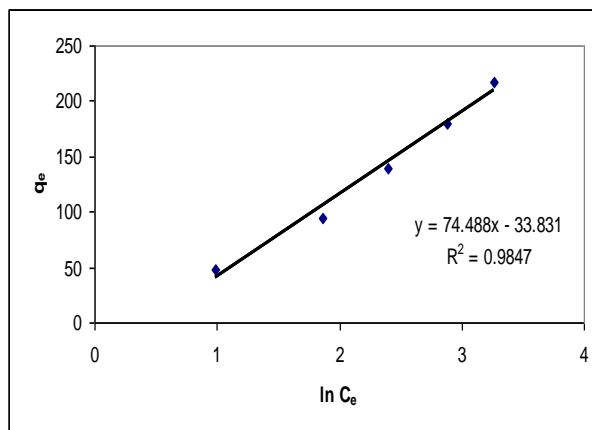
(c) MR

Figure (17): Tempkin isotherm for adsorption- dyes by using the activated carbon prepared ACRN3

Table (15): The values of Tempkin constants (B_T , K_T) and correlation coefficients which were got by their application on the experimental data for adsorption

Type Active carbon prepared	Dye	B_T	K_T	R^2
ACRO20	CR	117.48	0.5476	0.9795
	MO	73.795	0.4002	0.9496
	MR	61.137	0.4290	0.9393
ACRO25	CR	99.357	1.0764	0.9491
	MO	44.222	0.8800	0.9715
	MR	61.129	0.4581	0.9779
ACRN4	CR	156.45	0.8893	0.9869
	MO	107.18	0.4266	0.9798
	MR	68.855	0.4078	0.9555
ACRN3	CR	103.29	1.9579	0.9288
	MO	116.43	0.6330	0.9519
	MR	74.488	0.6350	0.9847

We can notice of the table(15) that the values of the constant B_T (which has a relation to the adsorbent capacity surface) are compatible to the theoretical adsorption capacity and got on Langmuir with the practical calculation of adsorption efficiency, whereas K_T is changing of inconstant mode and with variable has a relation to the bond energy between the dye and the activated carbon surface. Collectively, the results of application study of the three isotherms on the experimental data (for adsorption-studied systems) indicate that the model of Freundlich isotherm equation is more applicable to the results got in this study.

7: Kinetic study of adsorption

1: Pseudo first order equation

The pseudo first order equation sample (equation 15) which is so called Lagergren equation- was applied to the experimental data for adsorption dyes under study through drawing the relation between $\ln(q_e-q_t)$ in opposite to the time(min) to have linear correlation of slop was about($-k_1$) and section $\ln q_e$ in which the constants k_1 and q_e can be calculated respectively. The final results got were listed in the table(16) and explained in the figures(18,19,20, 21).

