

Removal of Methylene Blue Dye by Adsorption Using Low Cost Adsorbent from Agricultural Waste: Solanum Torvum

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Abstract: Activated carbon prepared from the stems of *Solanum Torvum* (STAC) was used to remove methylene blue dye (MB) from aqueous solutions. The activated carbon was characterized by Powder-XRD and Scanning electron microscopy (SEM). Various parameters such as initial dye concentration, contact time, pH and adsorbent dosage in a batch adsorption studies were investigated on the removal of methylene blue using STAC. Adsorption kinetics was found to follow pseudo-second-order kinetic model with a good correlation ($R^2 \approx 1$). Adsorption isotherms were modeled with Langmuir, Freundlich and Temkin isotherms at different temperatures. The data fitted well with the Langmuir isotherm. In addition, various thermodynamic parameters, such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) have been calculated. The adsorption process of methylene blue dye onto STAC was found to be spontaneous and endothermic process.

Keywords: *Solanum Torvum*, Methylene blue, Adsorption isotherms, Kinetics, Thermodynamics

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I. Introduction

One of the major problems based by the modern world is the pollution of water sources by effluents let out from the textile, paper, lather, food, tanneries, plastic and electroplating industries. In textile industries, the synthetic organic dyes are extensively used for dyeing cotton and polyester due to their high solubility and large tinctorial value. The wastewater from textile industries contains various pollutants which include acidic or caustic dissolved solids and different dyes. The dyes are non-biodegradable, carcinogenic, mutagenic and tetragenic and toxic to human beings, aqua systems and microorganisms [1-6]. Several methods like coagulation, flocculation or ozonation, oxidation, electrochemical precipitation, membrane separation and ultra-filtration have been tried to remove these harmful pollutants from the effluents. However, these methods are not preferred because of their high cost, economic disadvantage. However, the adsorption technique was found to be a popular technique for the dye removal. Generally, adsorbents provide large surface area, which adsorb contaminant molecules by physical or chemical interactions [7-9]. Now a days, there is a great attention focused on low cost activated carbon prepared from agricultural wastes [10, 11]. Numerous precursors have been used with success for the preparation of activated carbons including peat [12], bagasse [13], sawdust [14], olive stones [15], and husk [16], fruit peel [17], waste tee [18], and coffee grounds [19], *Phyllanthus reticulatus* [20].

II. Materials And Methods

2.1. Preparation of Adsorbate

Methylene blue (MB) dye (CI52015) from Sigma Aldrich was used without any further purification. A stock solution of MB was prepared by dissolving 1g of dye in 1000 ml of double distilled water and diluted to the required concentration.

2.2. Preparation of Activated Carbon (STAC)

Solanum Torvum stem was collected from local areas situated in and around Odathurai village, Tamilnadu, India. The plant stem was washed with distilled water to remove the impurities and dried for 7 days. The dried *Solanum Torvum* stem was treated with concentrated sulphuric acid in the ratio 1:1 (w/v). When the reaction subsided, the material was left in a hot air oven at 110 -140°C for a period of 24 hours. The dried mass was washed with large quantity of water to remove free acid and then dried at 110°C. The powdered material was subjected for activation at 800°C for a period of 10 minutes and used as adsorbent.

III. Characterization Of Adsorbent

3.1. Powder X-ray diffraction analysis

The X-ray diffraction pattern of the adsorbent is shown in Fig. 1. The adsorbent exhibit broad peaks at $2\theta = 25^\circ$ and the absence of a sharp peaks revealed a mostly amorphous structure, which is a beneficial property for well-defined adsorbent.

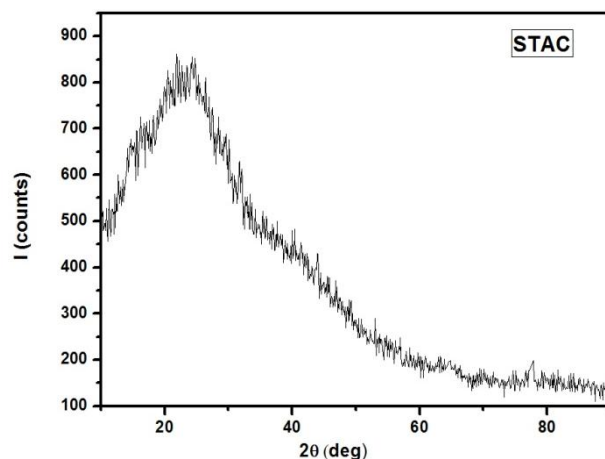


Fig. 1. Powder X-Ray diffraction pattern of STAC

3.2. SEM analysis

A scanning electron microscopy is a primary tool for characterizing the surface morphology and fundamental physical properties of an adsorbent. The SEM image of STAC is shown in Fig. 2. It is clear that, adsorbent appear to have number of pores and hence there is enhanced possibility for dye species to get trapped and adsorbed into these pores.

