Study of Kinetic and Thermodynamic Parameters Related to the Adsorption of Azo Dyes Orange-G over Alum Modified Activated Carbon

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Abstract

The study involves preparation of Aluminised activated carbon by treatment of the carbon with(0.1M)Alum ($KAl(SO_4)_2.12H_2O$). carbon prepared was used for the removal of Orange-G dyes from aqueous solution . The study involved the adsorption isotherm of the dyes over the aluminized carbon . The study assumes that the adsorption of dyes over activated carbon is pseudo first order Investigation of the effect of concentration, temperature, time and pH of the media was studied in detail to choose the suitable condition for the kinetic and thermodynamic studies .

الخلاصة

تتضمن هذه الدراسة تركيب الالومينيوم على الكاربون المنشط وعن طريـق معاملـة الكـاربون المنشط بـ(0.1M) من شب البوتاسيوم ($KAl(SO_4)_2.12H_2O$) وتم استخدام الكاربون المنشـط المحضـر لأزالة صبغة Orange-G في المحلول المائي . و كذلك دراسة حرارة الأمتزاز للصـبغة علـى الكـاربون المنشط كما افترضت هذه الدراسة ان امتزاز الاصباغ على الكاربون المنشط هو تفاعل من الرتبـة الاولـى كاذبة وقد تم دراسة تاثير التركيز ودرجة الحرارة والزمن والدالة الحامضية على الامتزاز وذلـك للحصـول على تفاصيل اكثر لأختيار الظروف المناسبة للأمتزاز و دراسة حركية وثيرموداينمكية هذا الامتزاز.

Introduction

Activated carbon is a collective name for a group of porous carboneous materials that exhibit appreciable surface area and micropores[1-4]. They are solid with a wide variety of pore and micropore sizes distribution .It can be prepared in different forms such as; powder , granules, pellets, fibers, cloths…..etc and can be used for many different applications for example gas-phase treatment and energy storge[5-7].

Activated carbon can be obtained from a large number of starting materials that could be a carbon precursor, which include petroleum residues, palm shells, wood, coconut shells, coals and pitch[8]. These materials are first pyrolyzed and carbonized at several hundred celcius degree. During this process the volatile fraction and low molecular weight products of pyrolysis are removed. The residual carbon materials were obtained. The resultant carbon rich materials were further activated by using oxidizing agents such as steam at high temperature or carbon dioxide in which the pores are formed as a result of activation. The yield of activated

carbon from raw material is in most cases less than 50% and sometimes below 10% [9-11].

Carbonization and activation can also be performed using inorganic chemicals such as zinc chloride, phosphoric acid …..etc., which is known to have a catalytic effect on the pyrolytic condensation. This sort of activation is termed as physical activation. Chemical activation has some advantage over physical activation interm of temperature and time. On the other hand chemical activation has some disadvantages such as corrosion and large amount of washing water. However, activation , which is either physically or chemically is not well understood yet and most of them are based on suggestions [12,13].

The presence of various functional groups on the carbon surface depends on the nature of the carbon precursor and the activation method employed in the manufacturing process. Furthermore, special post treatment can be used to modify the surface resulting in new surface functional group[13]. Over the last few decades many studies have been devoted to the characterization and evaluation of these centers by many analytical methods of varying degrees of sophistication [14]. The surface character is determined by the kind and the amount of the various heteroatom-containing functionalities and may be very complex (i.e-, phenolic, carboxylic, carbonylic, etheric, quinones and lactones). To adjust these properties for efficient and effective chromatographic separation special attention has been paid to structural complexity of carbonaceous materials, their heterogeneity as well as the diversity of the application. Activated carbon also contains to somextent ashes derived from starting materials. The mount of ash ranges from 1% to 5% . Ash consist mainly of silica, alumina, iron, alkaline and alkaline earth materials[15].

The functions of these ashes are not quantitatively clarified.

Adsorption from solution is relatively simple as no volume changes are involved. Modern analytical techniques can be easily adapted to measure concentration changes in solution during adsorption. Competitive adsorption may occur between the solvent and the solute in the same extraction process. Adsorption from solution may be further complicated because the solute may change chemically. On the other hand the solute concentration may change in the solution, thus concentration of an acidic molecule is a function of the pH of the solution due to both the non dissociated molecules and an associated ions[16].

Activated carbon is used to prevent the industrial pollution caused by dyes and especially azo dyes and their components. Adsorption of methylene blue from aqueous solution on the surface of activated carbons was accomplished under the optimized conditions of temperature, concentration , pH , duration time and quantity of adsorbent .

