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Kinetic study of adsorption methylene blue dye from aqueous solutions using activated carbon from starch

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ABSTRACT

In this article efficiency of activated carbon as a potent adsorbent of cationic dyes present in waste water was studied in this research. Activated carbon (AC) from starch was used to adsorb methylene blue (MB) from an aqueous solution. Various parameters such as adsorbent concentration, temperature, initial dye concentration, contact time, and pH were investigated and the optimum parameters were determined based on the experimental outcomes. The extent of methylene blue removal increased with the increased in contact time, adsorbent mass, solution pH and amount of adsorbent used. Thermodynamic parameters like the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also determined and they showed that the adsorption process was feasible, spontaneous, and exothermic in the temperature range of 293–333 K. The experimental equilibrium data were analyzed using the isotherms of Langmuir, Freundlich, and Tempkin. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes.

1. Introduction

Dyes have long been used in the dyeing, paper industries, printing, textiles, plastics, leather, cosmetics, pharmaceuticals and agri-food industries, but the effluents discharged by these industries pose certain risks and problems environmental [01]. These industries have shown a significant increase in the use of synthetic dyes as a coloring material. Since dyes have a synthetic origin and complex aromatic molecular structures, they are inert and difficult to biodegrade when discharged into waste streams [02].

The removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on biodegradation alone [03]. The Methylene blue has been studied because of its known strong adsorption onto solids, and it often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions [04]. Conventional wastewater treatments such as chemical coagulation, activated sludge, trickling filter, carbon ads orption and photo-degradation were used for the removal of dyes [05].

Many physicochemical methods have been tested, but only that of adsorption was considered to be superior to other techniques [06]. Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency, and effectiveness than other techniques [07-09]. This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations [10]. Adsorption is by nature a surface phenomenon, its performance being strongly related to

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the unique properties of specifically designed sorbent material. Adsorption process can be a physical adsorption which involve only relatively weak intermolecular forces, and chemisorptions which involve the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent [11].

Activated carbons are the most popular adsorbents used for the removal of toxic substances from water and due to its high surface area, porous structure, high adsorption capacity, special surface reactivity, good corrosion resistance and its inert nature, and stability over a wide pH range [12]. Therefore, development of activated carbon from comparatively low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability and ability to treat dyes in more concentrated forms [13-14]. In general, preparation of activated carbon is commonly realized by physical activation process or chemical activation process. Activated carbon is the most common adsorbent for the removal of many organic and inorganic contaminants [15]. The production of activated carbon consists of two phases: Carbonization and Activation [16].

In the present study, detailed are carried out to remove this dye by adsorption technique using activated carbon as an adsorbent. Various parameters affecting adsorption process, such as contact time, adsorbent concentration, initial dye concentration, temperature and pH were investigated. In addition, kinetic parameters were also calculated to determine adsorption mechanism was fitted into adsorption isotherms in order to give the best fit correlation.

2. Materials and methods

2.1. Adsorbate

The cationic dye, methylene blue (MB) was used as an adsorbate in this study of very high purity. It has the molecular formula $C_{16}H_{18}N_3SCl$ and the molecular weight of 319.85 g/mol. The chemical structure of MB is shown in Fig. 1. Double distilled water was employed for preparing all the solutions and reagents.

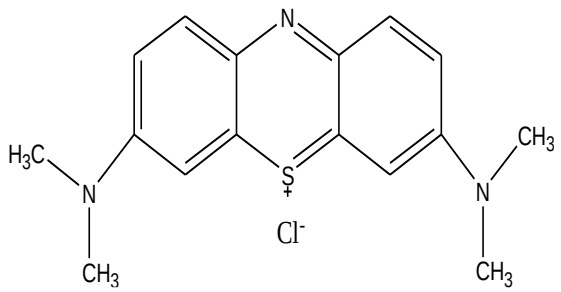

Figure 1. The structure of methylene blue.

2.2. Preparation and characterization of activated carbon

Starch is used for the preparation of activated carbon in this study. It was carbonized at 500 ºC for two hours in a horizontal tubular furnace under flow (20º/min) nitrogen. 10 g of the coal obtained by carbonization were mixed with 20 g of NaOH and 100 ml of distilled water and stirred for two hours. The mixture is put in an oven for 4 hours at 130° C, the product is then placed in the same calcination furnace, under nitrogen flow at 400° C, with a heating rate of 20° C and maintained at this temperature for 1 hour and a half. The resultant activated carbon was cooled at room temperature and was washed with Chlorydric acid 0.1 M then several times with hot distilled water. The material was then dried at 110 ºC for 24 hours.

