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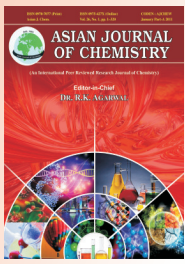

Removal of Methylene Blue from Synthytic Waste Water by Coconut Husk Fiber Based-Activated Carbon

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The adsorption of methylene blue on activated carbon fiber and granular activated carbon was studied in a batch system. The effects of initial concentration, agitation time, solution pH and temperature were examined. Langmuir and Freundlich models were applied to investigate adsorption isotherms. It was found that, the Langmuir model fits well with the experimental data in the case of activated carbon fiber, whereas both models fit the experimental data for adsorption of methylene blue on granulated activated carbons. The pseudo first-order, second-order and intra-particle diffusion models were used to examine the kinetics data. The results obtained showed that empirical kinetics data of both activated carbon fiber and granulated activated carbons were only well described by the second-order model. It was observed that the granulated activated carbons has adsorption performance higher than that of activated carbon fiber. Adsorption thermodynamics parameters were investigated and their values indicated that the adsorption of methylene blue on activated carbon fiber and granulated activated carbons were endothermic and spontaneous processes.

Keywords: Isotherm, Kinetics, Thermodynamics, Methylene blue, Coconut husk fiber, Activated carbon fiber.

INTRODUCTION

Methylene blue (MB) is the cationic dye that is frequently used for dyeing cotton, wool and silk[1]. Thus, wastewaters produced from chemical industries related to the use and synthesis of methylene blue are always polluted by this organic contaminants. Human exposed to these contaminated wastewaters suffer from tachycardia, methemoglobinemia, cyanosis, convulsions, dyspnea, irritation to the skin and gastrointestinal tract, nausea, vomiting and/or diarrhea[2,3]. Therefore, it is very important to remove the methylene blue from industrial wastewaters before its discharge to the environment. For this, various techniques like chemical precipitation, coagulation, solvent extraction, membrane filtration, reverse osmosis and adsorption have been applied for purification the industrial effluents from methylene blue[4]. It was reported by many researchers that the adsorption is the best and the most commonly method has been employed in wastewater treatment. This is due to its ability to eliminate methylene blue at any concentration at a relatively lower cost[3,4]. Conventionally, granulated activated carbon and powdered activated carbon (GAC and PAC) are the oldest and the most widely used adsorbents. The raw materials such as coal are non-renewable and relatively expensive[5]. It was also reported that the slow intraparticular diffusion in granulated activated carbons is a problem encountered in the using of adsorption technique to water treatment[6]. Moreover, powdered activated carbons due to its prattle nature, its usage in adsorption technique generates fine carbon[7]. Therefore, additional work such as separation of powdered activated carbons from the fluid after use is required[7]. Thus, the use of commercially granulated activated carbons and powdered activated carbons has been limited in recent years[8]. On the contrary, activated carbon fiber (ACF) has a high adsorption capacity and rate and easier to handle in a batch system compared to powdered and/or granular activated carbon[9]. For these reasons, activated carbon fibers have got much attention from many researchers as a new adsorbent for the purification of contaminated gaseous and liquid phases[10]. Various industrial fibers such as polyacrylonitrile[11], poly(*p*-phenylene terephthalamide)[12], Nomex [poly(*m*-phenylene isophthalamide)][13] and polyvinyl alcohol[14] have been used for the preparation of activated carbon fiber. The main negative aspect of the activated carbon fibers produced from manufactured fibers is its higher price compared to the commercial activated carbons[15]. Therefore, to increase the functionality and application capabilities of activated carbon fibers it would be sensible to use low-cost materials like natural fibers as precursors for the production of activated carbon fibers. Consequently, piassava fibers[16], kenaf fibers[17], cotton stalks[18], coconut shell fibers[19], jute and coconut fibers[10], coconut husk fiber[20,21] and oil palm fiber[5] were

used as low cost natural precursors for production of activated carbon fiber.

Although, the fibers obtained from coconut husk are abundant in tropical countries like Malaysia, have little ash content and are low-cost in comparison with industrial fibers, only one attempt has been carried out by Al-Aoh and his co-worker[22] to examine the adsorption performance of methylene blue, on activated carbon fiber from coconut husk fibers. The L_{19} orthogonal array of Taguchi experimental design method was applied by Al-Aoh[23] to optimize the experimental conditions for preparation of activated carbon fiber with higher adsorption performance towards methylene blue. He reported that some of experimental parameters are significant and the others have insignificant effects on the adsorption capacity of methylene blue on the prepared samples. Therefore, the main aim of this work was to investigate the adsorption parameters of methylene blue by coconut husk fibers based-activated carbon prepared under optimal conditions using L_9 orthogonal array of Taguchi method and AVOVA analysis.

