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Equilibrium and Kinetic Studies on the Adsorption of Methylene Blue from Aqueous Solution onto Activated Carbon Prepared from *Murraya koenigii* (Curry Tree) Stems

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In the present study, activated carbon is prepared from *Murraya koenigii* Stems (MKST) and used for the adsorption of methylene blue from aqueous solution. The nitrogen adsorption isotherms were used to characterize the pore properties of the activated carbon including the BET surface area, pore volume and pore diameter. The specific surface area of the prepared carbon is 508 m^2/g. Batch mode experiments were conducted to study the effect of adsorbent dosage on the adsorption of methylene blue. The equilibrium data fits well with Langmuir model with monolayer adsorption capacity of 123.46 mg/g. The adsorption kinetics was studied using pseudo-first order and pseudo-second order models. The rate of adsorption was found to conform to pseudo-second order kinetics with a good correlation. The results show that methylene blue interacts strongly with the prepared activated carbon and hence the adsorbent is good for the removal of methylene blue from aqueous solution.

Key Words: Activated carbon, Methylene blue, BET, Adsorption isotherm, Kinetics.

INTRODUCTION

The effluent from the textile industries is a major pollutant in the industrial sector, based on the volume of discharge and effluent composition[1]. Hence, effluent treatment is necessary to reduce the dye concentration to acceptable level before releasing into water bodies. Now-a-days, a lot of problems are encountered in the removal of dyes from effluents since these dyes are usually very stable and difficult to degrade after use and hence coloured effluents from the industries are treated by using various treatment techniques like adsorption[2], chemical coagulation[3], biodegradation[4], electrochemical oxidation[5,6], *etc*. Among these, adsorption is an effective method for the treatment of dye wastewater. Since activated carbon can adsorb dyes effectively from dilute solutions, adsorption by activated carbon is an advantageous process when compared to other methods.

In textile industry, methylene blue is a dye used for dyeing cotton, silk and wool. Generally, Basic dyes are toxic colourant[7] and have cationic properties that are due to the positive charge localized on the nitrogen atom and delocalized throughout the chromophoric system. Methylene blue causes eye burns, irritation to the gastrointestinal tract and acute exposure to methylene blue can cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans. Hence, removal of this dye form effluents is very important in the environmental aspect. Many biodegradable adsorbents have been studied for the adsorption of dyes like coir pith[8], neem leaf powder[9], sawdust[10], jute fiber carbon[11], curry tree seed[12], agricultural wastes[13], *etc*. still there is a need for highly effective adsorbents.

Murraya koenigii commonly known as curry tree[14] is plenty in the southern part of India a plant that is native to Asia. The stems of *Murraya koenigii* (curry tree) is an agricultural waste that is available throught the year. To produce a value added product from this agricultural waste it is proposed to convert it into activated carbon. The objective of the present work is to examine the adsorption and access the feasibility of using activated carbon prepared from *Murraya koenigii* (curry tree) stem as an adsorbent for the removal of methylene blue from aqueous solution.

EXPERIMENTAL

Methylene blue obtained for this investigation was from HiMedia Laboratories Pvt. Limited, Mumbai. The molecular structure of the dye is shown in Fig. 1. It is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$.

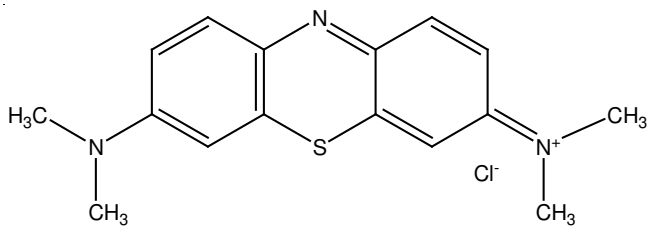

Fig. 1. Molecular structure of methylene blue

Preparation of activated carbon: *Murraya koenigii* stems were cut into small pieces of 2-3 cm and dried for 36 h at 393 K. The raw material is mixed with K_2CO_3 at an impregnation ratio of 1:1. The mixture is dried in an oven at 393 K for 24 h.