(b) MO

$y = -0.0697x + 4.7056$
$R^2 = 0.9627$

(a) CR

$y = -0.0817x + 5.3904$
$R^2 = 0.9106$
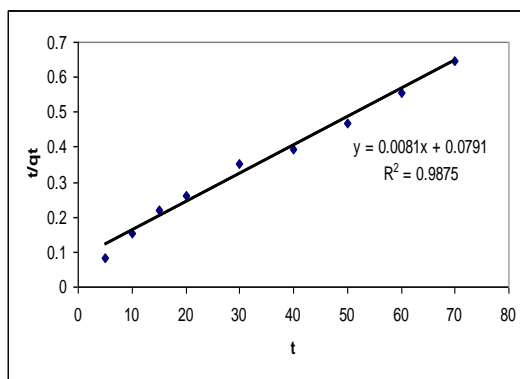

(c) MR

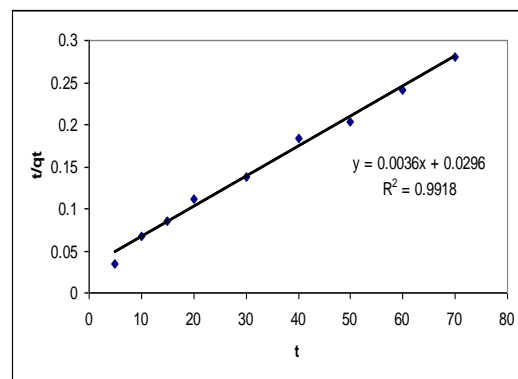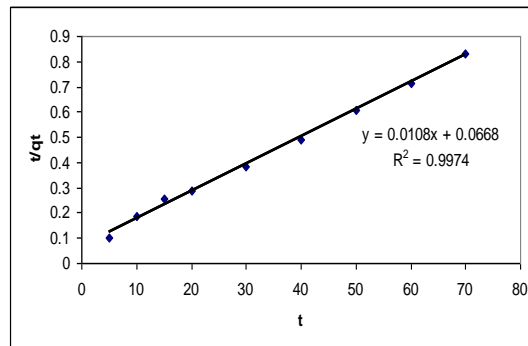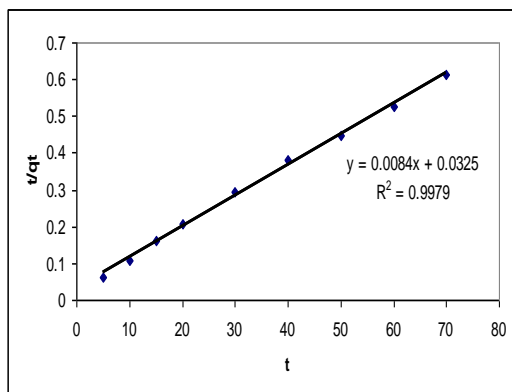$y = -0.069x + 4.2069$
$R^2 = 0.9568$
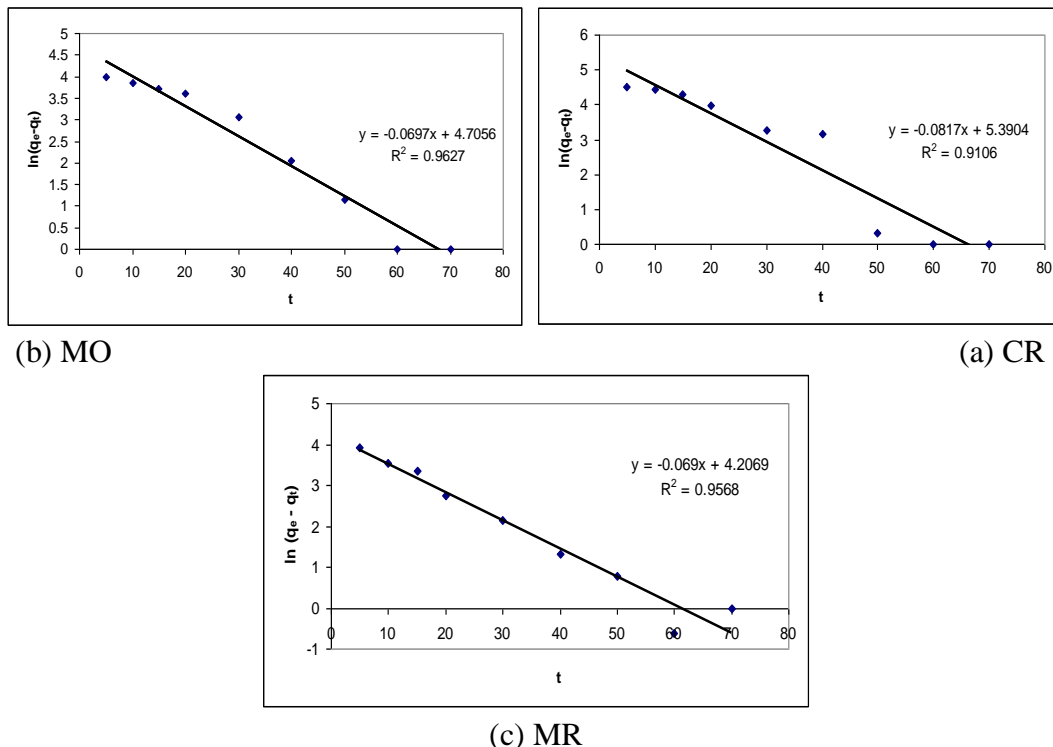
Figure (18): The relation between ln (qe – qt) in opposite to the time(minute) for the dyes by using the activated carbon prepared ACRO20

(b) MO

(a) CR

$y = -0.0724x + 4.6557$
$R^2 = 0.9372$

$y = -0.0781x + 5.5596$
$R^2 = 0.9335$

(c) MR

$y = -0.0629x + 3.8457$
$R^2 = 0.9496$
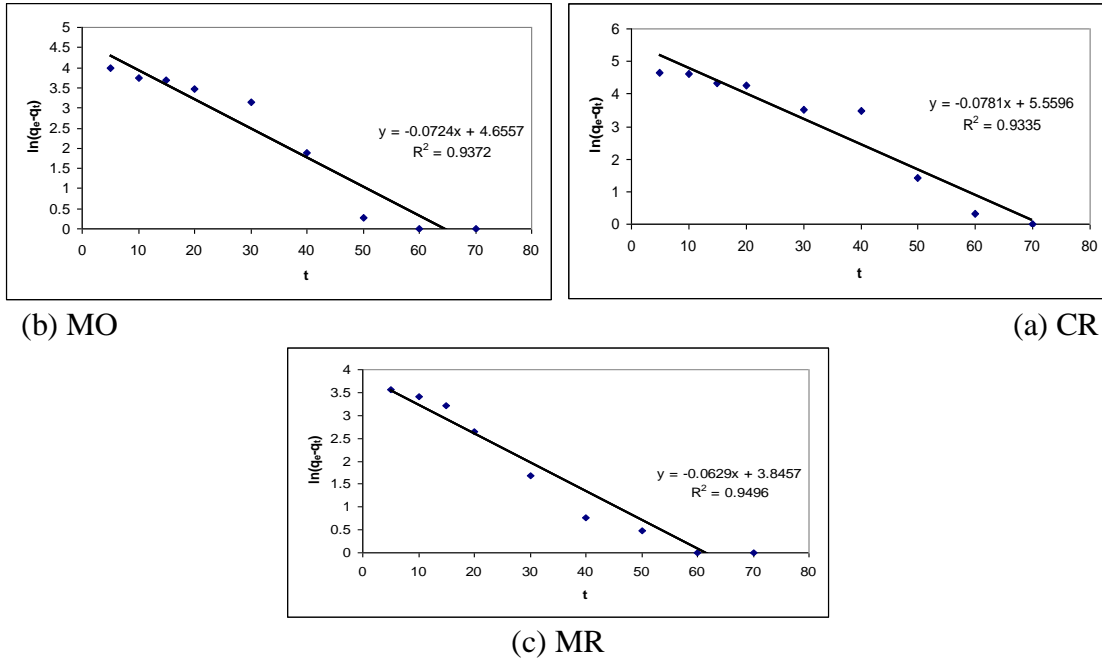
Figure (19): The relation between ln (qe – qt) in opposite to the time(minute) for the dyes by using the activated carbon prepared ACRO25

