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An eco-friendly non-conventional adsorbent from silk cotton fiber for the removal of methylene blue dye

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Highly porous activated carbon fiber with excellent surface area has been prepared using silk cotton fiber as a precursor. The Activated Silk Cotton Fiber (ASC) has well developed porosity with rose flower like structure. The BET surface area of the prepared adsorbent is 1041.08 m^2/g with a total pore volume of 0.4944 cm^3/g. The adsorption capability of the prepared adsorbent ASC has been analyzed using methylene blue (MB) dye. The effect of *p*H indicates that ASC has its maximum adsorption at a *p*H of 10. On analyzing the kinetics of MB adsorption, the pseudo-second order kinetic model describes the adsorption with good r^2 value of $0.9895 < r^2 < 0.9997$. The maximum Langmuir monolayer adsorption capacity is found to be 80.65 mg/g at 45°C. The experimental results and the thermodynamic studies prove the physisorption nature of MB adsorption onto ASC.

Keywords: Adsorbent, Silk cotton, Microwave, Kinetics, Isotherm studies

Discharge of untreated waste water into water streams and stagnant water bodies has created lot of imbalance to the natural ecosystem. Textile, paper, printing, paint and plating industries release lot of wastewater containing non-biodegradable organic dyes which are persistent for a long period of time in the ecosystem. Dyeing industries in particular consumers of the huge quantity of dyes and they are responsible for the discharge of large quantity of highly coloured wastewater into nearby land and water streams. Dye bearing wastewater is highly harmful for the aquatic animals due to their poisonous and non-biodegradable nature. High poisonous nature of dyes is caused by the presence of complex aromatic molecular structure, which also makes them more stable against conventional degradation methodologies.

Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually throughout the world, of which about 20-30% is wasted in industrial effluent during textile dyeing and finishing processes[1]. Many dyes may also cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system[2]. Beyond the above said problems some dye molecules are suspected to be more carcinogens and mutagens[3].

Complete removal of dye molecules present in wastewater is a challenging task in these days. Many treatment techniques like chemical coagulation[4], foam flotation[5], electrolysis, chemical oxidation[6], photochemical degradation[7], membrane filtration[8], biological treatment and adsorption[9] etc. have been used in the past for the removal of dyes from dye bearing wastewater. The scope of these technologies is limited either in the form of high cost or poor selectivity towards all types of pollutants. Adsorption using activated materials is one of the most widely used technology for the removal of various kinds of pollutants present in the water and wastewater. The cost of commercial activated carbon is not affordable for small scale industries. In this context the production of an activated carbon from a renewable, easily available and low cost precursor is highly warranted.

Many agricultural by products and agro-wastes like coir pith[10], banana pith[11], sugarcane dust[12], rice husk[13], orange peel[14], apple pomace and wheat straw[15], neem husk[16], and industrial by products like fly ash, bottom ash, red mud[17,18] etc**.** have been tried as a low cost adsorbent for the treatment of wastewater.

In the present study, silk cotton fibers, (an eco-friendly and renewable source of carbon) is used as a precursor for the preparation of an activated carbon using microwave hydrothermal heating process. The precursor (silk cotton fiber) is available in plenty in countries like India and most parts of Asia. The advantage of the precursor is not only available in plenty also it is renewable with short span of time with very good yield. In the last few decades, usage of microwave for synthetic applications has grown rapidly. Microwave heating has been widely used in research and industrial purpose due to its direct interaction with matter. The major advantage of using microwave is that the treatment time can be considerably reduced, more economical and also the process is pollution free one[19].

Methylene blue (MB) is a heterocyclic aromatic dye, commonly used for dyeing cotton, wool and silk dyeing industries. It produces vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis when enters into human body[20]. The removal of MB dye using a low cost adsorbent can serve amicable solution for the pollution.

Experimental Section

The precursor, Silk cotton fiber collected from in and around the Erode district of Tamilnadu, India. The fibers are dried in sunlight for 3 days and used without any pre treatment. All the chemicals used for the study are analytical grade reagents supplied by Aldrich-India (>99 % purity). Double distilled water is used as a solvent as well as for all dilutions.

Preparation of activated carbon fibers

The precursor soaked with 0.5% (W/V) solution of $FeCl_3$ for one hour. After one hour of impregnation, the fibers were removed from the solution and carbonized in microwave oven at 600W for 05 min. The carbon is washed with plenty of water to remove any residual chemicals. The washed carbon activated in microwave oven in an N_2 atmosphere at 600W for 10 min, labeled as ASC and stored in tight lid container for further studies.