The samples were loaded in a ceramic boat and placed in a tubular furnace under high purity N_2 (99.99 %) flow of 150 cm^3/min. The sample is heated to 800 °C and it is maintained at that temperature for 0.5 h. The reactor is then cooled to room temperature under N_2 flow and the sample is repeatedly washed with water until the filtrate become neutral. The sample is dried at 373 K for 1 day to prepare the adsorbent used for the study. The carbon is finally crushed and they are sieved to particle size of 125-150 mesh and stored in plastic bottles for adsorption studies.

Characterization: The surface area of the prepared carbon is measured by N_2 adsorption at -196 ºC using micromeritics ASAP 2020 surface area analyzer. Prior to the analysis, the sample was outgassed at 150 ºC for 12 h. The differential pore volume and pore size distributions were calculated using a Horvath and Kawazone model[15] and BJH model[16]. The median pore width was calculated using Horvath and Kawazoe method.

Batch adsorption experiments: The effect of adsorbent mass on the amount of dye adsorbed was determined by using 50 mL of dye solution of initial dye concentration of 80 mg/L with different amount of the adsorbent (0.02, 0.04, 0.06, 0.08, 0.10, 0.12 g) in orbital shaker at room temperature for an equilibrium time of 8 h. The sorption equilibrium experiments were done by using a fixed adsorbent mass in 50 mL of the dye solution at different initial dye concentrations. The samples were centrifuged and the supernatant solution was analyzed at the wavelength of maximum absorbance (668 nm) using a spectrophotometer (ELICO:SL 207). Kinetic experiments were carried out using mechanical stirrer in the concentration range of 80 to 200 mg/L. The percentage of dye removal and the amount adsorbed on to unit weight of the adsorbent mass was calculated using the equations:

$$\text{Percentage of dye removal} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

The amount of adsorption at equilibrium q_e (mg/g) was calculated by:

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_e)V}{M} \qquad (2)$$

where C_i and C_e are the liquid phase concentrations of the dye at initial and equilibrium concentrations (mg/L), respectively. M is the mass (g) of adsorbent and V is the volume of dye solution (mL).

RESULTS AND DISCUSSION

Characterization of the adsorbent

Nitrogen adsorption/desorption isotherm of the prepared activated carbon: A qualitative information on the adsorption process and the extent of surface area available to the adsorbate is given by the shape of the adsorption isotherm. The N_2 adsorption isotherm of the activated carbon prepared from *Murraya koenigii* stems (MKST) at -196 ºC is shown in Fig. 2. The adsorption isotherm is classified as type I isotherm indicating that the carbon is mainly microporous[17] in nature. The presence of hysteresis indicates the presence of mesopores on the surface of the carbon. The amount of nitrogen adsorbed on the adsorbent gradually increases in the whole relative pressure range, implying that this carbon contains a small amount of mesopores. The prepared carbon exhibits a moderately developed porosity with a specific surface area of 508 m^2/g and the single point adsorption total pore volume of pores (< 913.205 Å) is 0.2939 cm^3/g. The BJH average pore radius (2 V/A) is 15.834 Å and median pore width by Horvath and Kawazoe is 8.857 Å. The presence of micropores and mesopores in the activated carbon prepared from *Murraya koenigii* stems is given by pore size distribution calculated by Hovarth and Kawazone method and the differential pore volume plot is given by the Fig. 3.