(b) MO

(a) C R

$y = -0.0587x + 3.9461$
$R^2 = 0.944$

$y = -0.0749x + 5.379$
$R^2 = 0.9693$
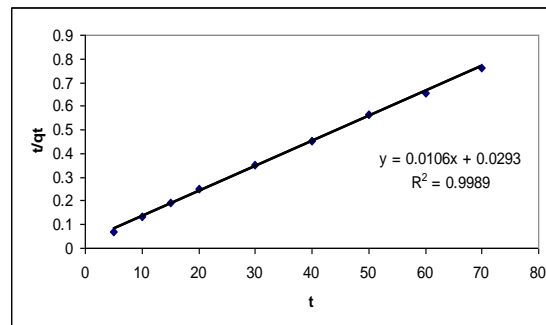
(c) MR

$y = -0.064x + 3.7166$
$R^2 = 0.9261$

Figure (20): The relation between ln (qe – qt) in opposite to the time(minute) for the dyes by using the activated carbon prepared ACRN4

(b) MO

(a) CR

$y = -0.0584x + 3.7835$
$R^2 = 0.9442$

$y = -0.0589x + 3.8452$
$R^2 = 0.9659$

(c) MR

Figure (21): The relation between ln (q$_e$ – q$_t$) in opposite to the time(minute) for the dyes by using the activated carbon prepared ACRN3

Table (16): the values of velocity constants and the theoretical-practical adsorption capacity for the pseudo first order;the quantity of the activated carbon: 0.01g at 25C°

Type Active carbon prepared	dye	q$_e$(exp)mg/g	q$_e$(calc)mg/g	k$_1$(min^{-1})	R^2
ACRO20	CR	231.292	219.203	0.0817	0.9106
	MO	106.056	110.564	0.0697	0.9627
	MR	82.406	67.148	0.069	0.9568
ACRO25	CR	249.512	259.718	0.0781	0.9335
	MO	108.02	105.182	0.0724	0.9372
	MR	84.022	46.791	0.0629	0.9496
ACRN4	CR	252.192	216.805	0.0749	0.9693
	MO	113.912	51.733	0.0587	0.944
	MR	88.332	41.124	0.064	0.9261
ACRN3	CR	257.766	46.768	0.0589	0.9659
	MO	118.494	43.969	0.0584	0.9442
	MR	91.562	26.692	0.0486	0.9662

By noticing the indicator in the figures(18, 19, 20, 21), we find that it represents weak-linear relations and it indicates the value R^2 listed in the table(16), as well as the calculated values q$_e$(calc) of the got straight lines sections do not be coincident with the values calculated experimentally q$_e$(exp), accordingly, it is not possible to regard this adsorption process from the first order reactions, even if the resulted forms of applying this equation have given rather good correlation coefficients.

2: Pseudo-second order equation

The pseudo second order equation-model (equation 16) was applied on the experimental data for adsorption dyes on the activated carbon through drawing the relation between t/q$_t$ in opposite to the time(min). The values of the slop and straight lines section got by the graphic representation were used to calculate the values of velocity constant (k$_2$) (g.mg^{-1}.min^{-1}) and the adsorption capacity at the equilibrium (mg/g)q$_e$ respectively. The results got are explained in the table(17) and drawn graphically in the figures (22, 23, 24, 25).
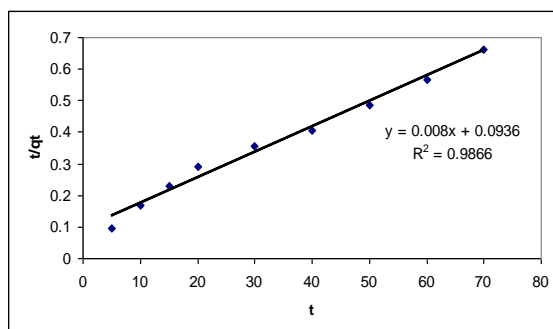
(b) MO
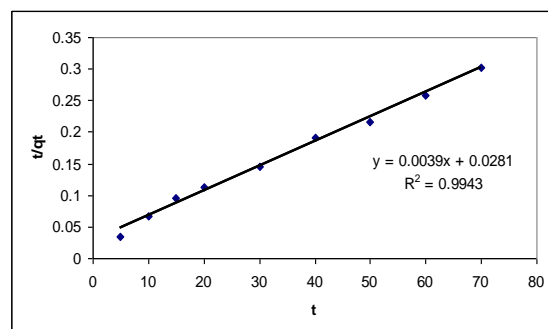
(a) CR
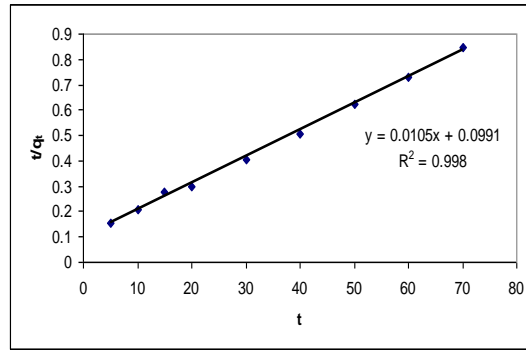
(c) MR

