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Kinetic and Thermodynamic study of The Adsorption Of Methylene Blue Over Magnetic Activated Carbon

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الخلاصة:

تتضمنت هذه الدراسة تركيب الحديد Fe^{+3} على الكاربون المنشط وعن طريق معاملة الكاربون المنشط بـ (0.25M) من كبريتات الحديديك المائية $Fe_2(SO_4)_3.5H_2O$ وقد استخدام الكاربون المنشط (المحضر) لأزالة صبغة Methylene blue في المحلول المائي . وكذلك دراسة حرارة الأ متزاز للصبغة على الكاربون المنشط وافترضت هذه الدراسة ان امتزاز هذه الصبغة على الكاربون المنشط هو تفاعل من الرتبة الثانية كاذبة ، بالإضافة الى دراسة تاثير التركيز ودرجة الحرارة والزمن والدالة الحامضية على الامتزاز وذلك للحصول على تفاصيل اكثر لأختيار الظروف المناسبة للأمتزاز و دراسة حركية وثيرموداينمكية هذا الامتزاز.

Abstract

The study involves preparation of magnetic activated carbon by treatment of the carbon with(0.25M) $Fe_2(SO_4)_3.5H_2O$ Carbon prepared was used for the removal of methylene blue dyes from aqueous solution. The study involved calculation of heat of adsorption of the dyes over the magnetic carbon. The study assumes that the adsorption of dyes over activated carbon is pseudo second order. Investigation of the effects of concentration, temperature, time and pH of the media were studied in detail to choose the suitable conditions for the kinetic and thermodynamic studies.

Introduction

Activated carbons are microporous carbonaceous materials were used for refining beet sugar and coloured materials which stimulated rapid growth in adsorption research. Many research works have been published in the activated carbon and its industrial applications.[1,2]

Activated carbon is applied to a group of porous materials formed mainly from carbon that exhibit a recognizable apparent surface area with large micropore volume.[3,4] They are solid with a wide variety of pores size and micropores. Activated carbon can be prepared in different forms such as powder, granule, pellet, fiber cloth and others.[5,6]

It can be prepared from a large number of sources such as palm shells, wood coconut shells, coals,carbon fibers and pitch. Activated carbon adsorbs molecules from both liquid and gaseous phase depending on the specific surface area,pore size distribution and surface oxygen functional group (also denoted as surface complexes). Activated carbon is a unique material in terms of its variable microporosities and amphoteric character. It is also essentially hydrophobic and adsorb species from aqueous solution apparently ignoring the presence of the water provided that the surface are relatively free of surface oxygen complexes[7].

The process of preparing activated carbon involving first pyrolysis of the materials and carbonization at high temperature. During this process the volatile fraction and low molecular weight products of pyrolysis are removed while the residual carbonaceous materials remained.

In the physical activation the samples are typically treated between 800-1100 ˚C with an oxidant gas, mainly CO_2 or steam, so that pores on the surface of the carbon are cleared [2].

Activated carbon also contains to some extent ashes derived from starting materials. Ash consist mainly of silica, alumina, iron, alkaline and alkaline earth metals [8].

Chemical activation offers well-know advantages over physical activation, which can be summarized as follows:

1) it uses lower temperatures and heat treatment times.
2) It is usually carried out in one stage.
3) the carbon yields obtained are typically higher.

On the other hand chemical activation has some disadvantages such as the need for washing stage after heat treatment and the more corrosive behavior of the chemical activation has been carried out using one of two activating agents: phosphoric acid or zinc chloride[9,10].

In the case of chemical activation with phosphoric acid, lignocellulosic material are preferred as precursors [11]. At low degree of activation, the activated carbons do not have highly developed areas and they are essentially microporous, where as at higher activation degrees, the surface area and the micropore volume increase, but there is also a remarkable increase in the mesopore volume and a widening of the micropore size distribution [12]. while in physical activation, in the case of activation with phosphoric acid, both high adsorption capacity and narrow micropore size distribution cannot be achieved, however, for activated carbons that need a well developed mesoporosity, for example, for gasoline removal, phosphoric acid is a very suitable activation method [13].