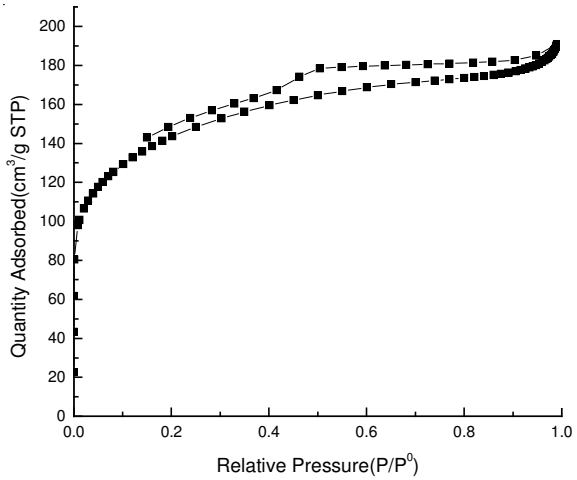

Fig. 2. Nitrogen adsorption/desorption isotherm of the prepared activated carbon

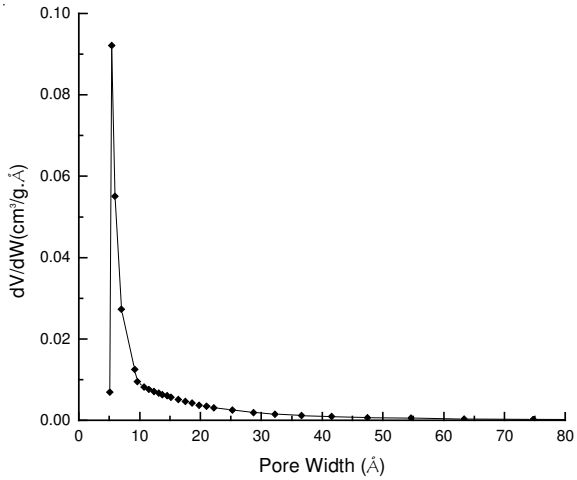

Fig. 3. Horvath-Kawazoe differential pore volume plot for the prepared activated carbon

Effect of adsorbent dosage: The amount of dye adsorbed (mg/g) and the percentage dye removal with increase in adsorbent dosage is shown in Fig. 4. The carbon dosage was varied in the range of 0.02 to 0.12 g and the adsorption of methylene blue for a dye concentration of 80 mg/L was studied.

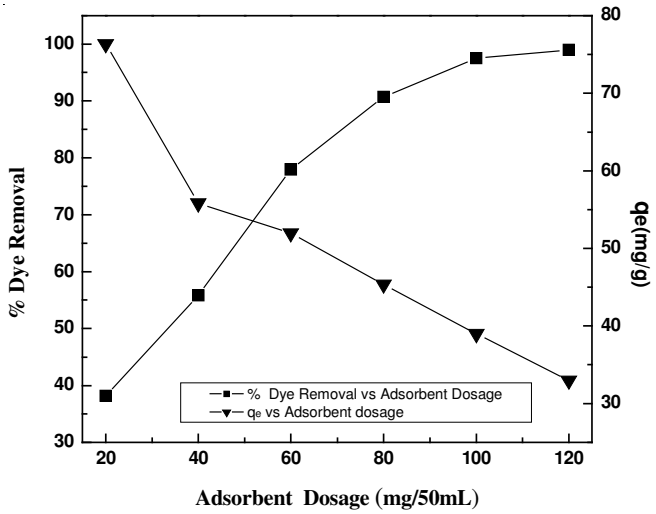

Fig. 4. Percentage of dye removal *versus* adsorbent dosage (C_0 = 80 ppm; V = 0.05 L; t = 8 h)

The percentage dye removal increased from 38.16 to 98.99 % for an adsorbent dosage of 0.02 to 0.12 g. This is due to the increased surface area and availability of more adsorption sites. An adsorbent dosage of 0.12 g was required to attain 98.99 % dye removal. When the adsorbent and the solute concentration are low then the adsorption rate is low. On the other hand, when the adsorbent to the solute concentration is high then the adsorption is more onto the adsorbent surface and hence there is a decrease in the solute concentration in the solution. At high adsorbent to solute concentration, the adsorption is high on the adsorbent surface and hence the solute concentration in the solution decreases. This is due to the adsorption of a fixed amount of dye on a fixed mass of the adsorbent.

Adsorption isotherm: The equilibrium adsorption data is described by using equilibrium isotherm equations. Adsorption equilibrium is necessary to design and analyze the adsorption process that plays a major role in understanding the adsorption process[18]. The parameters obtained from the various models provide important information on the surface properties and mechanisms of the sorbents. When a dye molecule occupies a specific site then no further adsorption can take place at that site. The Langmuir[19], Freundlich[20] and Temkin[21] isotherms were tested.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \text{ or } C_e/q_e = 1/Q_m K_L + C_e/Q_m \quad (3)$$

$$q_e = K_F C_e^{1/n} \text{ or } \log q_e = 1/n \log C_e + \log K_F \quad (4)$$

$$q_e = RT/b \ln (K_T C_e) \text{ or } q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