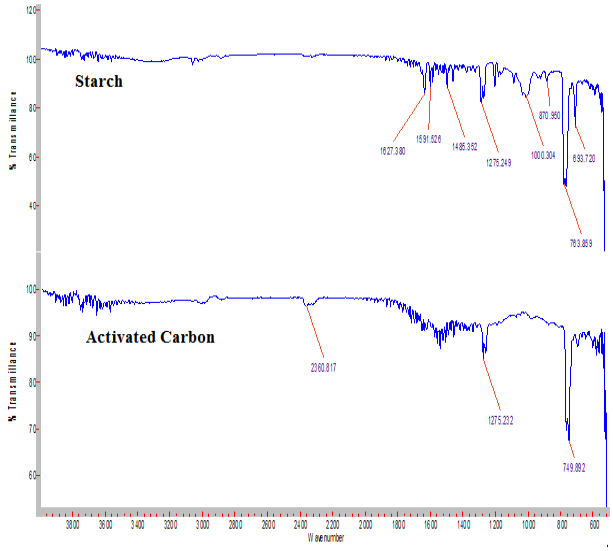

Figure 2. FT-IR spectra of Starch and Activated Carbon

Fig. 2 shows the FT-IR spectra of the Starch and Activated Carbon. When comparing the two spectra, we can show the disappearance of many absorption bands in the activated carbon spectrum as a result of carbonization and activation process (Fig.2). This suggests the decomposition of these groups and subsequent release of their by-products as volatile matter by chemical activation at high temperature. In the spectra of starch, the peaks at (870.950, 763.859 and 693.720) 1/cm are related to the C-O-H vibration. The peak located at 1000.304/cm assigned to C-O-C elongation, and the peak at 1275.249/cm are assigned to CH_2, CH deformation. In the FT-IR of activated carbon, the peak located at 749.892/cm related to the aromatic CH and the peak observed at 1275.232/cm corresponds to the existence of C-O esters, and the band at 2360.817/cm, correspond to CO_2 elongation.

2.3. Batch adsorption studies

A stock solution of methylene blue was prepared by dissolving its 1.0 g/L distilled water. The stock solution was diluted accordingly to obtain fresh solutions of desired concentrations.

To determine the dye concentration, 0.10 g of activated carbon were stirred with 20 mL of MB concentration of

200 mg/L for 90 min.

The remaining concentration of methylene blue was determined by measuring the absorbance at 665 nm using a UV/Visible spectrophotometer (OPTIZEN 1412V). The removal efficiency was calculated using the equation:

Removal efficiency (%) = $[(C_0-C_e)/C_0] \times 100$

Where, C_0 = Concentration of methylene blue in the sample solution before treatment C_e= Concentration of methylene blue in the sample solution after treatment.

3. Result and discussion

3.1. Effect of adsorbent mass

The effect of the mass of active carbon on the adsorption of methylene blue has been carried out for six different mass (25, 50, 75, 100, 125 and 175 mg) in 20 mL of the same particle size. The removal efficiency of methylene blue dye is also graphically shown in fig.3. That the MB removal increased sharply with an increased in the adsorbent mass from 20 to 100 mg. This may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents [17]. However, no significant changes in removal efficiency were observed beyond 100 mg adsorbent mass.

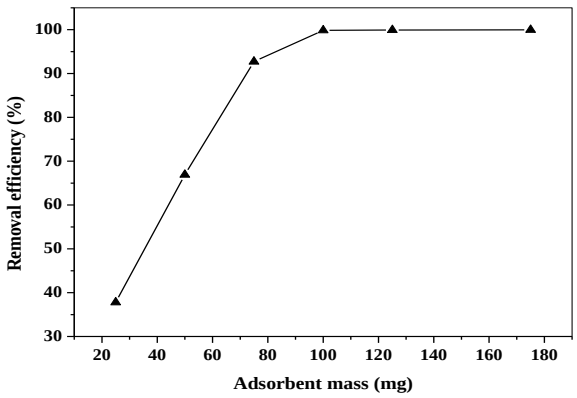

Figure 3. Effect of adsorbent mass on methylene blue removal.