The concentration of dye was determined spectrophotometrically on the basis of the relation between absorbance and percent concentrations. At acertain wave length ,adsorption before and after treatment gives the amount of dyestuff separated from effluent. The results are treated using the Langmuir and Freundlich isotherm. The values of activation energy , enthalpy change and entropy change were also evaluated [17] .The saw dust activated carbon was prepared and used to study the adsorption of the water- soluble organic dyes. The maximum adsorption capacities for a cridine orange, Bismarck brown,

crystal violet, malachite green, methyl green, nile blue, safranin and Saturn blue LBRR 200 ranged between 34 and 59 mg g^{-1} dry adsorbent. The adsorption followed both freundhich and Langmuir adsorption isotherms. A change in pH value can increase the dye adsorption on modified sawdust Thus it is interesting material for further study and potential applications[18].

To the best of our knowledge no such work has been carried out before on the adsorptive property of some azo dye(orang G) over Alum-treated activated carbon.

Experimental

1. Drying of the activated carbon

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

2. Loading of aluminum in the form of Al^{3+} over the active carbon

25 gm of predried carbon sample was added to 200ml of 0.1M alum($KAl(SO_4)_2.12H_2O$). The mixture of carbon and alum solution was shaked mechanically for six hours at room temperature (25-30°C). The mixture was allowed to settle for another additional hour. The mixture was filtered and washed with nonionic water till no acidity detected . The treated carbon was shiny in colour. The carbon was allowed to dry to constant weight at 80°C (i.e the melting point of the alum). The weight of the sample (25gm)was increased to 29.1gm.

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

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

The kinetic and thermodynamic study require to find out the best amount of the adsorbant and adsorbet in order to follow the colour changes from the beginning of the adsorption to require time a certain . The amount of activated carbon required was 0.1gm, on the other hand the amount of Orange-G was 80ppm to follow the adsorption.

4. study of the equilibrium required time

The study involved preparation of nine samples of the same concentration (80ppm)from Orange-G. The amount of carbon added to each sample is 0.1gm and sample was shaked for (10-90) minute, the best time for the adsorption and equilibrium was found to be 60 minute.

5.Effect of dyes concentration

Nine samples of the Orange-G dye were prepared by dilution to 110-50ppm. The amount of carbon added was 0.1gm. The mixture was shaked for 60 min and filtered directly. The spectra in the visible region for filterates were measured on Cecil CE 1011 spectrophotometer. The absorbance of each sample were used to calculate the percentage absorbed dye.

6. Effect of temperature

The effect of temperature variation on the adsorption ability of carbon was studied using seven samples (80ppm), to which 0.1 gm of carbon was added The mixture was shaked for 60 minutes at 15-45°C, using 5°C increment, After filtration, absorbance was measured and the percentage of adsorption was calculated .

7. Effect of pH

The effect of pH after determining the ideal conditions (Conc., Temp., and Time), was studied in which five samples having the same concentration were mixed separately

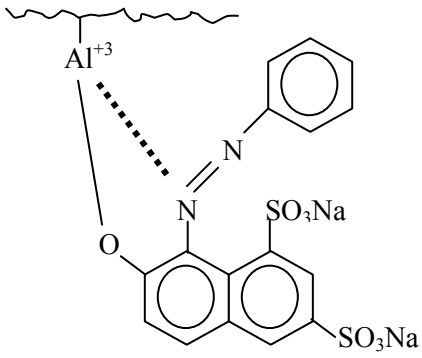
with 0.1 gm of carbon . The mixture was shaked for the same time and at each pH. After adsorption was finished, the absorbance measured and the percentage of adsorption was calculated .

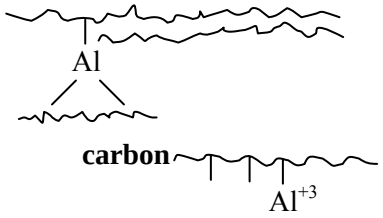
8. Kinetic study

In the kinetic study we recognize 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 variant 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. From the literature the adsorption of dyes on active carbon is considered as a pseudo first order reaction .

Discussion

The work involves treatment of commercial activated carbon (BDH grade) with potassium alum($KAl(SO_4)_2.12H_2O$). The treatment process was conducted through physically mixing of the carbon with 0.1M solution of the alum for 6hr. After filteration of the excess alum and thoughly washing with deionized water the prepared sample was dried at room temperature for 24hr and then at 75-80°C. The difference in the weight of sample before and after treatment was determined 4.10 gm. In this treatment the metal ion Al^{3+} is expected to enter the pores of the carbon and to make stable chellate to the dyes as in,





The aluminized activated carbon was used in the kinetic and thermodynamic study of Orange-G adsorption.

Before studying the kinetic of dyes adsorption, the dyes used was recrystalised from ethanol. The suitable concentration used in the adsorption was 50-110 ppm at 25°C(water bath temperature). The result of the adsorption is calculated from standard curve of orange G dyes at 478nm. The results are given in Table 1 and Figure 1.

The data of the adsorption of orange-G at different concentration follow a linear first order equation that of the type y=0.0403X + 0.0211.