Preparation of adsorbate

All the chemicals used are reagent grade. Cationic dye methylene blue with a molecular formula ($C_{16}H_{18}ClN_3S$) M.W: 319.85, C.I No. 52015, λmax: 665 nm, (E. Merck, India) was chosen as the adsorbate. A stock solution containing 1000 mg of the dye per liter was prepared by dissolving 1.22 g of dye (Dye content is 82 %) in 1000 mL of double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required.

Batch mode adsorption studies

The adsorption experiments were carried out in 200 mL tight lid glass bottle (Borosil-R) by agitating 100 mg of adsorbent with a 200 mL of the aqueous dye solution. The effect of *p*H was studied by adjusting the *p*H of the adsorptive solution from 2 to 11 using 0.1N HCl and 0.1N NaOH. All other kinetic experiments were carried out at the normal *p*H (normal *p*H of MB solution is 8.2) of the dye solution. The contents of the flasks were agitated with the help of a temperature controlled orbital shaker (REMI Make). After the specified time, the sample is taken out from the shaker then centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 min and un-adsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio UV-visible spectrometer (BL-192) at 665 nm. All the experiments were conducted in duplicate and mean of the two values were taken for calculation. Maximum deviation is 4%.

Amount of adsorbed dye per gram of adsorbent were calculated with the following equations[21]:

$$q_e = (C_0 - C_e)\frac{V}{W} \quad \ldots (1)$$

$$\text{Percentage of dye removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad \ldots (2)$$

where, C_0 and C_e (mg/L) are the liquid-phase concentrations of dye initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Desorption studies

Desorption studies as a function of *p*H were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. After adsorption experiments the dye loaded carbon washed gently with double distilled water to remove any un-adsorbed dye if present. Exactly 500 mg of the dye loaded carbon agitated above the equilibration time with 50 mL of double distilled water of various pH and then the concentration of dye solution measured as stated above.

Results and Discussion

Adsorbent characteristics

The carbon ASC prepared using microwave heating found to have excellent porosity and high surface area. The carbon ASC has a BET surface area of 1041.08 m^2/g and a total pore volume of 0.4944 cm^3/g. The surface characteristics of the activated carbon fibers is given in Table 1.

The scanning electron microscopic image of the prepared carbon fiber is shown in Fig. 1. Two stage microwave irradiation of silk cotton fiber along with $FeCl_3$ catalyst produces highly porous three dimensional carbon structures. Well developed pores and great amount of roughness were observed in the SEM images of ASC (Fig. 1). The iodine value is an indication of the ability of an adsorbent to remove small pollutant molecules. The carbon ASC truly has the adsorption capacity towards large organic molecules and metal ions.

Effect of *p*H

The influence of solution *p*H on the adsorption of MB onto ASC studied over a *p*H range of 2 to 11. The variation of MB adsorption with respect to *p*H is shown in Fig. 2. The adsorption of MB onto ASC is low at lower *p*H. The MB is a cationic dye with $–N^+(CH_3)$ groups in its structure. At lower *p*H the surface of ASC become positively charged which makes some sort of repulsive force with the positively charged dye molecules. Since below the pH_{zpc} the carbon surface become positively charged, which will minimize the adsorption of MB. If the *p*H goes above pH_{ZPC} of ASC, the surface of ASC become negative and hence the negatively charged carbon surface forms chemical affinity with the positive charged dye molecule[22]. As a result of this affinity, the resistance of the boundary layer surrounding the adsorbent weakens. When the *p*H of solution further increased, there is no appreciable change in adsorption. The adsorption could have been controlled by pore diffusion as there is no much variation in adsorption after a *p*H of 8.0.

Table 1 — Surface characteristics of the activated carbon fibers

S. No	Parameter	Value
1	S_{BET} (m^2/g)	1041.08
2	Total volume (cm^3/g)	0.4944
3	Micropore volume (cm^3/g)	0.3411
4	Mesopore volume (cm^3/g)	0.1791
5	Average pore diameter (nm)	2.09
6	Iodine number (mg/g)	565.06
7	pH_{zpc}	5.05
8	Density (g/cm^3)	0.49
9	Yield (%)	47.71

Fig 1 — FESEM image of ASC fiber

Desorption of MB from ASC surface decreases with increase of *p*H from 2 to 9 and then there is no appreciable variation when the *p*H further increased above 9. As shown in Fig. 2, the maximum percent of desorption observed at *p*H 2.0 was 41.2%. Good amount dye molecules desorbed at a *p*H of 2.0 indicates that the dye molecules are attached on the carbon fiber with very weak forces of attraction. Higher percentage of desorption proves the physisorption mechanism for the adsorption of MB onto ASC.