3.2 Effect of initial dye concentration

The removal efficiency is highly dependent on the initial concentration of solution of adsorbate. The adsorption studies were investigated at 293.15K the concentration range of 100, 200, 400, 600, 800 and 1000 mg/L. The results are shown graphically given in fig.4.

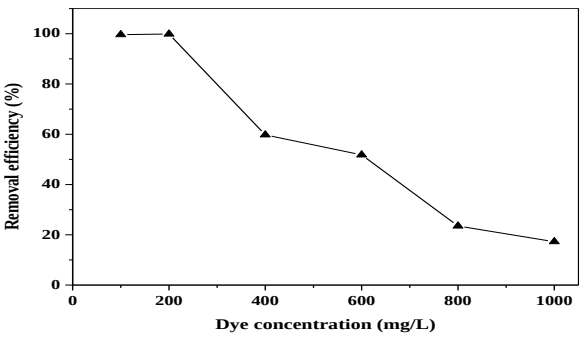

Figure 4. Effect of initial concentration on adsorption of MB with CA.

The total accumulation of methylene blue increased with increasing initial concentration was probably due to more contact of adsorbent sites with methylene blue [18]. The initial concentration 200 mg/L was chosen for the next method optimization work.

3.3. Contact Time Effect

In adsorption studies, effect of contact time plays vital role irrespective of other experimental parameters effecting adsorption kinetics. Adsorption experiments were carried out for different contact time.

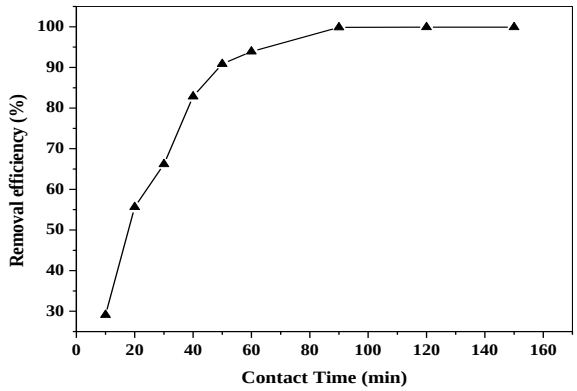

Figure 5. Effect of Contact Time in Methylene Blue Removal.

The extent of dye removal by activated carbon increased with the increased of contact time, the results are shown in figure 5. The removal of methylene blue by adsorption using activated carbon was found to be rapid at the initial period of contact time between 10 to 50 min and then become stability with the increase of contact time. This is due the strong attractive forces between the dye molecules and the adsorbent, fast diffusion onto the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium. [19]. Based on these results, ninety minutes (99.85%) was taken as the equilibrium time in kinetic adsorption experiments.

3.4. Effect of pH

The effect of pH on the removal of methylene blue in the presence of activated carbon varied between 2.7 and 10.5, as it can be seen in Figure 6. When initial pH of the dye solution was increased the percentage removal increased from lower to higher.

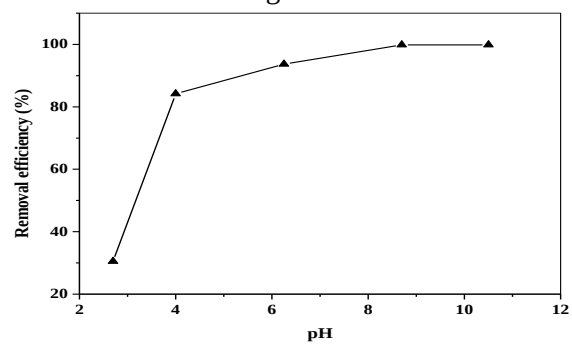

Figure 6. Effect of pH on MB adsorption (= 200 mg/L, concentration of adsorbent = 5 g/L, temp. = 30°C and contact time = 90 min).

The methylene blue removal efficiency by activated carbon was increased from 30.50 to 99.86% upon changing the pH from 2.7 to 10.5, respectively. The increasing trend of removal of dye with increasing pH is dependent on the nature of the adsorbent. This result indicates that removal of dye using activated carbon having different surface characteristics (acidic or basic) will have an influence of pH [20].