Figure (22): The relation between t/q_t in opposite to the time(minute) for dyes by using the activated carbon prepared ACRO20

(b) MO

(a) CR

(c) MR

Figure (23): The relation between t/q_t in opposite to the time(minute) for dyes by using the activated carbon prepared ACRO25

(b) MO
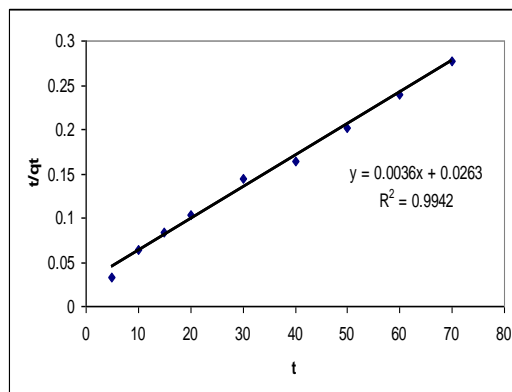
(a) CR
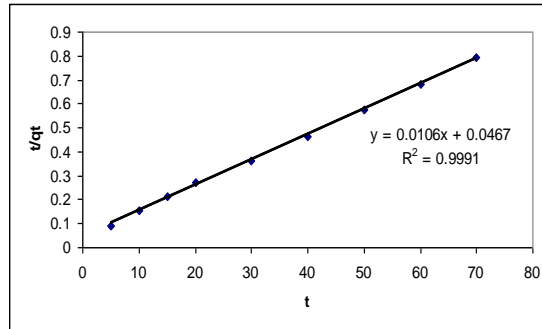
(c) MR

Figure (24): The relation between t/qt in opposite to the time(minute) for dyes by using the activated carbon prepared ACRN4
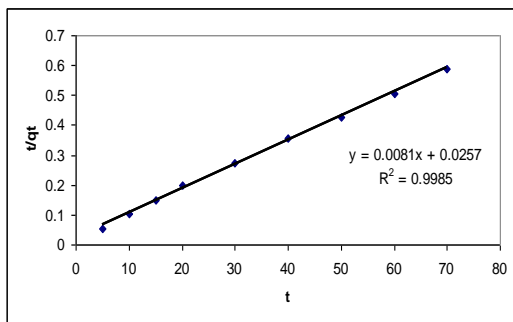
(b) MO
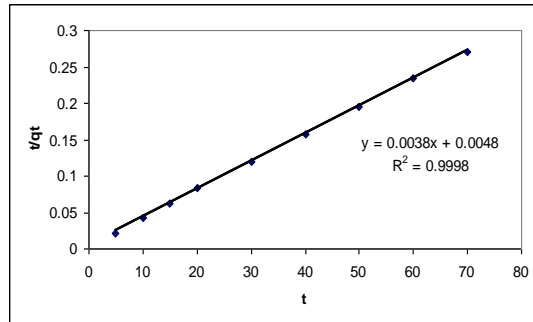
(a) CR


(c) MR

Figure (25): The relation between t/qt in opposite to the time(minute) for dyes by using the activated carbon prepared ACRO20

Table (17): The values of the velocity constants and the theoretical-practical adsorption capacity of the pseudo second order;the quantity of the activated carbon: 0.01g at 25C^{o}

Type Active carbon prepared	dye	q_e(exp)mg/g	q_e(calc)mg/g	k_2 (g.mg^{-1}.min^{-1})	h (mg.g^{-1}.min^{-1})	R^2
ACRO20	CR	231.292	256.410	0.00054	28.887	0.9943
	MO	106.056	125	0.00068	7.648	0.9866
	MR	82.406	95.238	0.00111	7.537	0.998
ACRO25	CR	249.512	277.777	0.00043	26.770	0.9918
	MO	108.02	123.456	0.00082	9.568	0.9875
	MR	84.022	92.592	0.00174	12.283	0.9974
ACRN4	CR	252.192	277.777	0.00049	31.164	0.9942
	MO	113.912	119.047	0.00217	28.157	0.9979
	MR	88.332	94.339	0.00240	18.726	0.9991
	CR	257.766	263.157	0.00300	199.329	0.9998

ACRN3	MO	118.494	123.456	0.00255	35.804	0.9985
	MR	91.562	94.339	0.00383	32.109	0.9989

Looking carefully at the results listed in the two tables(16 and 17), we find the other way round was found in the pseudo first order equation, the application of the pseudo second order equation gave excellent linear relations. This was indicated by the values of correlations coefficients (R^2) which their values were about (0.998 - 0.9998), in addition to that, the values of the calculated adsorption capacity of straight lines slop were more compatible to the experimental values in the process of the adsorption systems under study, this leads to the indication that it is suitable to the kinetic equation (of the pseudo second order).

3: Elovich kinetic equation

The Elovich kinetic equation (equation 17) was applied on the experimental data for the adsorption of dyes under study, on the activated carbon. The results got were listed in the table(18) and they were represented graphically by the shown drawings (26,27,28,29).