EXPERIMENTAL

Preparation and characterization of the adsorbents: Coconut husk fiber-based activated carbon was prepared in a horizontal tube furnace under optimized conditions. The optimized parameters were; activation temperature of 600 °C, 50 % w/v $ZnCl_2$ concentration, activation time of 3 h and 3 days of soaking time. The commercial granular activated carbon (GAC; CAS No. 64365-11-3) was obtained from Sigma Aldrich (Germany). The specific surface areas (S_{BET}) of activated carbon fiber and granulated activated carbons were measured by N_2 adsorption (at 77.40 K), using a surface analyzer (Sorptomatic Thermo Finnigan 1990, U S A). The *t*-method was used to determine the pore structure of these adsorbents. The pH at the point of zero charge of the prepared activated carbon fiber was determined by using the batch equilibrium method, as described by Babic *et al.*[24]. The surface morphology of the adsorbents used in this work was studied by scanning electron microscopy (LEO 1455 VP, England).

Adsorbate: Methylene blue (28514 FLUKA) with purity ≥ 95 %, molecular weight 319.85, empirical formula $C_{16}H_{18}ClN_3S.xH_2O$ and having maximum wave length at 618 nm, was supplied by Sigma-Aldrich (U.S.A.). A stock solution of 10000 mg/L was prepared by dissolving 10 g of methylene blue (MB) in 300 mL distilled water and diluted to 1000 mL. The test solutions were prepared by diluting of this stock solution to the required concentrations using distilled water.

Adsorption procedures

Effect of the initial adsorbate concentration: Experiments on the effect of the initial concentration of methylene blue were performed in eight 30 mL amber bottles each containing 25 mL of methylene blue solution at different initial concentrations (50-1000 mg/L). Certain amount (0.03 g) of the prepared activated carbon fiber was then added to each bottle. The bottles were mounted on a rotational shaker and shaken at 150 rpm, at room temperature (30 ± 1 °C) and without any pH adjustment, for four days to reach equilibrium. After reaching the equilibrium the samples were through a 0.45 µm membrane filter paper under suction. The concentrations of methylene blue in the filtrate before and after adsorption were measured by UV-visible spectrophotometer (Shimadzu, Japan) at 618 nm. The same procedures were repeated with granulated activated carbons as the adsorbent. The amounts of methylene blue adsorbed onto both adsorbents were calculated by eqn. 1.

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

where C_o and C_e (mg/L) are the initial and final concentrations of methylene blue, respectively, W (g) is the mass of adsorbent used, q_e (mg/g) is the adsorption amount per unit gram of the adsorbent at equilibrium and V (L) is the volume of the solution.

Adsorption isotherms: Adsorption of 200, 300, 400, 600 and 800 mg/L of methylene blue solution onto fixed amounts (0.03 g) of activated carbon fiber and granulated activated carbons were carried out at 30, 45 and 60 °C in a batch system. These experiments were performed by adding 25 mL of each solution to 30 mL amber bottles each of which contained the required amount of activated carbon fiber or granulated activated carbons. The amber bottles were sealed and placed in an incubator shaker without any pH adjustment. The bottles were shaken at an agitation speed of 150 rpm for four days to reach equilibrium. The mixtures were filtered and the final concentrations of methylene blue in the filtrate were diluted and measured by UV-visible spectrophotometer (Shimadzu, Japan) at the methylene blue maximum wavelength (618 nm). The amounts of methylene blue adsorbed at equilibrium, q_e (mg/g) were calculated from eqn. 1. The results obtained were used for determination of the adsorption capacities and thermodynamic parameters. The effect of temperature was also investigated using these results.

Adsorption kinetics: To investigate the effect of agitation time and kinetic parameters, adsorption of 100 and 200 mg/L solutions of methylene blue on the activated carbon fiber and granulated activated carbons were investigated at various time intervals. The same procedures as described in the isotherm studies were applied. The amount of methylene blue adsorbed q_t (mg/g) at time *t* (min) was calculated from eqn. 2.