Effect of Initial dye concentration

The effect of initial dye concentration on the adsorption of MB onto ASC is shown in Figs 3a and 3b. It can be observed that the percentage of dye uptake was rapid at the beginning of adsorption and decreases slowly and finally reaches equilibrium at 70 min. Under given set of operating conditions

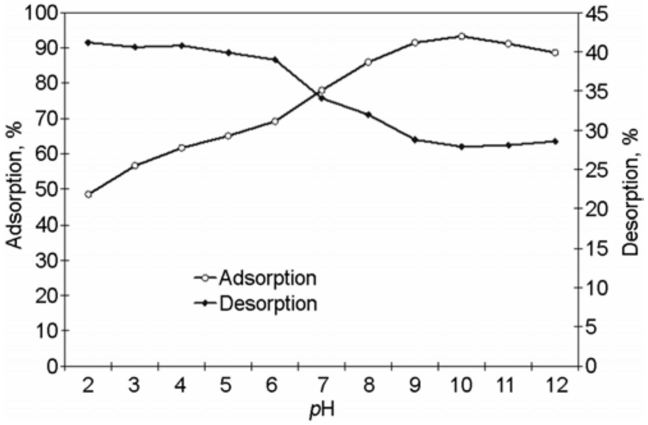

Fig 2 — Effect of *p*H for the adsorption and desorption of MB

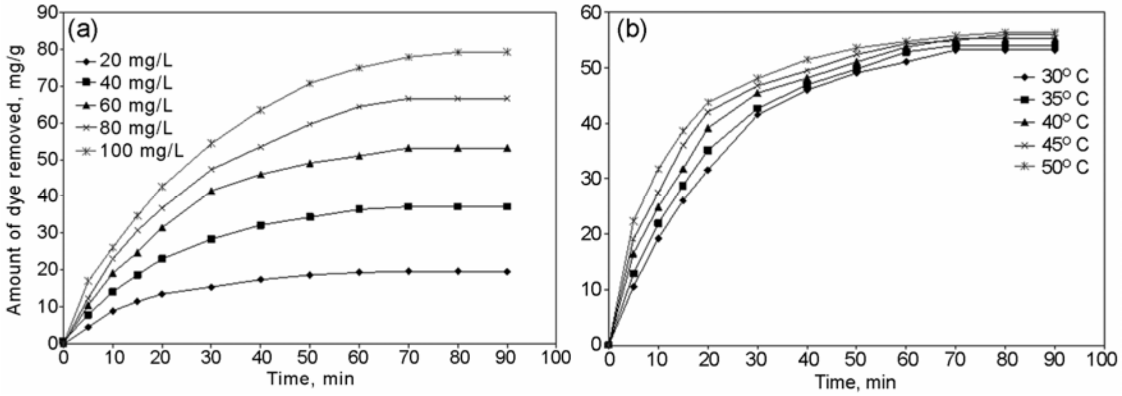

Fig 3 (a) — Effect of initial dye concentration for the adsorption of MB onto ASC; (b) — Effect temperature for the adsorption of MB onto ASC

greater percentage of MB adsorbed from its aqueous solution of lower concentration than for higher concentration. Up to 30 min of contact time, the rate of adsorption is 1.817 to 0.516 mg/g/min and than at middle of the adsorption process, the rate of adsorption slightly decreased to 1.111 to 0.281 mg/g/min and then finally reaches equilibrium at 70 min. Even though the percentage of adsorption decreases with respect to increase of initial dye concentration, the amount of dye adsorbed per gram of adsorbent increases 19.68 mg/g to 79.13 mg/g on increasing the concentration from 20 mg/L to 100 mg/L.

At lower concentrations, the ratio of the initial number of moles of dye to the available surface area is low and subsequently the fractional adsorption becomes independent of initial dye concentration. However at higher concentration, the available sites for the adsorption becomes fewer and hence the percentage removal of dye is dependent upon the initial dye concentration. The adsorption curves for the adsorption of MB onto ASC are smooth and continuous indicating the formation of monolayer coverage on the surface of adsorbent and equilibrium time is independent of initial concentration of dye.

Kinetics of adsorption

Batch experiments were conducted to explore the rate of MB adsorption onto ASC by varying the initial dye concentrations from 20 to 100 mg/L at a fixed temperature. The effect of temperature was studied by fixing the initial dye concentration at 60 mg/L and varying the solution temperature from 30 to 50°C.