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries, colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. further more,many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.[14]

The material prepared was used to study the adsorption of selected water –soluble organic dyes the adsorption isotherms followed Langmuir, generalised Freundlich generalised Langmuir and Langmuir –Freundlich adsorption patherns: maximum adsorption capacities for a cridine orange, Bismarck brown, crystal violet malachite green, methyl green, nile blue, safranin O and Saturn blue LBRR 200 ranged between 34 and 59 mg.g^{-1} dry adsorbent: a change in pH value can increase the dye adsorption ferro fluid-modified sawdust is thus an interesting material for further study and potential application.

The study compared the efficiencies of two activated carbon for removing methylene blue dye from aqueous solutions using treated and untreated activated carbon. the activated carbon used in this study is a commercial product prepared by activation with an acidic agent, the other is treated activated carbon (TAC), which was prepared in our laboratory by activation of the commercial activated carbon (AC)with potassium hydroxide. It has been shown that KOH. activated carbon is essentially microporous with high surface area [15]. Magnetic separation is a promising technique for adsorption of difficult to handle samples. Magnetic nano and micro particales have already been applied in various area of biosciences biotechnology, and environmental technology. It used for example for separation of cells isolation and purification of proteins and peptides.

Application of magnetic particales are of special interest in relation to environmental technology Both small scale (analytical) and industrial – scale processes have been developed. Magnetic particales are helpful for preconcentrating target xenobiotics from large sample volumes to allow assay using chromatograghy or spectroscopy techniques [16].

In this study results obtained spectrophotometerically were discussed in the from of vant hoff and lagergreen equation. The work involves the adsorption of methylene blue from aqueous solution on the surface of natural adsorbent the concentration of dye was determind spectrophotometrically on the basis of relation between absorbance and concentration percent [17].

Experimental

1- **Drying of the activated carbon**

15 gm of powdered activated carbon of commercial BDH grade of a powdered form was dried in an oven at 120˚C for 4 hrs.The sample was kept closed for use in the next step.

2- **loading of iron in the form of Fe^{+3} over the active carbon**

15 gm of predried crbon sample was added to 10 gm of $Fe_2(SO_4)_3.5H_2O$ and added to 100 ml of distilled water.The mixture of carbon,ferrous sulfate and water was reflex for 21 hrs.the mixture was allowed to settle for another additional hour. The mixture was filtered and washed with deionized water till no acidity detected. The treated carbon was shiny in colour. The carbon was allowed to dry to constant weight at 150˚C.

Note: the sample must be kept in a desiccator under vaccum due to its high hygroscopcity character.

3- **Optimum activated carbon amount and dyes concentration to reach the equilibrium**

The study required to find out the best amount of the adsorbent and adsorbed in order to follow the colour changes from the beginning of the adsorption to the required time. A certain amount of activated carbon required was 0.02 gm on the other hand the concentration of methylene blue was 230 ppm to follow the adsorption.

4- **Study of the equilibrium required time**

The study involved preparation of six samples of the same concentration (230 ppm) from methylene blue the amount of carbon added to each sample is 0.02 gm and samples was shaked for (10-35) minute, The best time for the adsorption and equilibrium was found to be 30 minute.

5- **Effect of dye concentration**

Six samples of methylene blue were prepared by dilution in the range of (200-250) ppm. The amount of carbon added was 0.02 gm. The mixture was shaked for 30 minute and filtered directly. The spectra in the visible region for filterates were measured on Cecil CE 1011 speactrophotometer. The absorbance of each sample were used to calculate the percentage absorbed dyes.

6- Effect of temperature

The effect of temperature variation on the adsorption ability of carbon was studied using five samples (230 ppm) to which 0.02 gm of carbon was added. The mixture was shaked for 30 minutes at 10-35˚C using 5˚C increment after filteration. Absorbance was measured and percentage of adsorption was calculated.