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where, q_t is the amount of methylene blue adsorbed at time *t* (mg/g). Co and C_t (mg/L) are the liquid phase concentrations at initial and any time *t*, respectively. V is the volume of the solution (L) and W is the mass of adsorbent (g). The results obtained were used to investigate the effect of contact time as well as the adsorption kinetics.

Effect of solution pH: A series of 600 mg/L methylene blue solutions at various initial pH (2-11) were prepared by the addition of either HCl or NaOH. 25 mL of each of this solution was added to a 30 mL amber bottle containing 0.03 g of either activated carbon fiber or granulated activated carbons. The bottles were then sealed, placed on a rotational shaker and shaken for four days at 150 rpm and room temperature (30 ± 1 °C). The adsorbent was separated from the aqueous phase by filtration through a membrane filter paper. The final concentrations of methylene blue and adsorption amounts at equilibrium were measured and calculated.

RESULTS AND DISCUSSION

Characterization of the activated carbons: The results of some important physical properties such as surface area, pore structure and pH_{ZPC} of the activated carbon fiber and granulated activated carbons are summarized in Table-1. It can be observed from this table that granulated activated carbons has a larger surface area, larger total pore volume, larger mesopore volume and higher mesopore percentage than that of activated carbon fiber. This indicates that the adsorptive properties of the former are better than that of the latter. The pH_{ZPC} was found to be 7.6 and 6.4 for activated carbon fiber and commercial granular activated carbon, respectively.

TABLE-1
CHARACTERISTICS OF THE ACTIVATED CARBONS

Type of activated carbon	Activated carbon fiber	Granular activated carbon
Specific surface area (m^2/g)	956.898	1061
Total pore volume (cm^3/g)	0.448	0.559
Micropore volume (cm^3/g)	0.350	0.328
Mesopore volume (cm^3/g)	0.098	0.231
Average pore diameter (Å)	18.73	21.06
Micropore (%)	78.13	58.68
Mesopore (%)	21.87	41.32
pH_{ZPC}	7.6	6.4

Fig. 1 (a) and (b) represents the SEM images of the prepared activated carbon fiber and commercial granulated activated carbons, respectively. It can also be observed from this figure that the number of pores on the surface of the prepared activated carbon fiber is higher than that of commercial granular activated carbon. This indicates that the granulated activated carbon has average pore diameter higher than that of activated carbon fiber. Hence the granulated activated carbons is more effective in adsorbing methylene blue. Moreover, this observation is in agreement with the results from surface analysis.

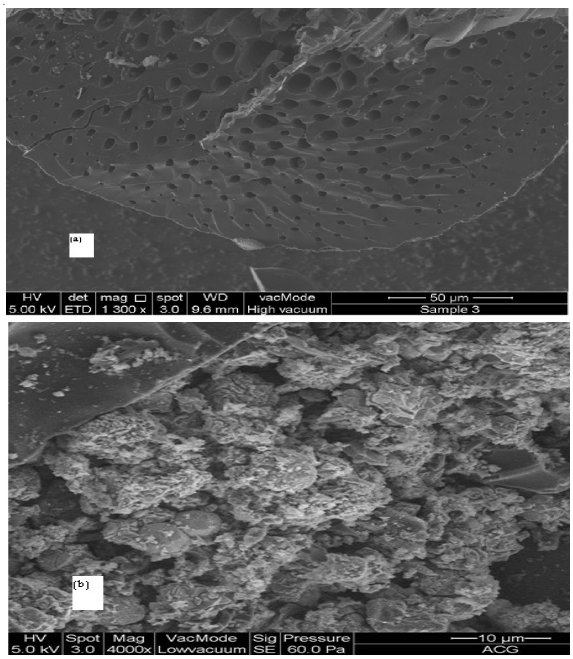

Fig. 1. SEM images of (a) activated carbon fiber and (b) granular activated carbon

Adsorption studies

Effect of initial adsorbate concentration on the adsorption process: The effect of the initial concentrations of methylene blue on its adsorption capacity at equilibrium was investigated (Fig. 2). This figure shows that the amount of methylene blue adsorbed on activated carbon fiber increased with increasing initial concentrations from 50 to 400 mg/L, whereas the adsorption ability of methylene blue on the granular activated carbon increase as the initial concentration of methylene blue increased in the range of 50-600 mg/L. This means that an increase in initial methylene blue concentration resulted in increasing the solute uptake. Similar observations have been reported[25-27].