where q_e is the amount of dye adsorbed per unit weight of adsorbent (mg/g), C_e the concentration of the dye solution (mg/L) at equilibrium and K_L is the constant related to the free energy of adsorption (L/mg). Q_m is the maximum adsorption capacity. The values of Q_m and K_L were calculated from the slope and intercept of the linear plot (Fig. 5). K_F is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and 1/n is the adsorption intensity. The constant B = RT/b and it is related to the free energy of adsorption and K_T is the Temkin isotherm constant (L/g) where these constants can be calculated from a plot of q_e *versus* ln C_e. The various isotherm constants were calculated from the linear form of the model and the results are given in Table-1. The R^2 value of 0.9986 for Langmuir model proves that this model fits better with monolayer coverage of methylene blue on the prepared activated carbon.

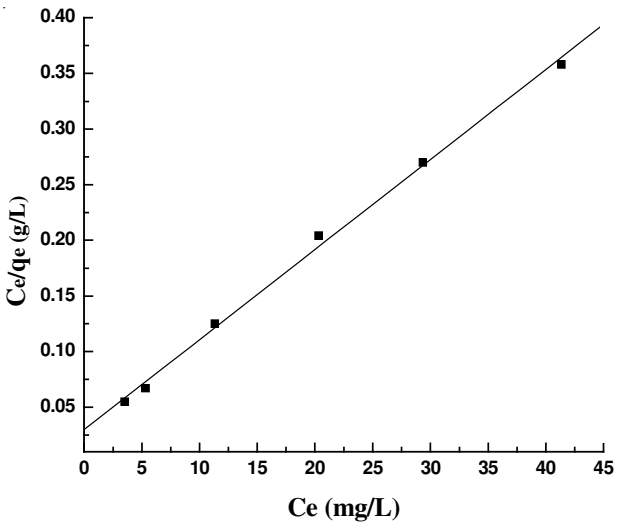

Fig. 5. Langmuir Adsorption Isotherm for methylene blue onto MKST

An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called the equilibrium parameter, R_L, which is defined by the equation[22]:

$$R_L = 1/1 + K_L \times C_0 \quad (6)$$

The value of R_L indicates the type of isotherm to be favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavourable ($R_L > 1$) or irreversible $R_L = 0$, where K_L is the Langmuir constant and C_0 is the highest initial dye concentration (mg/L). The value of R_L was found to be in the range of 0.042-0.019 for different dye concentrations, which suggests that the adsorption of methylene blue is a favourable process.

The Freundlich model assumes that the adsorption of methylene blue occurs on a heterogeneous surface with the total adsorption increasing with an increase in concentration. The value of n in the range of $0 < n > 1$ represents favourable adsorption conditions[23]. A plot of log q_e *versus* log C_e (Fig. 6) used to calculate the Freundlich constant K_f and n. The value of n was found to be 4.48, which indicate favourable adsorption of methylene blue by the prepared activated carbon.

The linear form of the Temkin equation is used to analyse the adsorption data and is observed that the R^2 value (0.9923) is good when compared to the Freuendlich isotherm, which proves the applicability of Temkin isotherm (Fig. 7). It is observed that the R^2 for Langmuir > Temkin > Freuendlich. The experimental results and the equilibrium data were well represented by the Langmuir and Temkin isotherm with a good coefficient of determination R^2 (0.9986 and 0.9923) and hence this confirms the monolayer coverage of methylene blue on to the activated carbon prepared from *Murraya koenigii* stems.