7- Effect of pH

Effect of pH after determining the ideal condition (conc. Temp. and Time) was studied in which five samples having the same concentration were mixed separately with 0.02 gm of carbon. The mixture was shaked for the same time and at each pH. After adsorption was finished the absorbance measured and the percentage of adsorption was calculated

DISCUSSION

In this research work we aimed to change the porosity of the carbon surface and to increase its ability in the removal of minute amount of azo dyes from aqueous solution. The process involved treatment of a known weight of carbon with $Fe_2(SO_4)_3.5H_2O$ for 24 hours under reflux condition, after cooling to room temperature and washing thoroughly with distilled water.

The magnatised carbon was dried in an oven at 150˚C for 10 hours. The weight of sample was recorded and a noticeable increase was recorded (1.5%). The prepared carbon was used to study kinetic of the dyes adsorption and to calculate the thermodynamic parameters. The study required to vary the conditions in term of quantity of adsorbent, time, temperature and the suitable concentration of the dyes.

The study refers that the optimum a mount of carbon (0.02 g) and the best dye concentration (230 – 250 ppm). The optimum condition for adsorption is 25˚C and 30 minutes. The results of the applications of beers low for constructing the calibration curve for absorbance at λmax 661 nm in visible region is given Table 1 and Figure 1 below

Table 1: The absorbance of different concentration of methylene blue

Conc. ppm	Absorbance (nm)
20	0.149
40	0.298
60	0.462
80	0.596
100	0.754
120	0.894
140	1.040
160	1.172
180	1.341
200	1.501

The results in the Figure(1) indicate a linear equation suitable for calculation of the concentration in the study.

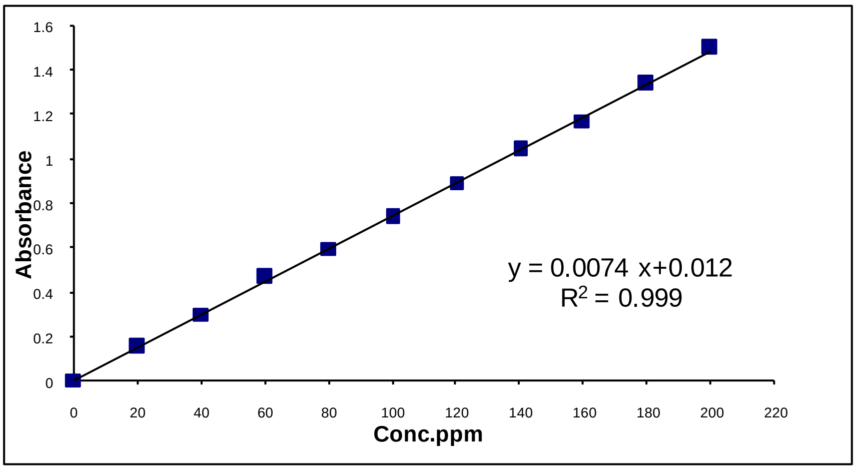

Figure 1: Standard calibration curve of the methylene blue at different concentration at 661 nm

The study revealed that the concentration below 200 ppm does not give any absorbance which lead us to used the concentration range of 200 - 250 ppm at λmax 661 nm. The results obtained are given in Table 2.

Table 2: Variation of concentration of the dye treated by activated carbon with the percentage adsorbed and adsorption capacity

Conc. of dye before adsorption (ppm)	Percentage of dye adsorbed	(q_e) Adsorption capacity (mg/g)
200	83.35	208.3
210	84.20	221.0
220	86.15	236.8
230	90.57	260.0
240	89.57	268.8
250	89.43	279.3
260	89.45	290.0

On the other hand changing the time from (2 -35)minutes indicates that, the adsorption of the dye is very fast in the first two minutes,then decreases gradually and reached to equilibrium after 35 minutes as shown in the Table 3.

Table 3: Effect of time on the adsorption of methylene blue.

Time (min)	Percentage of dye adsorbed	Adsorption capacity q_t (mg/g)
2	70.08	201.4
4	72.63	208.7
6	74.74	214.7
8	75.61	217.4
10	77.02	221.4
15	80.70	232.0
20	87.75	252.2
25	87.52	251.6
30	88.63	253.7
35	88.12	253.3

The effect of temperature on the adsorption of the azo dyes was carried out between (25-45 C°) and at time of equilibrium as given Table 4.