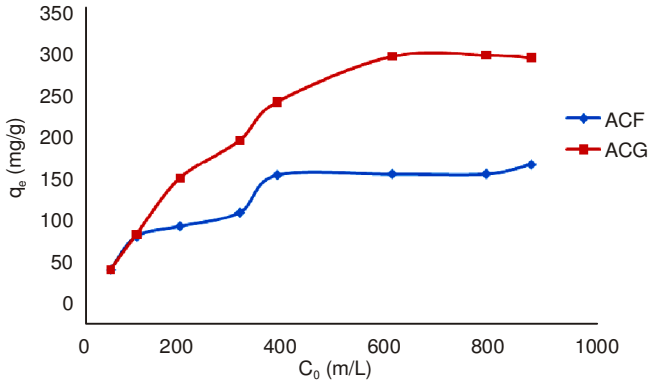

Fig. 2. Effect of initial concentration on the adsorption of methylene blue on activated carbon fiber (ACF) and granular activated carbon (ACG)

On the other hand, the amount adsorbed (q_e mg/g) is almost constant at initial concentrations of over 400 mg/L and 600 mg/L for activated carbon fiber and granular activated carbon, respectively. This can be explained by the fact of all adsorption sites became saturated after these initial concentrations. Moreover, it can also be observed from Fig. 2 that the adsorption efficiency of activated carbon fiber towards methylene blue is lower than that of granular activated carbon. This is because granular activated carbon has a higher surface area, larger pore diameter, higher total pore volume, higher mesopore volume and larger mesopore percentage (Table-1), which makes it more effective in adsorbing the dye. Similar observation was reported by Fernandes *et al.*[28].

Adsorption isotherms: The linear forms of the Langmuir (eqn. 3) and the Freundlich (eqn. 4) models were employed in this work in order to investigate the adsorption behaviour for activated carbon fiber and granulated activated carbon towards methylene blue at three different temperatures (30, 45 and 60 °C).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (3)$$

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

where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_{max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e is the concentration of the adsorbate at equilibrium (mg/L), K_L (L/mg) is the Langmuir constant and K_F (mg/g) $(L/mg)^{1/n}$ with 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. If the value of 1/n is between 0 and 1 the adsorption is favorable[29].

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless factor called equilibrium parameter R_L which is defined by eqn. 5.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where, K_L is the Langmuir constant and C_0 is the initial adsorbate concentration. The value of R_L indicates the type of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The plots of C_e/q_e *versus* C_e for activated carbon fiber and granulated activated carbons are shown in Figs. 3 and 4, respectively. In addition the plots of ln q_e against ln C_e are represented in Figs. 5 and 6 for activated carbon fiber and the commercial granulated activated carbons, respectively. The isotherms parameters of Langmuir (q_{max} and K_L) and Freundlich (K_F and n) with the corresponding correlation coefficients (R^2) were calculated and their values listed in Table-2. The values of R_L were also calculated according to eqn. 5 (Table-2).

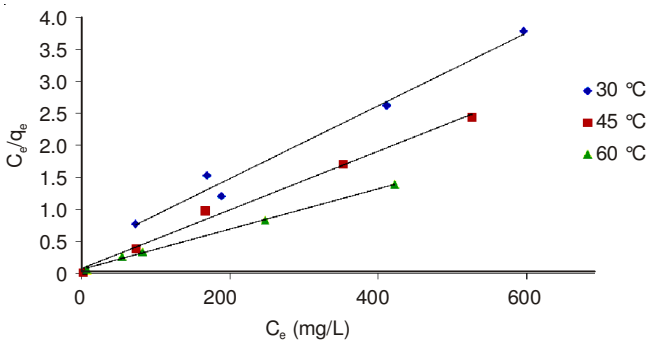

Fig. 3. Langmuir isotherm model for the adsorption of methylene blue on activated carbon fiber at three different temperatures (30, 45 and 60 °C)