(b) MO

(a)CR

(c) MR
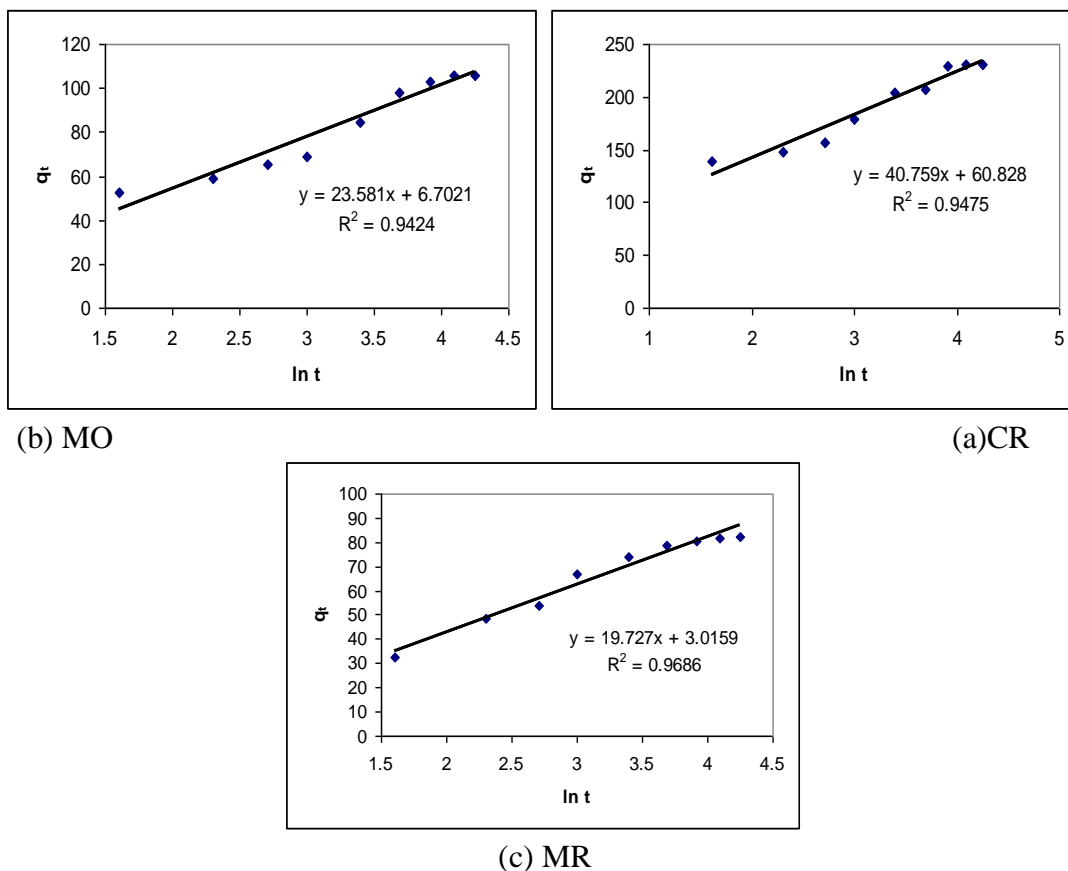
Figure (26): The relation between qt in opposite to lnt for the dyes by using the activated carbon prepared ACRO20

(b) MO

(a) CR
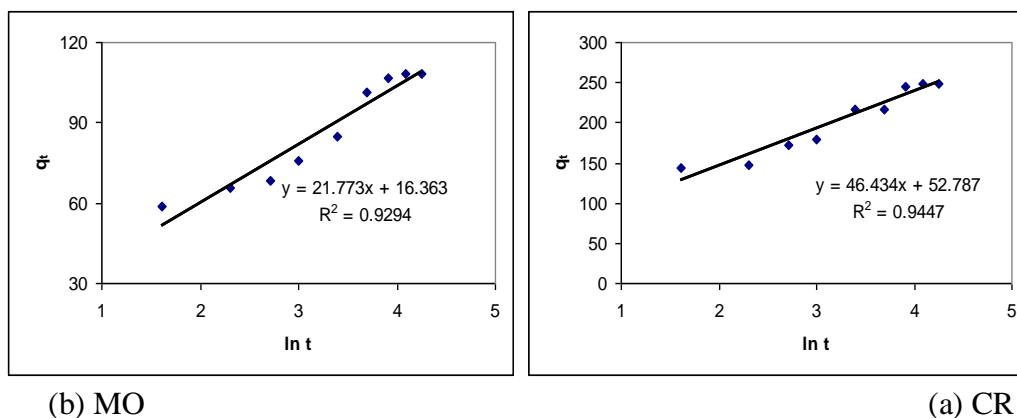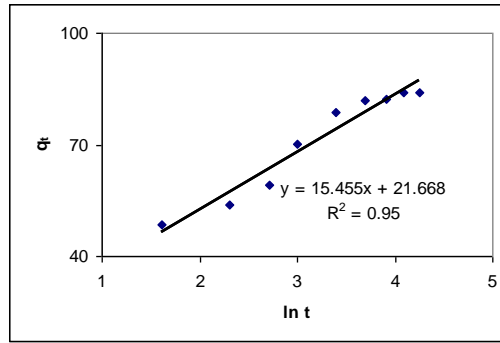
(c) MR