Pseudo-first order kinetics

The pseudo first order rate expression suggested by Lagergren is given as[23]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad \text{... (3)}$$

where, q_e and q_t are the amount of dye adsorbed on sorbent at equilibrium and time t (mg/g) and k_1 is the first order rate constant (min^{-1}). The value of $k_1$and q_e can be determined from the slope and intercept of a plot of log (q_e -q_t) versus t (figure not shown) at various initial dye concentrations and temperature are presented in Table 2. The calculated q_e values for all MB concentrations and various temperatures obtained from the pseudo-first order kinetic model show a deviation from the experimental values. The correlation coefficient value found to be $0.997 > r^2 > 0.9608$ indicates the poor fitness of pseudo-first order kinetic model for the adsorption of MB on to ASC. The pseudo-first order rate constant varies from 5.343×10^{-2} to 6.425×10^{-2} min^{-1} for the range of concentrations under investigation and it varies from 5.343×10^{-2} to 5.804×10^{-2} min^{-1} for the range of temperatures studied. The pseudo-first order rate constant does not show any sequential variation with respect to increase of concentration or temperature. The pseudo-first order plot at various concentrations and temperature shows that during the initial period of adsorption it follows first order and in the later stages of adsorption, the plot deviates from straight line, suggesting that the pseudo-first order kinetics is applicable for the initial 20 min of contact time and deviates in the later stages of adsorption. The results indicate that the sorption of MB onto ASC is not diffusion controlled and the process does not follow the pseudo-first order kinetics.

Pseudo-second order kinetics

The linearized form of pseudo second order rate expression is given as[24]:

Table 2 — Results of kinetic studies for the adsorption of MB onto ASC

Parameters	Initial dye concentration, mg/L					Temperature °C				
	20	40	60	80	100	30	35	40	45	50
q_e exp.(mg/g)	19.68	37.21	53.14	66.52	79.13	53.14	54.00	55.20	55.92	56.33
Pseudo first order kinetics										
$k_1\times10^{-2}$ (min $^{-1}$)	6.425	5.965	5.343	5.758	5.366	5.343	5.804	5.527	5.481	5.619
q_e cal(mg/g)	21.99	43.35	58.22	84.66	97.23	58.22	59.29	53.49	49.29	45.39
r^2	0.9778	0.9669	0.9964	0.9608	0.9622	0.9964	0.9737	0.9846	0.9896	0.9922
Pseudo second order kinetics										
$k_2\times10^{-3}$ (g/mg/min)	2.44	0.92	0.56	0.37	0.31	0.56	1.04	1.26	1.47	1.77
h	1.4229	2.1409	2.8003	3.1260	3.6900	2.8003	3.4990	4.4623	5.5249	6.9252
q_e cal(mg/g)	24.15	48.31	70.92	91.74	108.70	70.92	58.14	59.52	61.35	62.50
r^2	0.994	0.9933	0.9895	0.9929	0.994	0.9895	0.9958	0.998	0.9991	0.9997
Elovich model										
α (mg/g/min)	0.184	0.090	0.061	0.048	0.041	0.061	0.065	0.070	0.076	0.083
β (g/mg)	2.929	4.415	5.859	6.743	7.955	5.859	7.156	9.420	12.662	18.607
r^2	0.9797	0.9849	0.9811	0.9886	0.9836	0.9811	0.9848	0.981	0.9755	0.9738
Intra particle diffusion model										
k_{id}(mg/g/min^{½})	0.7309	0.3331	0.2794	0.1305	0.1243	0.2794	0.2412	0.2538	0.2905	0.4329
r^2	0.9743	0.9999	0.9901	0.9985	0.9841	0.9901	0.9968	0.9999	0.9927	0.9848