Table 4: Effect of temperature variation on the adsorption dye.

Temperature (C°)	Percentage of dye adsorbed	Adsorption capacity q_e
25	90.88	261.2
30	89.47	257.2
35	87.75	252.2
40	85.32	245.3
45	83.31	239.5

The results indicate that the adsorption of dyes over magnetized carbon is exothermic and the amount of dyes adsorbed decreased with increasing the temperature.

The effect of initial pH of the medium on the dyes adsorption indicates from Table 5 that as the acidity decreased the amount of dyes adsorbed increased. This may be explained the generation of positive charge on the amino group of the dyes and the positive charge of the sulfur. These two charges make repullsion off and reduce the adsorption

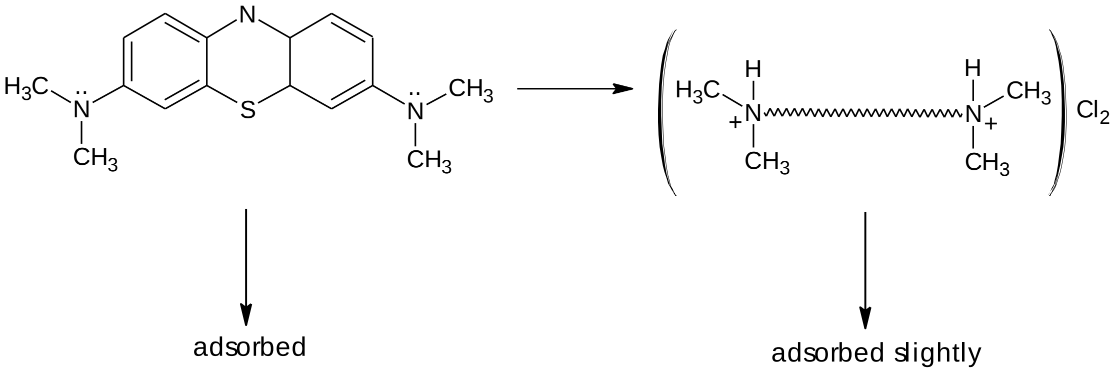

Table 5: Effect of pH on the adsorption dye

pH	Percentage of dye adsorbed	Adsorption apacity q_e
3	79.64	228.9
4	81.23	233.5
5.6	87.10	250.4
7	93.45	268.6
9	94.10	270.5

Kinetic study

In the kinetic study we recognized that, the adsorption of the dyes is very fast and require to be adjusted in term of concentration, time and temperature. The study used the same concentration of dyes amount to carbon at constant temperature, while the time is varied between zero-10 minute. The mixture was shaked for the given time. The remaining dye was filtered in each case and its absorbance was determined.

In order to study the adsorption kinetic over magnetised activated carbon, the amount adsorbed was determined between (2-10 minutes) as shown in Table 6.

Table 6: Effect of time (2-10) min. on the adsorption

Time (min)	Percentage of dye adsorbed	Adsorption capacity at equilibrium q_e	Adsorption capacity at variation time(q_t)
2	70.08	253.7	201.2
4	72.63	253.7	208.7
6	74.74	253.7	214.7
8	75.61	253.7	217.4
10	77.02	253.7	221.3

By using the lagergren first order and pseudo-second order rate equations that have been most widely used for the adsorption of an adsorbate from an aqueous solution, which are expressed by the equations

$$\text{Ln}\,(q_e - q_t) = \text{Ln}\,q_e - k\,t \qquad \text{Lagergren first order equation}$$

$$\frac{t}{q_e} = \frac{1}{kq_{e^2}} + \frac{1}{q_e}t \qquad \text{second order equation}$$

where q_e and q_t are the amount of dye adsorbed per unit unit mass of the adsorbent (in mg g^{-1}) at equilibrium time and time (t) respectively, and k is the rate constant. The q_e can be calculated by the equation

$$q_e = \frac{Ci-Ce}{m} * \frac{V}{1000}$$

where Ci is the inital dye concentration (mg/L), Ce the concentration of dye at equilibrium(mg/L), m the amount of adsorbent (g) and V the solution volume(mL).