Figure (27): The relation between qt in opposite to lnt for the dyes by using the activated carbon prepared ACRO25
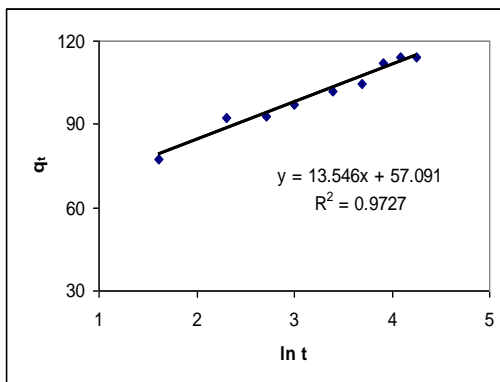
(b) MO
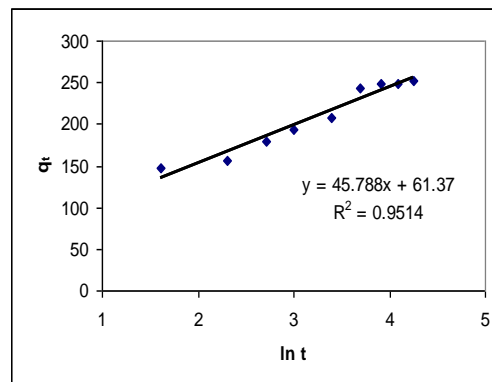
(a) CR
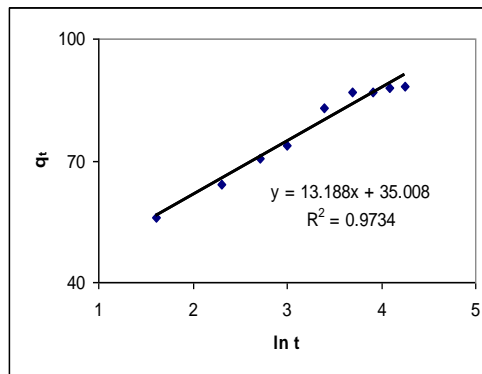
(c) MR

Figure (28): The relation between qt in opposite to lnt for the dyes by using the activated carbon prepared ACRN4
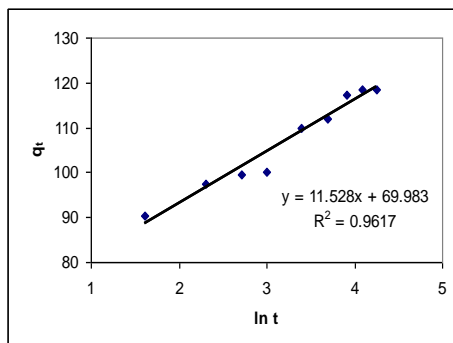
(b) MO
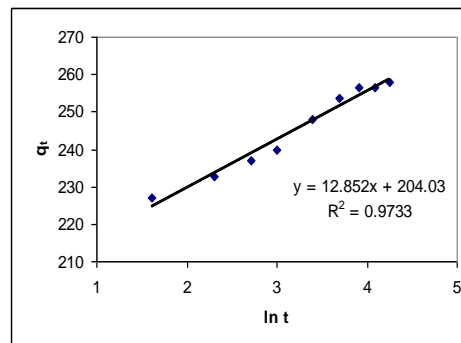
(a) CR
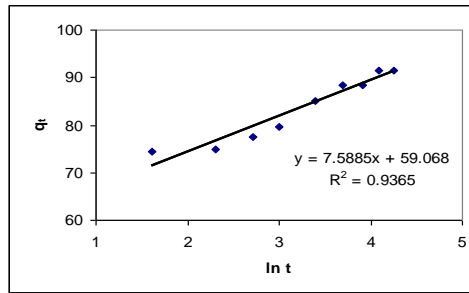
(c) MR

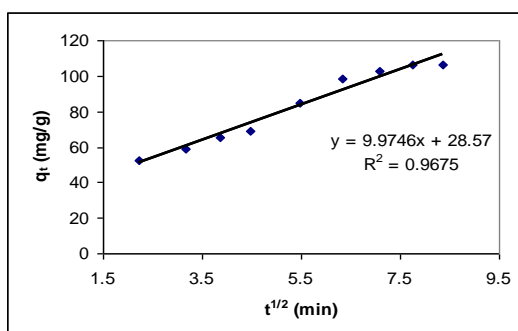**Figure (29): The relation between qt in opposite to lnt for the dyes by using the activated carbon prepared ACRN3**

Table (18): The values of Elovich constants (α, β) and the correlation coefficients which were got by applying them on the experimental data for adsorption, the quantity of the activated carbon: 0.01g and at 25C⁰

Type Active carbon prepared	dye	Conc.(mg/L)	$(g.mg^{-1}) \beta$	$(mg.g^{-1}.min^{-1}) \alpha$	R^2
ACRO20	CR	139.332	0.0245	181.537	0.9475
	MO	65.466	0.0424	31.337	0.9424
	MR	53.86	0.0506	23.027	0.9686
ACRO25	CR	139.332	0.0215	3.914E24	0.9447
	MO	65.466	0.0459	46.192	0.9294
	MR	53.86	0.0647	62.802	0.95
ACRN4	CR	139.332	0.0218	175.239	0.9514
	MO	65.466	0.0738	916.900	0.9727
	MR	53.86	0.0758	187.577	0.9734
ACRN3	CR	139.332	0.0778	100831764.7	0.9733
	MO	65.466	0.0867	4994.031	0.9617
	MR	53.86	0.1317	18235.256	0.9365

The results got by the application of Elovich equation(listed in the table 18) indicate that the primary velocity(α) is compatible to what has been noticed and got by the application of the pseudo second order equation.