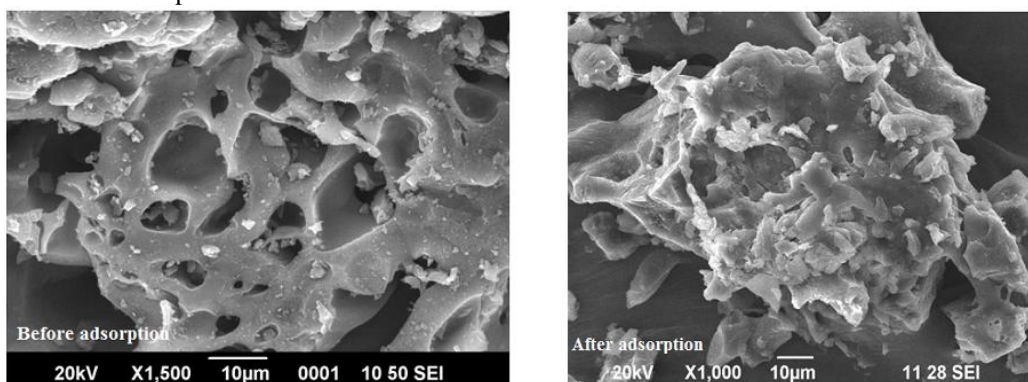


Fig. 2. SEM analysis of STAC

IV. Batch Adsorption Studies

Adsorption experiments were carried out in a 250 mL of Erlenmeyer flask containing known amount of adsorbent with MB dye solution. All the experiments were carried out at natural pH (except for effect of pH). The effect of contact time was studied using 100 mg of the adsorbent per 100 mL of dye solution at various concentrations. The effect of adsorbent dose was studied by varying the adsorbent dose. The effect of pH was studied in the pH range of 2-11 taking 100 mg of adsorbent and 100 mL of adsorbate.

V. Adsorption Studies On The Removal Of Dyes

5.1. Effect of agitation time and initial dye concentration

The experiments were carried out using initial concentrations 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L. The dye removal at equilibrium was found to decrease from 94.64% to 92.02% (Table 1) and the quantity of the dye adsorbed increased from 9.46 mg/g to 36.81 mg/g when STAC was used as adsorbent (Fig. 3). The curves obtained as shown were single, smooth and continuous leading to saturation suggesting possible monolayer coverage of dyes onto the surface of the adsorbent.

Table 1 Effect of agitation time and initial dye concentration of removal of Methylene blue

| Agitation time t (min) | 10 (mg/L) | 20 (mg/L) | 30 (mg/L) | 40 (mg/L) |
|------------------------|-----------|-----------|-----------|-----------|
| | % R | % R | % R | % R |
| 0 | 0 | 0 | 0 | 0 |
| 10 | 55.36 | 37.14 | 30.77 | 29.81 |
| 20 | 76.79 | 61.43 | 46.15 | 44.90 |
| 30 | 85.71 | 78.57 | 64.10 | 62.69 |
| 40 | 87.50 | 85.71 | 74.36 | 73.08 |
| 50 | 88.39 | 87.14 | 82.05 | 80.96 |
| 60 | 91.07 | 90.00 | 88.46 | 86.63 |
| 75 | 93.75 | 92.86 | 92.69 | 91.63 |
| 90 | 94.11 | 93.86 | 92.95 | 91.92 |
| 120 | 94.64 | 94.29 | 93.59 | 92.02 |