Figures 2 and 3 show the Lagergreen first order and pseudo-second order plots, respectively. As shown, the pseudo-second order plot gives a straight line with correlation coefficient, R^2 =0.999 and k=0.016(g.mg^{-1}

min^{-1}), indicating that the applicability of the pseudo-second order equation was the best result as compared to the Lagergreen first order plot with R^2 =0.982 and k=0.059 only as well as the values of both (q_e) experimental and theoretical is almost similar. the value of (q_e) theoretical (250) from the graph and (q_e) experimental (253.7).

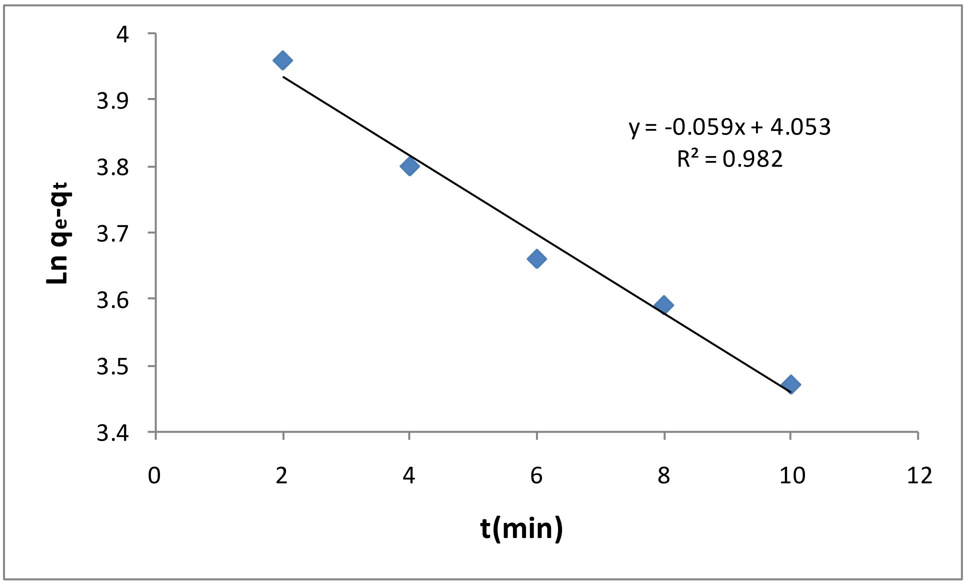

Figure 2: Lagergreen first order rate plot for methylene blue adsorption by magnetic activated carbon