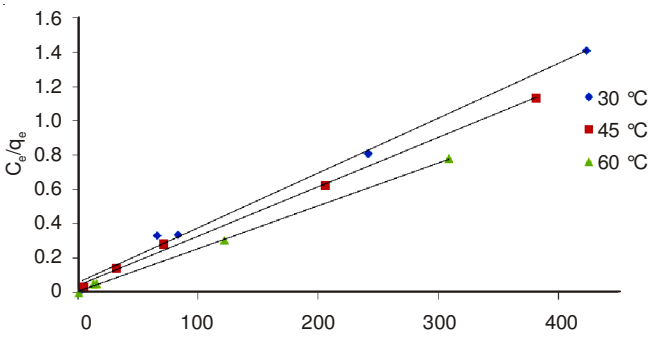

Fig. 4. Langmuir isotherm model for the adsorption of methylene blue on granulated activated carbons at three different temperatures (30, 45 and 60 °C)

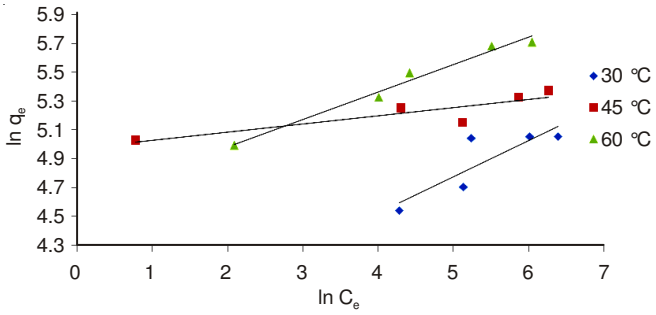

Fig. 5. Freundlich isotherm model for the adsorption of methylene blue on activated carbon fiber at three different temperatures (30, 45 and 60 °C)

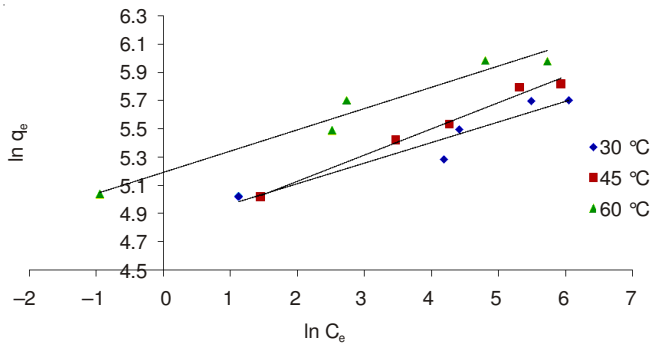

Fig. 6. Freundlich isotherm model for the adsorption of methylene blue on granulated activated carbons at three different temperatures (30, 45 and 60 °C)

The values of R_L and 1/n (Table-2) were found to be between 0 and 1, indicating that both activated carbon fiber and granulated activated carbons adsorb methylene blue favorably under the conditions studied. In case of the activated carbon fiber, the correlation coefficients (R^2) for the Langmuir model are more than that of the Freundlich isotherm model, indicating that the former offers a better fit than the latter. This confirms that the surfaces of the activated carbon fiber used in this work are uniform and the adsorption sites are of the same type. Similar results have been reported for the adsorption of methylene blue on cedar sawdust and crushed brick[30]. On the other hand, the correlation coefficients (R^2) values for the Langmuir and Freundlich isotherm models are over 91 for adsorption of this dye on granulated activated carbons. This suggests that both models satisfactorily fit the adsorption of methylene blue on the commercial granulated activated carbons.

Table-2 showed that the values of q_{max} and K_F obtained for granulated activated carbons are higher than that of

TABLE-2
LANGMUIR AND FREUNDLICH PARAMETERS AND THE SEPARATION FACTORS (R_L) FOR THE ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON FIBER AND GRANULATED ACTIVATED CARBONS AT THREE DIFFERENT TEMPERATURES (30, 45 AND 60 °C)

Adsorbent	Temperature (°C)	Langmuir isotherm				Freundlich isotherm			
		q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)(L/mg)$^{1/n}$	1/n	n	R^2
Activated carbon fiber	30	175.44	0.016	0.074	0.983	33.88	0.251	3.98	0.731
	45	217.39	0.063	0.020	0.994	144.68	0.057	17.54	0.799
	60	312.50	0.050	0.025	0.998	100.13	0.190	5.26	0.980
Granulated activated carbon	30	312.50	0.050	0.025	0.994	124.20	0.146	6.85	0.912
	45	344.83	0.066	0.019	0.998	116.50	0.186	5.38	0.988
	60	400.00	0.248	0.005	0.999	180.06	0.150	6.67	0.956

activated carbon fiber, which indicate that the former has better adsorption efficiency than the latter. This is due to the higher surface area and higher percentage of mesopores for granulated activated carbons (Table-2), hence is more effective in adsorbing methylene blue.