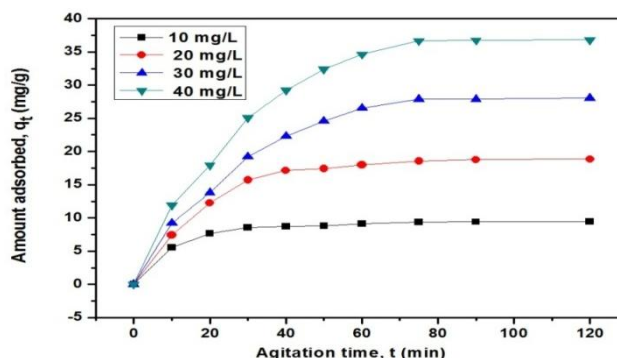


Fig. 3. Effect of agitation time and initial dye concentration of removal of Methylene blue

5.2. Effect of adsorbent dose

In this study 50 mL of dye solution of different initial concentrations were agitated with different doses of the adsorbent ranging from 10 mg to 120 mg for a time 1 hour. The flasks were withdrawn and the contents were analyzed after separation. The results indicate that the given initial concentration of the dye solution, the percentage of removal of dye increased with increase in adsorbent dose, reached a maximum with a particular amount adsorbent and then remained also constant with further addition of the adsorbent. The effect of adsorbent dose on MB by STAC was observed that the removal efficiency increased with increase in adsorbent dose from 10 to 70 mg and then remains almost constant (Fig. 4). The data in Table 2 indicate, the amount adsorbed per unit mass of the adsorbent decreases with increase in adsorbent dose [21].

Table 2 Effect of adsorbent dose on removal of Methylene blue

| Weight of adsorbent (mg) | qt (mg/g) | | |
|--------------------------|-----------|-----------|-----------|
| | 10 (mg/L) | 20 (mg/L) | 30 (mg/L) |
| 10 | 11.61 | 14.57 | 20.19 |
| 20 | 8.48 | 11.79 | 17.50 |
| 30 | 7.44 | 11.62 | 16.22 |
| 40 | 6.92 | 10.93 | 15.05 |
| 50 | 6.61 | 10.26 | 14.58 |
| 70 | 5.99 | 9.98 | 14.04 |
| 100 | 4.74 | 9.43 | 13.92 |
| 120 | 3.97 | 7.87 | 11.78 |

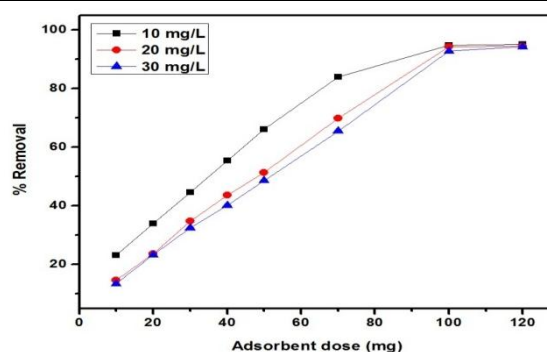


Fig. 4. Effect of adsorbent dose on removal of Methylene blue

5.3. Effect of pH

In this study, the maximum removal of MB was observed under strongly basic conditions (pH = 11.0) is shown in Fig. 5. It shows that with increase in pH of the solution there is increase in adsorption for MB. The data of percentage removal is given in Table 3. A positively charged adsorbent surface at low pH value does not favour adsorption of the cationic dye due to electrostatic repulsion. At high pH values the electrostatic attraction between the negatively charged adsorbent surface and the cationic dye increases leading to maximum adsorption. Thus in the case of MB, the adsorption increases with increase in pH²¹.

Table 3 Effect of solution pH on removal of Methylene blue

| Dye concentration | 10 (mg/L) |
|--------------------------------|-----------|
| Initial pH of the dye solution | % Removal |
| 2 | 3.57 |
| 3 | 7.14 |
| 4 | 10.71 |
| 5 | 13.04 |
| 6 | 13.75 |
| 7 | 14.29 |
| 8 | 18.04 |
| 9 | 21.43 |
| 10 | 27.14 |
| 11 | 27.68 |

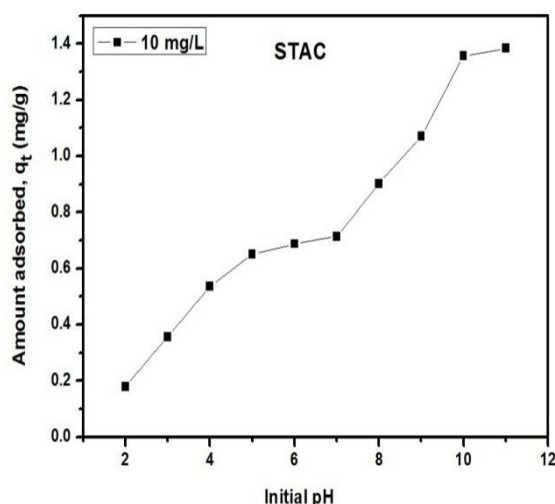


Fig. 5. Effect of solution pH on removal of Methylene blue

VI. Adsorption Isotherms

6.1. Langmuir isotherm

The adsorption of dyes at different temperatures have been analysed the linear form of Langmuir model is expressed by,