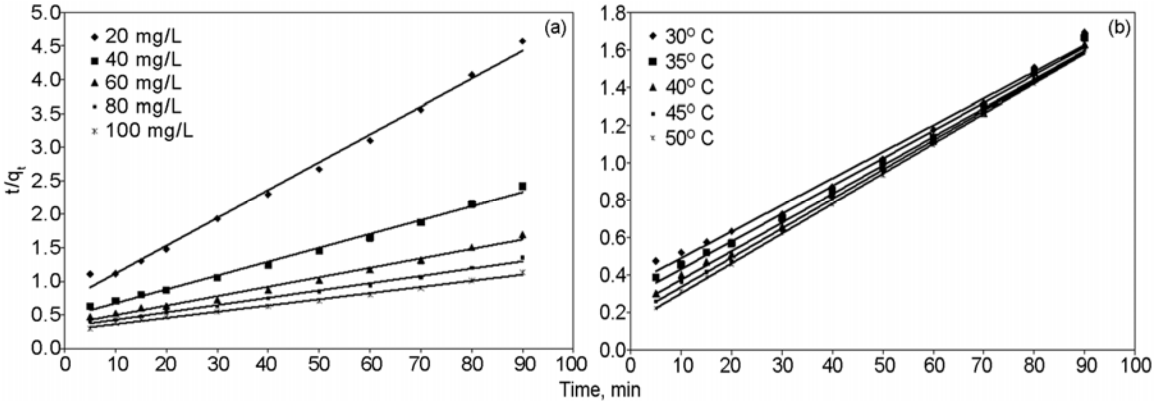

Fig 4 (a) — Pseudo-second order plot for the adsorption of MB onto ASC at various concentrations; (b) — Pseudo-second order plot for the adsorption of MB onto ASC at various temperatures

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \text{... (4)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad \text{... (5)}$$

where, k_2 is the pseudo-second order rate constant (g/mg/min). The values of q_e and k_2 can be determined from the slope and intercept of the plot of t/q_t versus t. The second-order rate constants were used to calculate the initial sorption rate, given by the following equation: h = $k_2.q_e^2$.

The pseudo-second order plot for the adsorption of MB onto ASC at various initial dye concentrations and temperatures are shown in Figs 4a and 4b and the results are presented in Table 2. The pseudo-second order rate constant decreases from 2.44×10^{-3} to 0.31×10^{-3} g/mg/min on increasing the initial dye concentration from 20 to 100 mg/L and it increases from 0.56×10^{-3} to 1.77×10^{-3} g/mg/min on increasing the solution temperature from 30 to 50°C. The increase of rate constant with increase in temperature indicating that the sorption system reached equilibrium faster at high temperature. This may be due to an increase in the probability of collision between active surface binding sites and the adsorbate and a decrease in thickness of boundary layer of the adsorbent at high temperature. The q_e value calculated using pseudo-second order kinetic model show slight deviation from the calculated q_e values for all the range of concentration and temperature under investigation. The initial sorption rate, h increases while increasing the concentration as well as the solution temperature. When the concentration increases, the number of dye molecules around the sorbent surface increases which lead to high initial sorption rate.

The high value of correlation coefficients $0.9895 < r^2 < 0.9997$ indicates better fitness of the data for the adsorption of MB onto ASC and also it indicates that the adsorption follows pseudo-second order kinetics.

Elovich Model

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as the following[25]:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad \text{... (6)}$$

Integrated linear form of the equation can be written as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad \text{... (7)}$$

where, α (initial adsorption rate) and β (desorption constant) were calculated from the slope and intercept of the plot of lnt versus q_t (figure not shown).

The initial adsorption rate α decreases from 0.184 to 0.041 mg/g/min on increasing the initial dye concentration from 20 to 100 mg/L and it increases from 0.061 to 0.083 mg/g/min on increasing the temperature from 30 to 50°C. This variation is consistent with the initial sorption rate obtained in the pseudo-second order rate expression. The desorption constant β increases from 2.929 to 7.955 g/mg on increasing the concentration from 20 to 100 mg/L and it increases from 5.859 to 18.607 g/mg on increasing the temperature from 30 to 50°C. At higher concentrations and temperatures the rate of forward and backward reactions of adsorption are more which is indicated by the high value of desorption constant (β). The correlation coefficient of Elovich model is moderately good with a value of $0.9738 < r^2 < 0.9886$.

Intra-particle diffusion model

When diffusion (internal surface and pore diffusion) of dye molecule inside the adsorbent is the rate-limiting step, then adsorption data can be presented by the following equation:

$$q_t = k_{id} \cdot t^{½} \quad \text{... (8)}$$

where, k_{id} is the intra-particle diffusion rate constant (in mg/g/min^{½}). The rate constant k_{id} directly evaluated from the slope of the regression line of q_t versus $t^{½}$ (figure not shown) and the results are presented in Table 2. The intra-particle diffusion constant decreases from 0.7309 to 0.1243 mg/g/min^{½} on increasing the initial dye concentration from 20 to 100 mg/L and it increases from 0.2794 to 0.4329 mg/g/min^{½} on increasing the temperature from 30 to 50°C.