Effect of temperature: It can be seen from Table-2 that the adsorption capacity of the activated carbon fiber and granulated activated carbons increases with rising temperature of the solution, indicating that the process is endothermic. This is owing to the increase in the mobility of methylene blue due to the increase in solution temperature. An adequate energy may also be required for additional number of molecules to undergo an interaction with the active sites at the surface[31]. Moreover, rising temperature may cause swelling of the internal structure of these adsorbents, enabling extra number of the dye molecules to penetrate them[32]. Similar trends were reported in the literature for the adsorption of methylene blue on activated carbon prepared from coconut husk[22].

Thermodynamic parameters: The enthalpy (ΔH°) and entropy (ΔS°) change values were computed from slopes and intercepts of the plotted lines (Fig. 7) according to eqn. 6, while the values of the free energy change (ΔG°) at three different temperatures were calculated from eqn. 7.

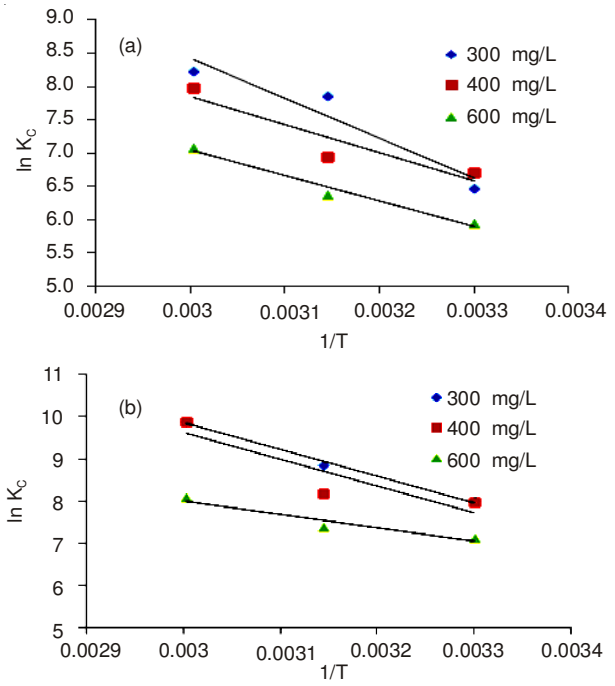

Fig. 7. Plots of $\ln K_c$ *versus* 1/T for the adsorption of methylene blue onto (a) activated carbon fiber and (b) granulated activated carbons at different dye concentrations

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where, R (8.314 J/mol K) is the universal gas constant, T (K) is the solution temperature, K_c (L/g) is the standard thermodynamic equilibrium constant defined by (q_e/C_e).

The calculated values of these parameters are summarized in Table-3. The positive values of ΔH° indicate that the adsorption of this dye on the activated carbon fiber or granulated activated carbons is endothermic in nature. This is in accordance with the results observed in earlier study on the effect of temperature.

The values of ΔH° (Table-3) are in the range of (31.702-49.341) and (26.987-52.179) for activated carbon fiber and granulated activated carbons, respectively. It was reported in the literature[8,34] that the adsorption enthalpy, ranging from 2.1 to 20.9 kJ/mol corresponds to a physical adsorption. Therefore, the values of ΔH° obtained in this work suggest that the adsorption of methylene blue on activated carbon fiber and/or granulated activated carbons can be classified as chemical adsorption. It was also found that in the case of the adsorption kinetics the experimental data is well described by the pseudo-second order model, indicating that the type of this adsorption is chemisorption. The positive ΔS° values suggest an increase in the randomness at the adsorbate-solution interface during the adsorption process.

The negative values of ΔG° suggest that the adsorption of methylene blue onto any one of these two adsorbent is spontaneous. It can also be observed from Table-3 that the values of ΔG° become more negative as the adsorption temperature is increased for each concentration, indicating that higher temperature is the most favorable condition for higher adsorption efficiency. In other words, the affinity of methylene blue molecules to adsorb onto the surfaces of activated carbon fiber and granulated activated carbons increases with rising temperatures. The results obtained in this work are in agreement with the results reported previously for the adsorption of methylene blue on kenaf core fibers[25] and jatropha curcas[8].