The results in the table indicate a fast adsorption of the dye between 5-30 ppm Table 2.

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

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

The results indicate that 50-60 minutes is the best time for equilibrium of the dye adsorption more over , the effect of increasing temperature was investigated between 15-45°C with 5°C increment , the best temperature

for the dyes adsorption is 25°C to give 85.68%.the adsorbed dyes below 25˚C increase which may be due to the formation of hydrogen bonding and some electrostatic adsorption forces .these forces started to decay after 25˚C due to the exothermic nature of the adsorption process and the energy added by increasing the temperature The results are given in Table5

ΔH of adsorption process was found by employing (vant hoff equation) from

Drawing equilibrium constant to the temperature variation study .

$$\text{Ln } K = \text{Ln } k_o \frac{\Delta H}{RT}$$

K^- = Equilibrium constant

k_o =Intercept

ΔH = Enthalpy of the reaction

R = 8.314(J.k^{-1}.mol^{-1})

T = (273+°C)

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

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

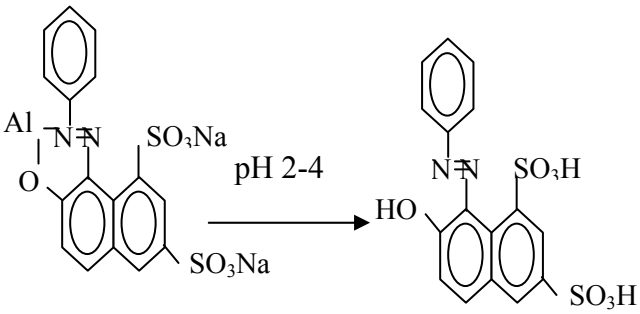
On the hand, ΔS was calculated using the following equation

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

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

The results of the equilibrium constant ,Δ H˚, ΔG˚, and ΔS˚ enthalpy of the reaction are given in Table 6 and Figure 2 explain the calculate of enthalpy from equilibrium constant.

Study of the pH effect of media on the adsorption of orange G indicates that increasing the acidity from 6.25 to 2 improves the adsorption of the dye in which we expect the following conversion.



However increasing the basisty from 6.25 to 11 shows great reduction in the adsorption of the dye which may be due to the formation of $Al(OH)_3$ salt, and could be reached to the solution that may prevent adsorption . the results for the study is given in table 7.

After variation of temperature , concentration and pH of the dye for the purpose of thermodynamic study we started studing the kinetic of the adsorption of dyes over aluminized activated carbon and noted that the adsorption of over the modified carbon is very fast at the interval of 1-10 min and the amount adsorbed after that start to slow down which may be due to the formation of second layer or multilayer. The results for the study is give in Table 8.

by employing largergreen equation and plotting the remained concentration of the dyes with time as given in the Figure 3.

Ln (a-x) = Ln a - k t equation largergreen

From the figure the value of the rate constant(k) is calculated,

k=7x10^{-2}sec^{-1}

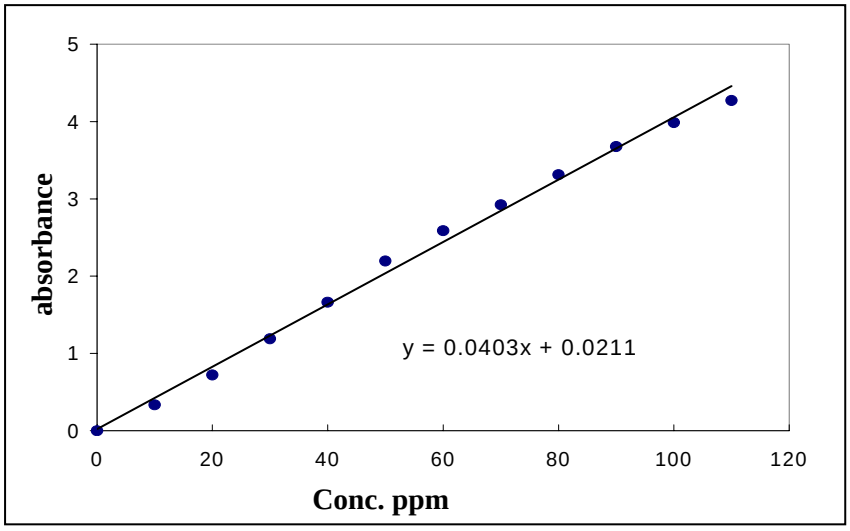
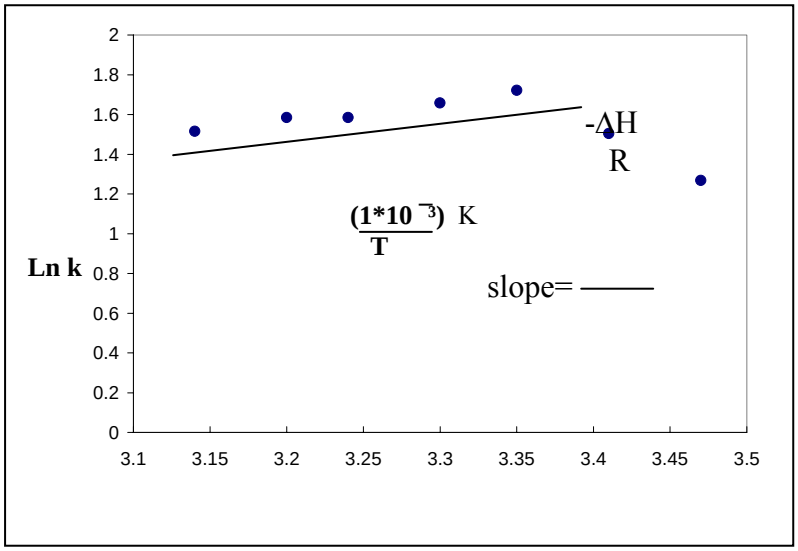