The r^2 values ranged from $0.9743 < r^2 < 0.9999$, indicates the applicability of intra-particle diffusion model suggested by Webber-Morris. The plot $\mathbf{q_t}$ versus $t^{½}$ does not pass through origin indicates that intra-particle diffusion is not the rate limiting step. It may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the adsorption of MB onto ASC.

Adsorption isotherm

The equilibrium isotherms are used to describe fitness of the experimental data for the selected adsorption system. The applicability of the selected adsorption system is analyzed using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) adsorption isotherm models.

Langmuir isotherm

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface[26]. Linear form of the rearranged Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \quad \text{... (9)}$$

where, Q_0 is a constant related to complete monolayer adsorption capacity (mg/g) and b_L is Langmuir constant related to apparent energy of adsorption L/mg. The constants Q_0 and b_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e (figure not shown) and results are presented in Table 3.

The maximum monolayer capacity Q_0 obtained from Langmuir isotherm plot is 80.65 mg/g for the

Table 3 — Results of Isotherm plots for the adsorption of MB onto ASC

Parameters	Temperature °C			
	30	35	40	45
Langmuir isotherm				
Q_0 (mg/g)	77.52	78.74	79.37	80.65
$b_L \times 10^{-3}$(L/mg)	0.0121	0.0122	0.0122	0.0122
r^2	0.9749	0.9885	0.99	0.9877
Freundlich isotherm				
n	2.38	2.74	3.02	4.34
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	17.04	22.22	26.06	34.01
r^2	0.9729	0.9303	0.9466	0.9884
Temkin isotherm				
b_T (J/mg)	144.14	170.74	177.87	196.85
a_T (L/mg)	1.627	3.998	5.577	11.650
r^2	0.9958	0.9977	0.9873	0.9811
Dubinin-Radushkevich isotherm				
q_D (mg/g)	61.05	62.09	66.58	62.92
$B \times 10^{-7}$(mol^2/J^2)	20.0	6.0	6.0	1.0
E (kJ/mol)	0.5	0.91	0.91	2.24
r^2	0.8392	0.8059	0.9071	0.6490

adsorption of MB onto ASC surface. The Langmuir constant related to energy of adsorption does not show any variation while increasing the temperature from 30 to 45°C.

The essential characteristics of Langmuir isotherm can be expressed by dimensionless constant called equilibrium parameter, R_L.

$$R_L = 1/\ (1+b_L.C_0) \quad \text{... (10)}$$

where, b_L is the Langmuir constant and C_0 is the initial concentration (mg/L). The value of R_L indicates the nature of the adsorption process as given below

$R_L > 1$ Unfavorable
$R_L = 1$ Linear
$0 < R_L < 1$ Favorable
$R_L = 0$ Irreversible

The R_L value ranges between zero and one for the range of temperatures studied indicate that the adsorption is favorable.

The value of R_L (dimension less constant separation factor) between 0 and 1 indicates that the adsorption of MB onto ASC is favorable for the range of temperatures studied. The correlation coefficient r^2 varies from 0.9749 to 0.9900. This suggests that the Langmuir isotherm provides a good model of the sorption of MB onto ASC.

Freundlich model

The Freundlich isotherm can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer sorption[27]. The Freundlich isotherm can be derived assuming a logarithmic decrease in enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

$$q_e = k_f C_e^{1/n} \quad \text{... (11)}$$

where, k_f is the measure of adsorption capacity related to bond energy and 1/n is the adsorption intensity of dye onto the adsorbent or it can also be called as surface heterogeneity.

The linear form of Freundlich equation is

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{... (12)}$$

A plot of log q_e vs log C_e gives a linear trace (figure not shown) with a slope of $1/n$ and intercept of log k_f and the results are presented in Table 3. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. When $1/n$ is < 1.0, the change in adsorbed concentration is greater than the change in the solute concentration.

As the value of Freundlich constant (k_f) increases, the adsorption capacity of adsorbent for a given adsorbate increases. The Freundlich constant k_f for the adsorption of MB onto ASC increases from 17.04 to 34.01 ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) on increasing the temperature from 30 to 45°C, which indicates that the adsorption favored by raise in system temperature. Another constant n related to adsorption intensity increases from 2.38 to 4.34, indicates that the adsorption of MB onto ASC is highly favorable. The r^2 value for Freundlich model is between 0.9303 to 0.9884 shows that Langmuir model is more appropriate to describe the adsorption system than Freundlich model.

Temkin isotherm model

The Temkin isotherm model contains a factor that explicitly takes into account the interactions between adsorbate and adsorbent species[28]. It further implies that the heat of adsorption of all the molecules in the layer would decrease linearly with the coverage involved in this interaction.