3.5. Adsorption Isotherms

In general, the adsorption isotherm describes how adsorbents interact with adsorbents and therefore it is critical in optimizing the use of adsorbents.

3.5.1. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites.

The Langmuir equation is written as [22] :

$$C_e/q_e=C_e/q_m+1/(K_L q_m)$$

Where q_e (mg/g) is the quantity of MB adsorbed per mass of activated carbon at equilibrium, q_m(mg/g) is the maximum adsorption capacity of the activated carbon, K_L (L/mg) is the Langmuir equilibrium constant related to the adsorption energy, and C_e is the concentration at equilibrium (mg/L).

When C_e/q_e was plotted against C_e, straight line with slope $1/q_m$ was obtained (Fig. 7), indicating that the adsorption of MB on activated carbon follows the Langmuir isotherm. The Langmuir constants 'K_L' and 'q_m' were calculated from this isotherm and their values are given in Table 1.

The essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless separation parameter R_L which is defined by [23]:

$$R_L=1/(1+K_L.C_0)$$

Where, K_L (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial concentration of BM in the liquid phase.

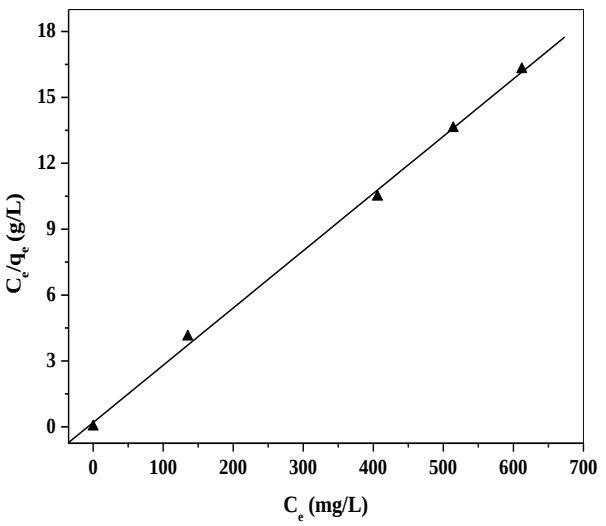

Figure 7. Application of the Langmuir model for the adsorption of methylene blue on activate carbon.

The initial dye concentration C_0 used in the adsorption isotherm studies was in the range of 100 to 800 mg/L and the corresponding values of parameter R_L are in the range 0.0694 - 0.0092. R_L values showed that the adsorption of MB was more favourable for the higher concentration than the lower one, which is due to the effect of the pore diffusion sorption phenomenon. The value of R_L indicates whether the type of the Langmuir isotherm is unfavorable (R_L> 1), linear (R_L= 1), favorable (0< R_L< 1) or irreversible (R_L= 0).

3.5.2. Freundlich Isotherm

The Freundlich equation for heterogeneous surface energy systems is given by [24] :

$$Ln(q_e)=lnK_F+(1/n)ln(C_e)$$

Where K_F and n are Freundlich constants, determined from the plot of $ln(q_e)$ versus $ln(C_e)$ (Fig. 8).

The parameters K_F and $1/n$ are related to sorption capacity and the sorption intensity of the system. The magnitude of the term (1/n) gives an indication of the favorability of the sorbent/adsorbate systems [25].

The results of Freundlich were calculated from this isotherm and their values are given in Table 1.

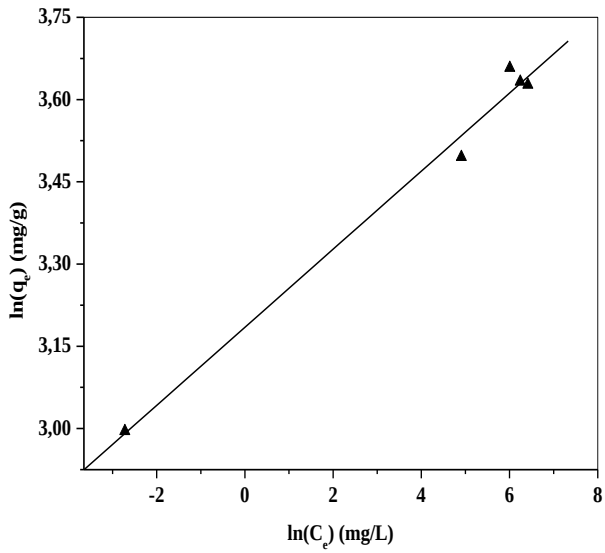

Figure 8. Application of the Freundlich model for the adsorption of methylene blue on activated carbon

3.5.3. Temkin Isotherm

Temkin isotherm includes the influences of indirect adsorbate/adsorbate interactions on adsorption isotherms and explains that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [26].