Figure1 standard calibration curve of the orange-G at different concentration at 478nm.



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

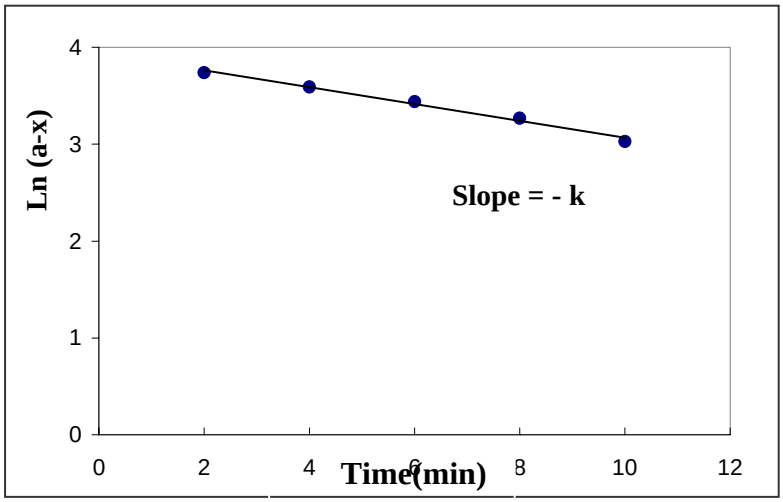


Figure 3 The relationship between time and Ln(a-x)

Table 1 The absorbance of different concentration of orange-G

conc. ppm	absorbance
10	0.336
20	0.721
30	1.190
40	1.663
50	2.196
60	2.588
70	2.923
80	3.312
90	3.676
100	3.986
110	4.272

Table(2): effect of concentration of orange-G over activated carbon at constant temperature (25˚C)and time(60min).

Primary conc. ppm	Finally conc. ppm
5	Zero
10	Zero
15	Zero
20	Zero
25	Zero
30	Zero
50	3.70
55	4.01
60	4.26
65	4.54
70	4.81
80	6.45
90	10.09
100	13.99
110	21.88

Table3 variation of concentration of the dyes treated with activated carbon and the percentage adsorbed .

Conc. Of dyes before adsorption(ppm)	Percentage of dye adsorbed
50	93.60
55	93.65
60	93.81
65	93.83
70	93.87
80	94.33
90	89.36
100	86.53
110	83.65

Table 4 effect of time on the adsorption of orange-G

Time min.	Percentage of dye adsorbed
10	79.28
20	83.00
30	83.03
40	84.64
50	85.39
60	85.39
70	86.38
80	86.38
90	86.38

Table 5 effect of temperature variation on the adsorption of dye.

Temperature	Percentage of adsorption
15	77.22
20	81.42
25	85.68
30	84.78
35	83.20
40	83.16
45	82.11

Table 6 values of thermodynamic parameters for adsorption of orange-G dyes adsorption

T (Kelvin)	K	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1} kel^{-1})
288	3.56	-3038.5	-9200.8	-21.39
293	4.52	-3663.7	-9200.8	-18.89
298	5.60	-4266.3	-9200.8	-16.55
303	5.25	-4176.7	-9200.8	-16.58
308	4.88	-4058.7	-9200.8	-16. 69
313	4.74	-4047.2	-9200.8	-16.46
318	4.55	-4005.4	-9200.8	-16.33

Table 7 effect of pH on the adsorption of dye.

pH	Percentage of adsorption
2	95.71
4	89.61
6.24	86.53
9	80.72
11	27.77

Table 8 effect of time variation on the amount of dye adsorbed to study the kinetic.

Time min	Percentage of adsorption
2	57.50
4	63.70
6	68.71
8	73.43
10	79.28

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