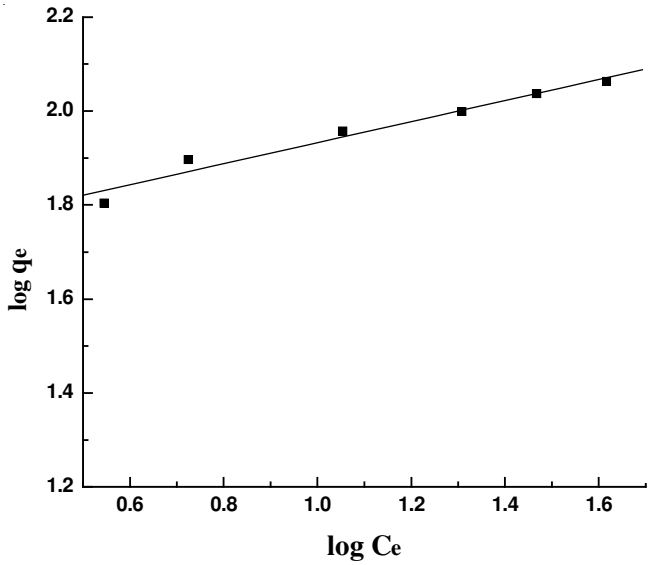

Fig. 6. Freundlich adsorption isotherm of methylene blue on to MKST

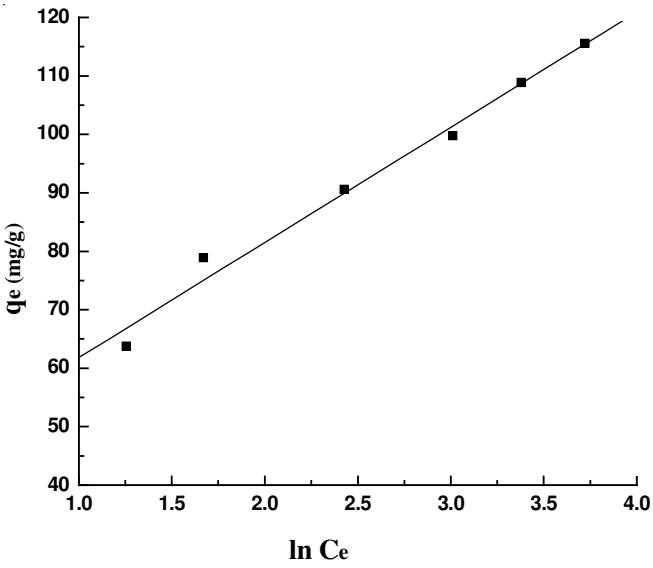

Fig. 7. Temkin isotherm of methylene blue onto MKST

Adsorption kinetics: Adsorption kinetics was investigated by pseudo first order[24] and pseudo second order[25] model. The linear form of pseudo first order reaction and pseudo second order model is given by:

$$\log (q_e - q_t) = \log q_e - k_1/2.303t \quad (7)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_t \quad (8)$$

The slope and the intercept of the plot of log (q_e-q_t) *versus* time (Fig. 8) and t/q_t *versus* time were used to determine the rate constant k_1 and k_2 and the results are given in Table-1. The R^2 value was observed in the range of 0.9548 to 0.9858 for dye concentrations from 80 to 200 ppm. Since the experimental q_e values and calculated q_e value do not agree with each other with low correlation coefficient, it is suggested that the pseudo first order model does not fit well.

The high R^2 value (> 0.9896) for different dye concentrations for the pseudo second order model (Fig. 9) proves that the adsorption kinetics follows the pseudo second order model. The q_e calculated from the pseudo second order model and the high R^2 value suggests that the pseudo second order model better represents the adsorption kinetics and it appears that chemisorption process[25,26] controls the adsorption process. The values of kinetic constants and qe for methylene blue adsorption onto MKST are given in Table-2.

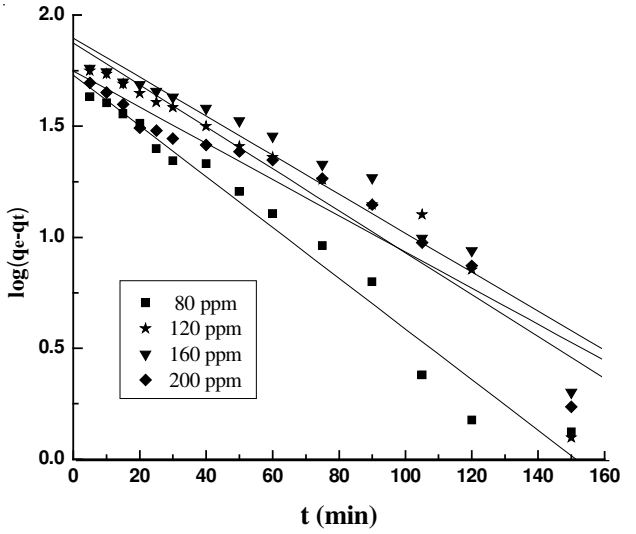

Fig. 8. Pseudo first order kinetics plot for the adsorption of methylene blue onto MKST