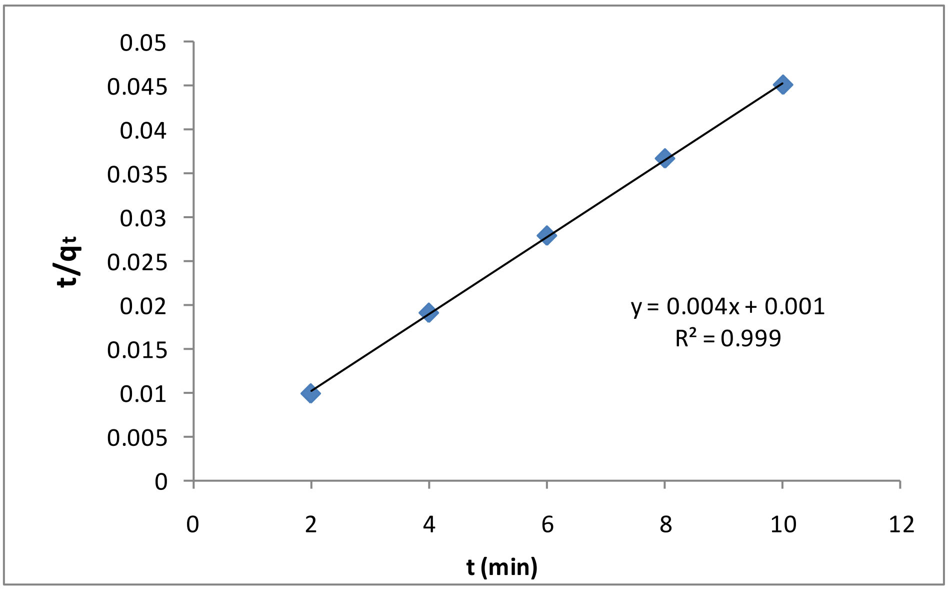

Figure3 Pseudo second order rate plot for methylene blue adsorption by magnetic activated carbon

Thermodynamic study

Calculation of the thermodynamic parameters for the adsorption of the dyes over activated carbon requires change the temperature between

(298- 318 C°). The equation used in the calculation of ΔH was (Vant Hoff equation) by drawing equilibrium constant resus the temperature variation as given in the Figure 3.

$$\text{Ln } K = \text{Ln } k_o - \frac{\Delta H}{RT} \qquad \text{(Vant Hoff equation)}$$

K = Equilibrium constant
k_o =Intercept
ΔH = Enthalpy of the reaction
R = 8.314($J.K^{-1}.mol^{-1}$)
T = (273+°C)

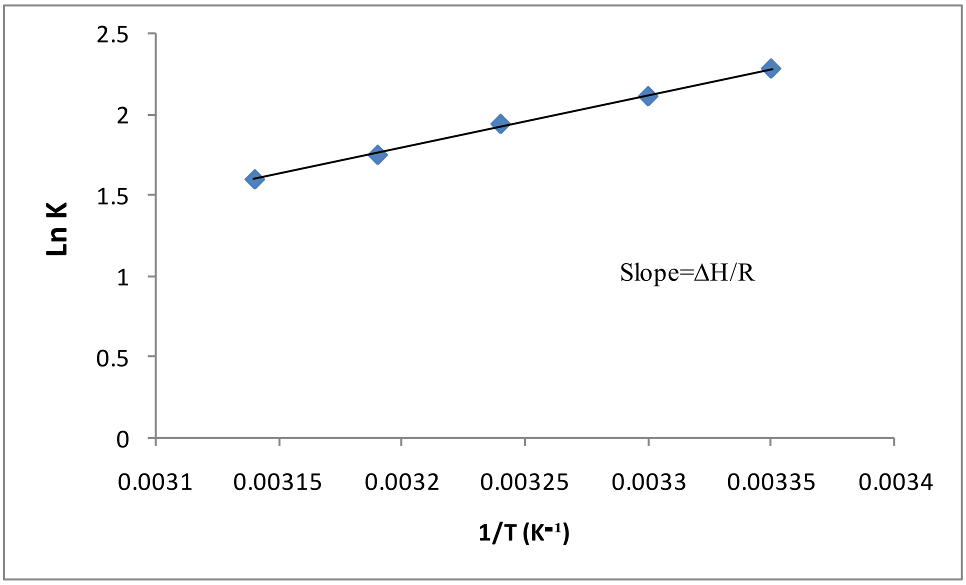

Figure 4: The relationship between Ln equilibrium constant and reciprocal of temperature in Kelvin.

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

$$\Delta G^\circ = - R\,T\,\text{Ln } K$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

The values of the equilibrium constant, ΔH°, ΔG° and ΔS° enthalpy of the reaction are given in Table 7.

Table 7: Values of thermodynamic parameters for adsorption of methylene bule dye.

T (Kelvin)	K	ΔH° (KJ.mol^{-1})	ΔG° (KJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})
298	9.86	-28.059	-5.648	75.20
303	8.33	-28.059	-5.315	75.06
308	7.02	-28.059	-4.967	74.97
313	5.81	-28.059	-4.589	74.98
318	4.99	-28.059	-4.250	74.87

The results of Table 7 indicate that, the adsorption of the dye is exothermic on magnetised carbon which is refer to positive charge on the carbon and the negative charge on the dyes.

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