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_0}$$

Where C_e is equilibrium concentration of dye (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_0 and b are the Langmuir constants correlated to adsorption capacity and rate of adsorption, respectively. A linear plot of C_e/q_e vs C_e is shown in Fig. 6. The values of Q_0 and b were calculated from the slope and intercept of the plots and the values are given in Table 4. The maximum monolayer adsorption capacity increases slightly with increase in temperature from 303 K to 333 K in the case of MB dye studied. The important features of the Langmuir isotherm was examined by the dimensionless constant separation term (R_L) to determine high affinity adsorption.

R_L was calculated as follows:

$$R_L = \frac{1}{1 + bC_0}$$

The values of R_L indicate the nature of the isotherms to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ (or) irreversible if $R_L = 0$. The R_L at different temperatures 303 K, 313 K, 323 K and 333

K were found to be between 0 and 1 in the concentration range studied for MB dye used in the present investigation, suggesting a favorable adsorption on the adsorbent.

Table 4 Data for Langmuir adsorption isotherm constants

| Temp. (K) | 303 | 313 | 323 | 333 |
|--------------|--------|--------|--------|--------|
| Q_0 (mg/g) | 50.63 | 51.63 | 54.64 | 59.24 |
| b (L/mg) | 0.1162 | 0.1274 | 0.1296 | 0.1250 |
| R^2 | 0.9899 | 0.9938 | 0.9926 | 0.9952 |

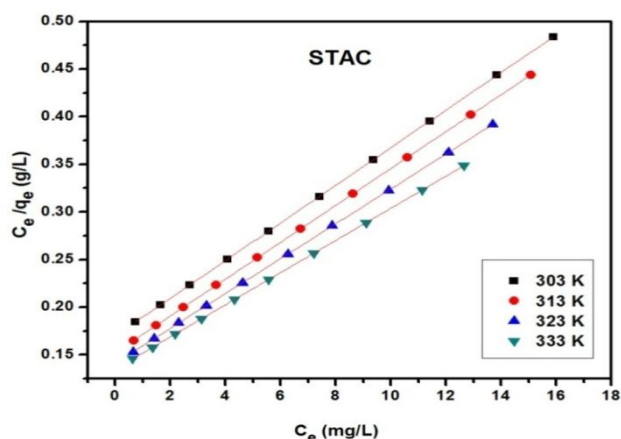


Fig. 6. Langmuir adsorption isotherm of Methylene blue

6.2. Freundlich isotherm

The Freundlich isotherm was represented by the following equation,

$$\log q_e = \log K_f + 1/n \log C_e$$

Where K_f and n are Freundlich constants represent adsorption capacity and intensity of the adsorbent respectively. The plot of $\log q_e$ vs $\log C_e$ shown in Fig. 7 indicates that the adsorption of MB dye favours the Freundlich isotherm to some extent. The Freundlich constants (K_f and n) are given in Table 5. The calculated values of n between 2 and 3 that represent good adsorption [22].

Table 5 Data for Freundlich adsorption isotherm constants

| Temp. (K) | 303 | 313 | 323 | 333 |
|--------------|--------|--------|--------|--------|
| K_f (mg/g) | 5.90 | 6.37 | 6.69 | 6.89 |
| n | 1.5220 | 1.5226 | 1.4868 | 1.4335 |
| R^2 | 0.9886 | 0.9861 | 0.9831 | 0.9827 |