The Temkin isotherm has been used in the following form [27]:

$$q_e = RT/b_T \ln(a_T) + RT/b_T \ln(C_e)$$

Where a_T (L/g) and b_T (J/mol) are the Temkin constants. The values of a_T and b_T can be calculated from the intercept and the slope of the linear plots obtained by plotting q_e versus ln C_e in fig. 9, respectively, and the results are listed in table 1.

Table 1. Langmuir, Freundlich and Temkin isotherm constants for MB.

Langmuir Y= 0.1945+0.0261 X			**Freundlich** Y=3.1846+0.0712 X			**Tempkin** Y= -12.2056+0.4899 X		
q_{max} (mg/g)	K_L (L/mg)	R^2	N	K_F ($mg^{1-1/n}.L^{1/n}.g^{-1}$)	R^2	a_T (L/g)	b_T (J/mg)	R^2
38.314	0.134	0.998	14.045	24.178	0.988	0.344	1.645	0.972

Table 2. Kinetic parameters for the adsorption of MB onto AC.

Pseudo first order model Y=1.706-0.022 X			**Pseudo second order model** Y=0.3597+0.0228 X		
K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg.min)	q_e (mg/g)	R^2
0.051	50.804	0.981	0.0014	43.859	0.992

The kinetics studies were conducted using pseudo-first order and pseudo second order models; for this purpose, log (q_e-q_t) and t/q_t versus time were plotted.

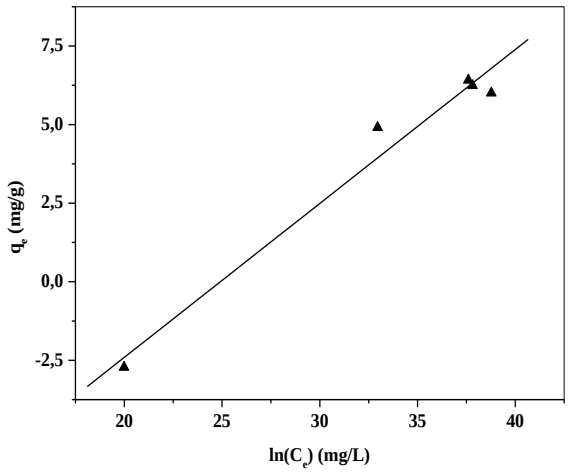

Figure 9. Application of the Temkin model for the adsorption of methylene blue on activated carbon

3.6. Adsorption Kinetics

The procedure of adsorption kinetic was identical to the adsorption equilibrium where the aqueous samples were withdrawn at different time intervals and the concentrations of dyes were similarly measured.

The quantity adsorbed by a unit mass of an adsorbent at equilibrium (q_e) at an instant, t, was calculated using the relations q_e=(q_0-C_t/m)V, where C_t (mg/L) is the liquid-phase concentration of a dye at time t (min).

The pseudo first order rate expression is given as [28]:

$$\log (q_e-q_t)=\log(q_e)-(k_1/2.303)t$$

The second order model is based on the solid phase adsorption capacity. The pseudo-second order model can be represented by the following Equation [29]:

$$t/q_t=(1/k_2\, q_e^2)+(t/\, q_e)$$

The plot of log log (q_e-q_t) as a function of time gives the straight line of slope equal to (-K_1/2.303) and the intercept equal to log (q_e). A plot of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept. q_e and q_t refer to the amounts of dye adsorbed (mg/g) at equilibrium and at each time, t (min), respectively, K_1 is the first order rate constant (min^{-1}) and K_2 is the pseudo second order rate constant (g/mg.min).

The results for the adsorption of MB on AC were applied to pseudo first and second order kinetic models and the results are presented in Table 2.