4: **The intra particle diffusion equation**

According to the intra particle diffusion equation, the dyes under study will be transform from their aqueous solution to the activated carbon surface, then, they will intervene to the pores found on the carbon surface by the intra particle diffusion, accordingly, the adsorption process will go through more than one speed and its activated energy differentiate in harmony with each passing phase, thereby, the intra particle diffusion model should be the fourth kinetic model which should be used in studying the determining step for the velocity of selected dyes adsorption on the activated carbon. This can be done through the (equation 18). The results got listed in the table(19) and they were represented graphically by the showing draw in the figures(30,31, 32, 33).
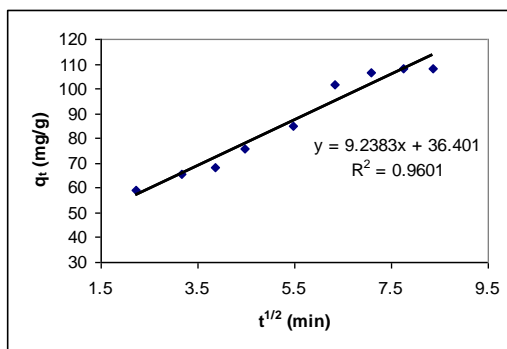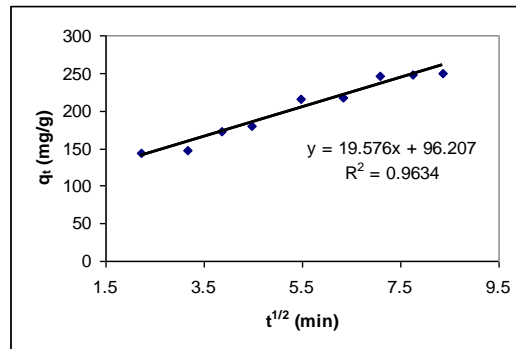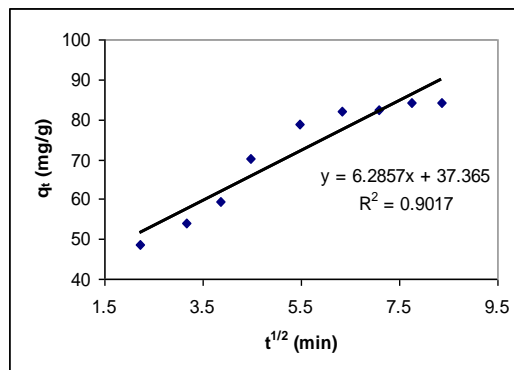

(b) MO
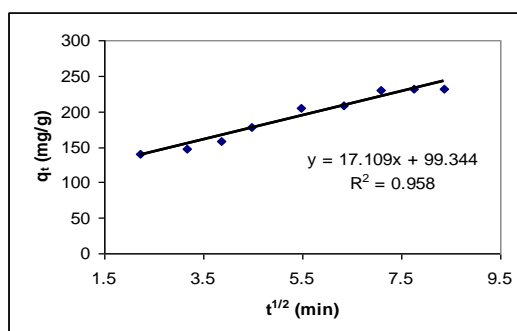
(a) CR
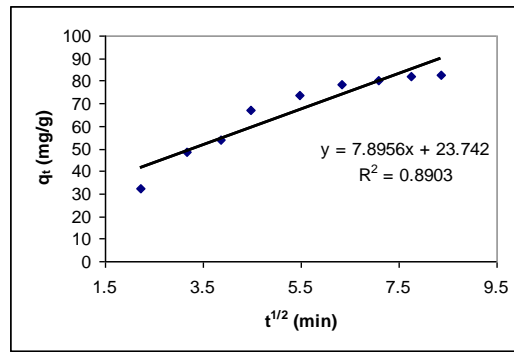
(c) MR

Figure (30): The relation between q_t in opposite to $t^{1/2}$ for the dyes by using the activated carbon prepared ACRO20
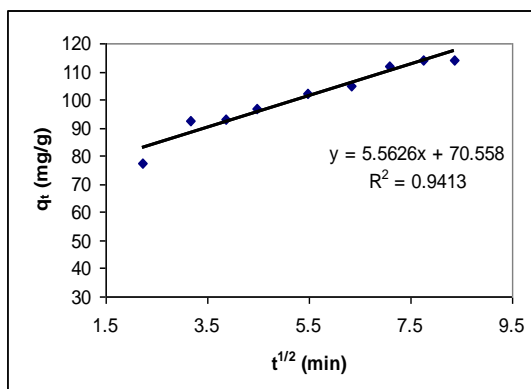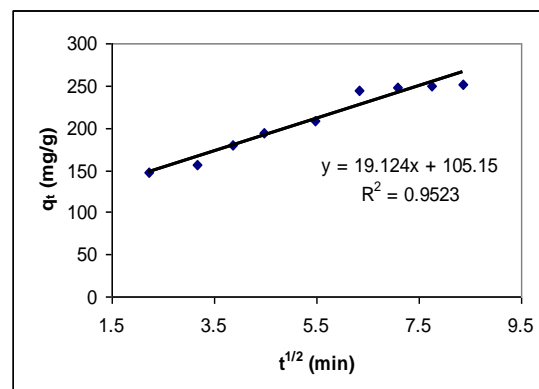