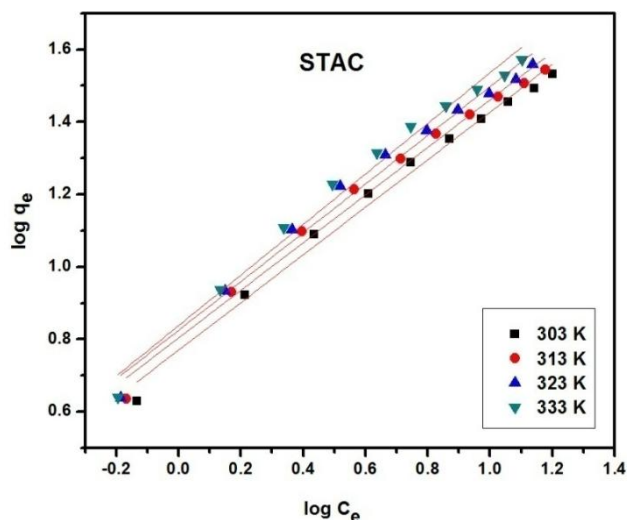


Fig. 7. Freundlich adsorption isotherm of Methylene blue

6.3. Temkin isotherm

Temkin considered the effects of some indirect adsorbate/adsorbate interactions on the adsorption isotherms. This isotherm is based on the fact that if the concentration is not too low or too high, because of these indirect interactions the heat of adsorption of all the molecules in a layer decreases linearly with coverage and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin equation has been applied commonly in the following form

$$q_e = (RT)/b_T \ln C_e.$$

In its linear form the Temkin isotherm can be simplified as

$$q_e = \beta \ln \alpha + \beta \ln C_e$$

The adsorption data were analyzed according to the linear form of the Temkin equation. The linear plots of q_e vs $\ln C_e$ are shown in Fig. 8. The values of constants α and β obtained from the slope and intercept of the plot, along with the values of regression coefficient are given in Table 6.

Table 6 Data for Temkin adsorption isotherm constants

| Temp. (K) | 303 | 313 | 323 | 333 |
|----------------|--------|--------|--------|--------|
| α (L/g) | 1.53 | 1.66 | 1.71 | 1.71 |
| β (mg/g) | 9.81 | 10.06 | 10.57 | 11.21 |
| R^2 | 0.9610 | 0.9656 | 0.9665 | 0.9668 |

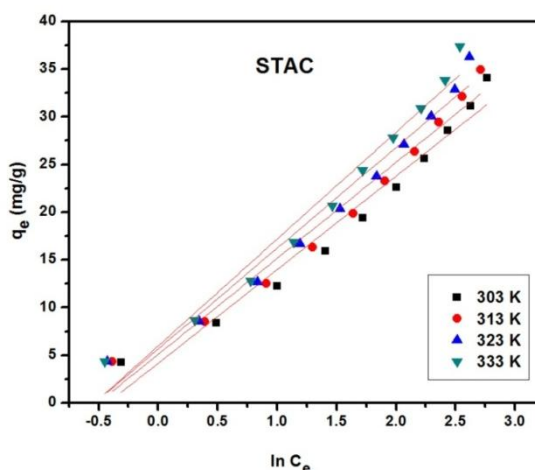


Fig. 8. Temkin adsorption isotherm of Methylene blue

VII. Adsorption Kinetics

In order to examine the kinetic of the adsorption process of MB on STAC, pseudo-first-order and pseudo-second-order kinetic models were studied.

7.1. Pseudo-first order kinetics

The rate constant of adsorption is determined from the pseudo-first-order rate expression given by Lagergren [23].

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

where, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (mg/g), t is the time (min) and k_1 is the pseudo first order rate constant (min^{-1}). The rate constant k_1 and q_e can be calculated from the slope and intercept of the graph plotted between $\log (q_e - q_t)$ vs t . The data revealed that the calculated values of q_e does not agree well with the experimental q_e values. The R^2 values are relatively low, indicates that the data does not fit into pseudo-first kinetics.

7.2. Pseudo- second order kinetics

The linear pseudo-second order kinetic equation is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where k_2 is rate constant of second order adsorption ($g\ mg^{-1}\ min^{-1}$). The plot of t/q_t vs t (Fig. 9) was linear. The values of q_e and k_2 can be calculated from the slope and intercept. From the results it is clear that the equilibrium adsorption capacity q_e increases and adsorption rate constant, k_2 , decreases with increase in the initial dye concentration. Based on the good agreement between the experimental and calculated q_e and high R^2 and low SSE values obtained (Table 7). For both the kinetic studies, good correlation coefficients were obtained ($R^2 \approx 1$) by fitting the experimental data to pseudo-second order than that for the pseudo-first order kinetic model.