TABLE-1
LANGMUIR, FREUNDLICH AND TEMKIN CONSTANTS FOR THE ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON PREPARED FROM MKST

Isotherm	Values
Langmuir	
q_m (mg/g)	123.46
K_L (L/mg)	0.28
R^2	0.9986
Freundlich	
log K_F (mg/g)	1.71
n	4.48
R^2	0.9825
Temkin	
K_T (L/mg)	8.47
B_1	19.7
R^2	0.9923

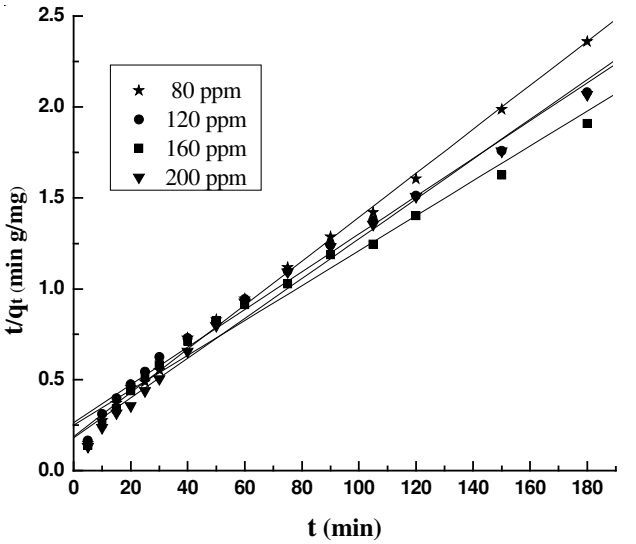

Fig. 9. Pseudo second order kinetics plot for the adsorption of methylene blue onto MKST

TABLE-2
KINETIC MODEL VALUES FOR THE ADSORPTION OF METHYLENE BLUE ON TO ACTIVATED CARBON PREPARED FROM MKST

Concentration (ppm)	q_e (mg/g)	Pseudo first order values		Pseudo second order values		
		k_1 min^{-1})	R^2	k_2 [g/(mg min)]	h	R^2
80	76.29	0.02630	0.9858	0.00077	5.28	0.9982
120	86.52	0.02171	0.9548	0.00041	3.78	0.9945
160	94.28	0.02022	0.9646	0.00037	3.99	0.9896
200	87.03	0.01876	0.9570	0.00066	5.53	0.9944

Table-3 gives the adsorption capacity of some of the adsorbents used for the adsorption of methylene blue. It is observed that the adsorption of activated carbon prepared from *Murraya koenigii* stem waste is comparatively good when compared with some of the adsorbents already reported in the literature for the adsorption of methylene blue from aqueous solution. The adsorption capacity (q_{max} value) of 123.46 mg/g suggests that the activated carbon prepared from *Murraya koenigii* stems is a good adsorbent for the removal of methylene blue from aqueous solution. The adsorption capacity of the adsorbent (q_{max}) prepared suggests that methylene blue is adsorbed easily by the activated carbon used in the present study.

TABLE-3
COMPARISON OF MAXIMUM ADSORPTION CAPACITY FOR METHYLENE BLUE ON OTHER DIFFERENT ADSORBENTS

Adsorbent	Adsorption capacity (mg/g)	Reference
Raw date pits	80.3	27
Coir pith	5.87	28
Hazelnut shell-based	76.9	29
Sawdust-walnut	59.17	29
Sawdust-pitch pine	27.78	29
Sawdust-Cherry	39.84	29
Sawdust-Oak	29.94	29
Curry tree Stem	123.46	Present study

Conclusion

The results show that the adsorbent has a good BET surface area of 508 m^2/g with a total pore volume of 0.2939 cm^3/g. The equilibrium data fitted well with the Langmuir isotherm, confirming the monolayer coverage of methylene blue onto MKST with a monolayer adsorption capacity of 123.46 mg/g. The dimensionless separation factor (R_L) value between 0 and 1 shows favourable adsorption. The kinetics of methylene blue adsorption on the prepared carbon follows pseudo-second order model. The material used in this study is an agricultural waste product, freely and abundantly available and hence it can be used as alternative to the other commercial activated carbons used for dye removal in wastewater treatment process.

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