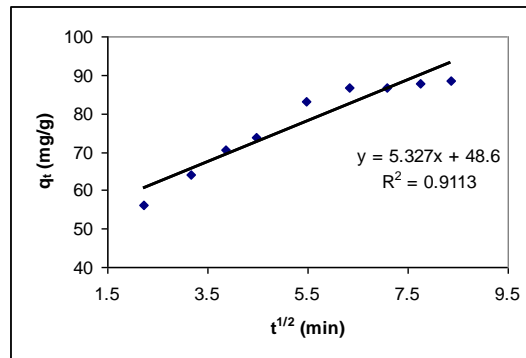(b) MO

(a) CR

(c) MR

Figure (31): The relation between q_t in opposite to $t^{1/2}$ for the dyes by using the activated carbon prepared ACRO25
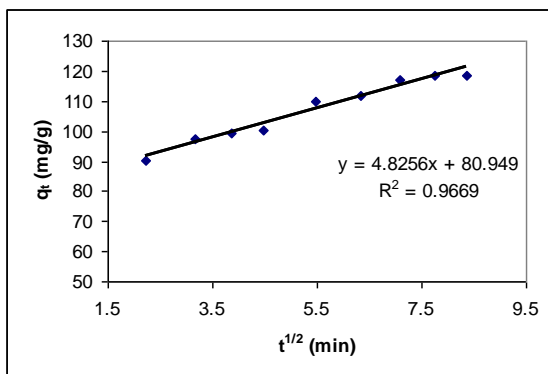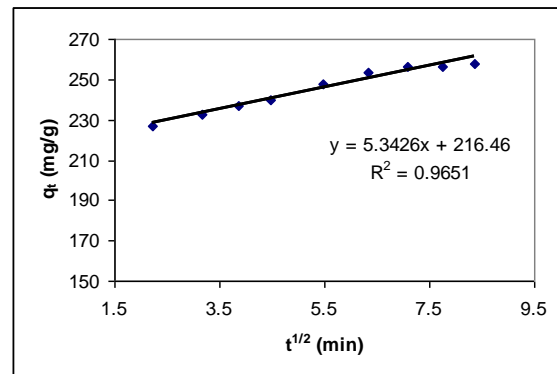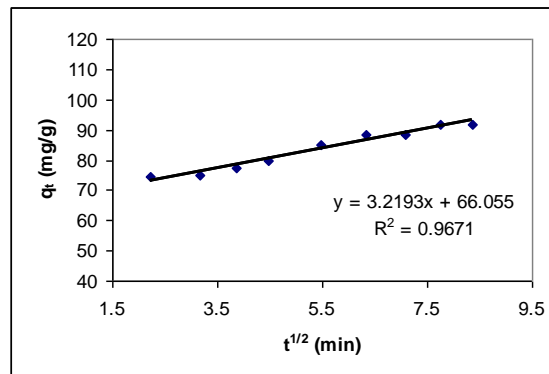

(b) MO

(a) CR

(c) MR

Figure (32): The relation between q_t in opposite to $t^{1/2}$ for the dyes by using the activated carbon prepared ACRN4

(b) MO

(a) CR

(c) MR

Figure (33): The relation between qt in opposite to t1/2 for the dyes by using the activated carbon prepared ACRN3

Table (19): The values of intra particle diffusion constants (k_{diff} , C) and correlation coefficients which were got by applying them on the experimental data for adsorption, the quantity of the activated carbon :0.01g and at 25C°

Type Active carbon prepared	dye	C_i(mg/L)	K_{diff}(mg.g^{-1}.min$^{-1/2}$)	C(mg/g)	R^2
	CR	139.332	17.109	99.344	0.958
ACRO20	MO	65.466	9.9746	28.57	0.9675
	MR	53.86	7.8956	23.742	0.8903
	CR	139.332	19.576	96.207	0.9634
ACRO25	MO	65.466	9.2383	36.401	0.9601
	MR	53.86	6.2857	37.365	0.9017

ACRN4	CR	139.332	19.124	105.15	0.9523
	MO	65.466	5.5626	70.558	0.9413
	MR	53.86	5.327	48.6	0.9113
ACRN3	CR	139.332	5.3426	216.46	0.9651
	MO	65.466	4.8256	80.949	0.9669
	MR	53.86	3.2193	66.055	0.9671

According to the results got in the table(19) and the figures got (30,31, 32, 33), the mechanism of the intra particle diffusion will form the only mechanism which is running the adsorption process, when the drawing of the relation between q_t in opposite to $t^{1/2}$ gives a straight line going through the original point. Because this does not happen, one can conclude that the process of intra particle diffusion plays a vital role in the process of dyes removal out of their aqueous solution by using the activated carbon prepared; but the experimental results suggest that they are not the only mechanism which is running and controlling on the dye adsorption.

Table (20): A comparison between the adsorption capability on the kinds of activated carbon prepared and the commercial activated carbon as for dyes from their aqueous solutions

Sample	Type Active carbon prepared	pH V:V Ethanol : Distillation Water %50	% Adsorption Dye CR pH=3.50 V:V Ethanol : Distillation Water %50	% Adsorption Dye MO pH=4.40 V:V Ethanol : Distillation Water %50	% Adsorption Dye MR pH=5.70 V:V Ethanol : Distillation Water %50
4	ACRO20	5.51	83.00	81.00	76.50
10	ACRO25	5.93	89.50	82.50	78.00
13	ACRN4	6.82	90.50	87.00	82.00
14	ACRN3	7.35	92.50	90.50	85.00
B.D.H*		4.36	78.00	77.00	71.50

We can notice of the results shown in the above table, that the capability related to the kinds of activated carbon prepared for adsorption dyes out of their aqueous solutions differentiate by depending on the chemical structure for dyes, but generally, they are higher than the capability of the commercial activated carbon for adsorption purposes.

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