Table 7 Table for Pseudo-second order kinetics

| Concentration (mg/L) | 10 | 20 | 30 | 40 |
|------------------------------|--------|--------|--------|--------|
| $k_2 \times 10^3$ (g/mg.min) | 15.585 | 3.443 | 1.093 | 0.805 |
| q_e exp (mg/g) | 9.46 | 18.86 | 28.08 | 36.81 |
| q_e cal (mg/g) | 10.05 | 21.54 | 30.65 | 40.10 |
| R^2 | 0.9992 | 0.9921 | 0.9831 | 0.9815 |
| SSE | 0.59 | 2.68 | 2.57 | 3.29 |

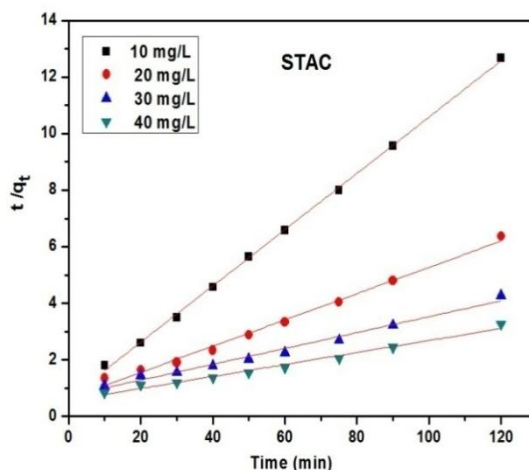


Fig. 9. Pseudo-second order kinetics of Methylene blue

VIII. Thermodynamic Studies

The thermodynamic parameters used to determine the feasibility of the adsorption process change in Gibbs standard free energy (ΔG^0), standard enthalpy of adsorption, (ΔH^0) and standard entropy of adsorption (ΔS^0) were determined from the slope and intercept of linear plots of $\ln K_c$ vs $1/T$ using the Van't Hoff equation (Fig 10).

$$\Delta G^0 = -RT \ln K_c$$

$$\ln K_c = \Delta S^0/R - \Delta H^0/RT$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Where R is the universal gas constant (8.314 J/mol. K). T is the temperature (K) and K_c is the Langmuir equilibrium constant. The negative value of ΔG^0 and positive value of ΔH^0 indicate that the adsorption process is spontaneous and endothermic in nature. The positive value of ΔS^0 indicated an increased randomness at the adsorbent- adsorbate interface of the adsorption process (Table 8).

Table 8 Thermodynamic data for Methylene blue

| Temp. (K) | ΔH^0 (kJ/mol) | ΔS^0 (J/Kmol) | ΔG^0 (kJ/mol) |
|-----------|-----------------------|-----------------------|-----------------------|
| 303 | 3.98 | 15.82 | -0.82 |
| 313 | | | -0.98 |
| 323 | | | -1.13 |
| 333 | | | -1.29 |

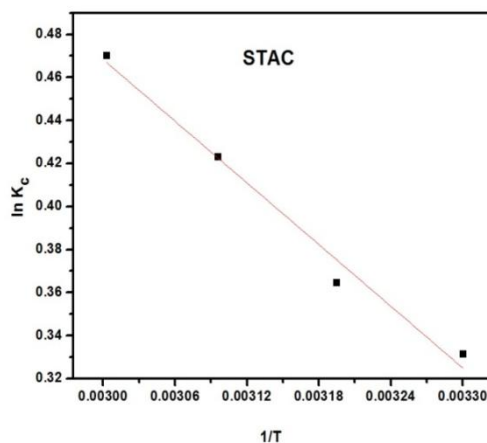


Fig. 10. Van't Hoff plot of Methylene blue

IX. Conclusion

The present study shows that an adsorbent can be prepared from *Solanum Torvum* stems with sulphuric acid activation. The amount of dye adsorbed varied with function of initial dye concentration, contact time, adsorbent dose and pH. The maximum removal of MB was observed at pH = 11.0. The Langmuir, Freundlich and Temkin adsorption isotherm models were used for the description of the adsorption equilibrium of MB dye onto STAC. The data were in good agreement with Langmuir isotherm. The kinetic data were tested for the models of pseudo-first order and pseudo-second order. The adsorption process follows the pseudo-second order model. The negative values of ΔG^0 and ΔH^0 positive obtained indicated that the MB dye adsorption process is a spontaneous and an endothermic.

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