The Temkin isotherm is applied in the following form

$$q_e = \left(\frac{\mathrm{RT}}{\mathrm{b_T}}\right) \ln\left(\mathrm{a_T}.C_\mathrm{e}\right) \quad \text{... (13)}$$

The linear form of Temkin equation is

$$q_e = \frac{RT}{b_T}\ln a_T + \frac{RT}{b_T}\ln C_e \qquad \text{... (14)}$$

where, b_T is the Temkin constant related to heat of sorption (J/mg) and a_T the equilibrium binding constant corresponding to the maximum binding energy (L/mg).

The Temkin constants were calculated from a plot of q_e versus C_e (figure not shown) and the results are given in Table 3. Analysis of the results derived from the Temkin plot show that the constant b_T increases from 144.14 to 196.85 J/mg on increasing the temperature from 30 to 45°C. At high temperature the kinetic energy of the dye molecules increases which ultimately increase the rate of desorption. Another constant a_T related to Temkin sorption potential increases from 1.627 to 11.650 L/mg while increasing the temperature from 30 to 45°C. The Temkin model correlation coefficient for the adsorption of MB onto ASC is $0.9811 < r^2 < 0.9977$ indicate that the Temkin model also demonstrates the adsorption of MB onto ASC with good degree of fitness.

Dubinin-Radushkevich isotherm

The D-R model was also applied to estimate the porosity apparent free energy and the characteristics of adsorption[29,30]. The D-R isotherm does not assume a homogeneous surface or constant sorption potential.

The isotherm proposed by Dubinin[29] has the following form

$$q_e = q_D.e^{-B\varepsilon^2} \qquad \text{... (15)}$$

Linear form of Dubinin-Radushkevich isotherm is

$$\ln q_e = \ln q_D - B\varepsilon^2 \qquad \text{... (16)}$$

where, q_D is the theoretical saturation capacity (mg/g), B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and ε is polanyi potential which is related to the equilibrium as follows;

$$\varepsilon = RT\ln(1+1/C_e) \qquad \text{... (17)}$$

where, R is the Universal gas constant (8.314 J/mol K)

A plot of ln q_e vs ε^2 gives a linear trace (figure not shown) and the constants q_D and B calculated from the slope and intercept as given in Table 3. The mean free energy of adsorption E calculated from B using the following equation

$$E = 1/(2B)^{½} \qquad \text{... (18)}$$

The maximum saturation capacity Q_D obtained from D-R isotherm model for the adsorption of MB onto ASC is 66.58 mg/g. This is consistent with the Langmuir monolayer adsorption capacity. The variation of Q_D is not sequential with respect to increase in temperature. The mean free energy of adsorption E varies from 0.5 to 2.24 kJ/mol on increasing the temperature from 30 to 45°C. The low mean free energy of adsorption indicates that the adsorption of MB onto ASC is dominated by physical forces of attraction with chemisorption a negligible role. The correlation coefficient is very low ($0.6490 < r^2 < 0.9071$) suggesting the poor fitness of D-R model for the present adsorption system.

Thermodynamic parameters

The thermodynamic parameters such as standard free energy change ΔG°, standard enthalpy ΔH°, and standard entropy ΔS° were also calculated to identify the influence of temperature on the adsorption process. These parameters were calculated using the following equation[31].

$$K_c = \frac{C_{ads}}{C_{sol}} \qquad \text{... (19)}$$

$$\Delta G^0 = -RT\ln K_c \qquad \text{... (20)}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad \text{... (21)}$$

where, K_c is the equilibrium constant, C_{ads} is the amount of MB (mg/L) adsorbed on ASC at equilibrium, C_{sol} is the equilibrium concentration of MB (mg/ L) in the solution, T is the solution temperature and R is a gas constant. The values ΔH° and ΔS° were evaluated from the slope and intercept of Vant Hoff plot of ln K_c versus 1/T and the results were presented in Table 4.

The negative Gibbs free energy -ΔG° indicates the more spontaneous nature of MB adsorption onto ASC and also the more negative ΔG° at higher temperature

Table 4 — Thermodynamic parameters for the adsorption of MB onto ASC

Temp, °C	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, kJ/mol
30	- 4.471	47.76	173.04
35	- 5.742		
40	- 6.634		
45	- 7.039		

substantiates that the adsorption is more favored by high solution temperature. The ΔH° for the adsorption of MB onto ASC is 47.76 kJ/mol depicts the physisorption nature of adsorption (the enthalpy value is < 80 kJ/mol for physisorption) and the positive sign indicates the endothermic nature of adsorption. The standard entropy change ΔS° for the adsorption of MB onto ASC is 173.04 J/K/mol indicate the increased randomness at the solid liquid interface during adsorption which is beneficial for a better adsorption system.