The correlation coefficient of second order kinetic model (0.992) is greater than for first order kinetic model (0.981). This confirmed that the rate limiting step is chemisorption.

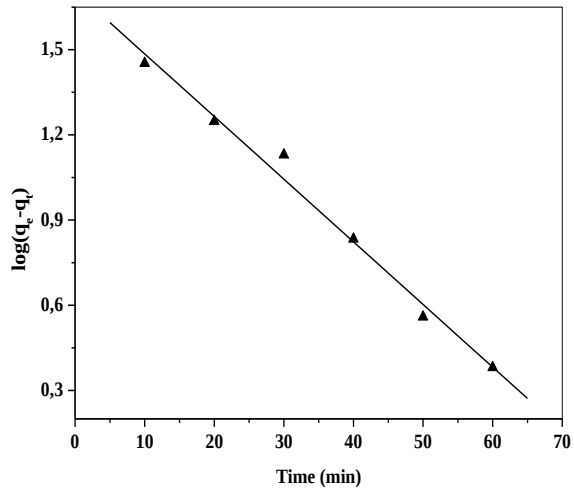

Figure 10. Application of pseudo-first order model of adsorption of methylene blue on activated carbon

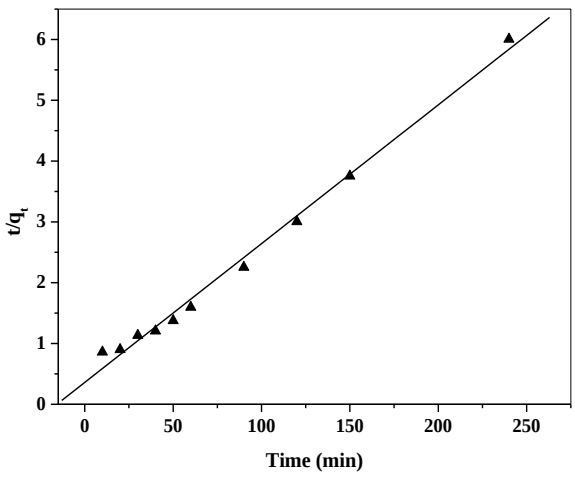

Figure 11. Application of the pseudo-second order model of methylene blue adsorption activated carbon.

3.7. Thermodynamics studies:

Various Thermodynamic parameters such as enthalpy ΔH°, entropy ΔS° and free energy ΔG° have been determined using Van't Hoff's plot.

ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot $\ln(q_e/C_e)$ vs. 1/T, ΔG° were calculated using equation $\Delta G° = -RT.\ln(q_e/C_e)$ values for different temperatures, where; q_e and C_e are the equilibrium concentration of methylene blue on the carbon activate (mg/g) and in the solution (mg/L), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). The negative value of ΔH° (-16.133 kJ/mol) indicating that the adsorption of MB onto the activated carbon occurred via is an exothermic physisorption processes. Negative standard free energy of adsorption indicates that the adsorption process is spontaneous in nature. The decrease in ΔG° with the increase of temperature indicates more efficient adsorption at higher temperature. Positive value of ΔS° suggests that the adsorption proceeds with increased randomness. The thermo dynamical parameters calculated are presented in Table 3.

Table 3. Thermodynamic parameter of MB adsorption onto AC

Table 3. Thermodynamic parameter of MB adsorption onto AC

ΔH (KJ/mol)	-16.133
ΔS (J/K.mol)	12.40
ΔG (KJ/mol)	-
T=293.15 K	-19.768
T=303.15 K	-19.892
T=313.15 K	-20.016
T=323.15 K	-20.140
T=333.15 K	-20.264

4. Conclusions

Kinetic and equilibrium studies were reported for the adsorption of methylene blue dye from aqueous solutions onto activated carbon prepared from starch which can be effectively used as an adsorbent for the removal of dye. Experimental data indicate that the adsorption capacity was dependent of operating variables such as pH, adsorbent quantity, initial dye concentration, contact time and temperature. The equilibrium data have been analyzed using Langmuir, Freundlich, and Temkin isotherms.

The thermodynamic parameters ΔH = -16.133 kJ/mol, ΔS = 12.40 J/mol K, and ΔG<0 indicate that the adsorption of MB onto AC is exothermic, spontaneous, and follows a chemisorption process.

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