Conclusion

Activated carbon fiber prepared from silk cotton using microwave irradiation can be conveniently used for the adsorption of methylene blue dye. The activated carbon fiber has the surface area of 1041.08 m^2/g. In all the concentrations and temperatures of study, rapid uptake of dye involved in the initial 30 min of contact time and the equilibrium reached at 70 min. The maximum sorption of MB is 93.3% at pH of 10.0. The adsorption of MB on to ASC follows pseudo second-order kinetics with high correlation coefficient. The mean energy of activation indicates that the adsorption of MB is physisorption in nature. Intra particle diffusion model proves that pore diffusion plays major in the dye adsorption. The adsorption isotherm data fits well for Langmuir isotherm models with high correlation coefficient. The positive enthalpy proves that the adsorption of MB onto ASC is endothermic in nature. ASC is a promising adsorbent for the removal of basic dyes from waste water.

References

1 Orfao J, Silva A, Pereira J, Barata S, Fonseca I & Faria P, *J Col Inter Sci*, 296 (2006) 480.
2 Kumar A, Chaudhary P & Verma P, *Sch J App Med Sci*, 1(2013), 111.
3 Khan T A, Sharma S & Ali I, *J Toxic Environ H Sci*, 3 (2011), 286.
4 Eren Z & Acar F N, *Desalination*, 194 (2006) 1.
5 Lin S H & Lo C C, *Environ Technol*, 17 (1996) 841.
6 Arslan I A & Bahnemann D W B, *Dyes and Pigments*, 47 (2000) 207.
7 Kanazawa H & Onami T, *Bull Chem Soc Japan*, 68 (1995) 2483.
8 Purkait M K, DasGupta S & De S, *Sep Purif Technol*, 37(2004) 81.
9 Garg V K, Kumar R & Gupta R, *Dyes and Pigments*, 62 (2004) 1.
10 Namasivayam C & Kavitha D, *Dyes and Pigments*, 54 (2002) 47.
11 Amin N K, *Desalination*, 223 (2008) 152.
12 Khattri S D & Singh M K, *Adsorp Sci Technol*, 17 (1999) 269.
13 Guo Y, Yang S, Fu W, Qi J, Li R & Wang Z, *Dyes and Pigments*, 56 (2003) 219.
14 Annadurai G, Juang R & Lee D, *J Hazard Mater*, B92 (2002) 263.
15 Robinson T, Chandran B & Nigam P, *Water Res*, 36 (2001) 2824.
16 Alau K K, Gimba C E & Kagbu J A, *Appl Sci Res*, 2 (2010) 456.
17 Namasivayam C & Arasi S E, *Chemosphere*, 34 (1997) 401.
18 Wang S, Boyjoo Y, Choueib A & Zhu Z H, *Water Res*, 39 (2005) 129.
19 Yacob A R, Wahab N, Suhaimi N H & Mustajab M K A A, *Int J Engg Technol*, 5 (2013) 214.
20 Vadivelan V & Kumar K V, *J Colloid Interf Sci*, 286 (2005) 90.
21 Tadjarodi A, Imani M & Kerdari H, *J Nanostruct Chem*, 3 (2013) 51.
22 Noroozi B, Sorial G A, Bahrami H & Arami M, *J Hazard Mater*, B139 (2007) 167.
23 Lagergren S, *Kun Sven Vetenskapsakad Handl*, 24 (1898) 1.
24 Ho Y S, McKay G, Wase D A J & Foster C F, *Adsorpt Sci Technol*, 18 (2000) 639.
25 Kavitha D & Namasivayam C, *Bioresour Technol*, 98 (2007) 14.
26 Langmuir I, *J Am Chem Soc*, 40 (1918) 1361.
27 Freundlich H, *Z Phys Chem*, 57 (1906) 387.
28 Temkin M J & Pyzhev V, *Acta Physiochim*, USSR 12 (1940) 217.
29 Dubinin M M, *Zhurnal Fizicheskoi Khimii*, 39 (1965) 1305.
30 Radushkevich L V, *Zhurnal Fizicheskoi Khimii*, 23 (1949) 1410.
31 Gopal N, Asaithambi M, Sivakumar P & Sivakumar V, *J Water Process Eng*, Article in Press (2014), http://dx.doi.org/10.1016/j.jwpe.2014.05.008