It can be seen from Table-3 that all of the thermodynamic parameters for the adsorption of methylene blue onto the prepared activated carbon fiber are smaller than that of the commercial granulated activated carbons, indicating that the adsorption affinity of the former towards methylene blue is lesser than that of the latter.

Effect of agitation time: Fig. 8 shows the adsorption uptake *vs.* the adsorption contact time at two initial methylene

TABLE-3
THERMODYNAMIC PARAMETERS OF METHYLENE BLUE ADSORPTION ONTO ACTIVATED CARBON FIBER AND GRANULATED ACTIVATED CARBONS (T = 303, 318, 333 K)

Adsorbent	Concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (KJ/mol K)	ΔG° (KJ/mol)			
				303 K	318 K	333 K	R^2
Activated carbon fiber	300	49.314	0.218	-16.74	-20.01	-23.28	0.916
	400	35.181	0.171	-16.632	-19.197	-21.762	0.862
	600	31.702	0.154	-14.96	-17.27	-19.58	0.972
Granular activated carbon	300	52.179	0.238	-19.935	-23.505	-27.075	0.995
	400	52.026	0.235	-19.179	-22.704	-26.229	0.806
	600	26.987	0.147	-17.554	-19.759	-21.964	0.919

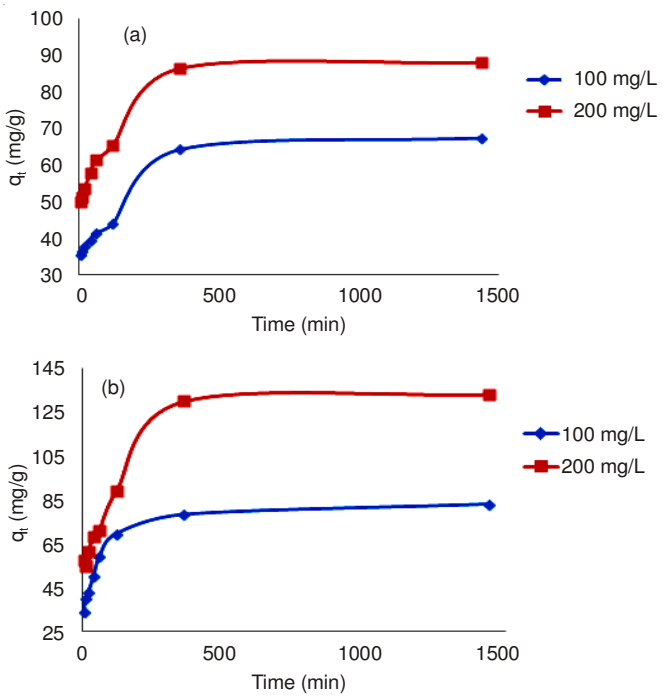

Fig. 8. Variation of the adsorption capacity of (a) activated carbon fiber and (b) granulated activated carbons with adsorption time at 100 and 200 mg/L concentrations of methylene blue (T = 303 K, W = 0.03 g, V = 25 mL)

blue concentrations (100 and 200 mg/L) for activated carbon fiber and granulated activated carbons, respectively. The amount of methylene blue adsorbed increased with increasing agitation time and then reached a plateau. The equilibrium contact time was 6 h for both adsorbents. Similar results have been reported for the adsorption of methylene blue on graphene[33,34].

Adsorption kinetic studies: Adsorption of methylene blue onto these adsorbents at two initial dye concentrations (100 and 200 mg/L) was investigated for several time intervals. The experimental data were analyzed by linearized-integral forms of the pseudo-first-order (eqn. 8), pseudo-second-order (eqn. 9) and intra-particle diffusion (eqn. 10) kinetic models.

$$\log (q_e - q_t) = \log q_e - K_1 \frac{t}{2.303} \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

$$q_t = K_{dif} \sqrt{t} + C \quad (10)$$

where, q_e and q_t are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at any time *t*, K_1 is the rate constant (h^{-1}). K_2 (hg/mg) is the rate constant for the pseudo-second-order adsorption kinetics. K_{dif} $(mg/gh)^{1/2}$ and C are intra-particular diffusion constants.

The values of pseudo-first-order parameters (K_1 and q_e) were calculated from the slopes and intercepts of the plots of log (q_e-q_t) *versus t*, which are presented in Fig. 9 for activated carbon fiber and granulated activated carbons. These values along with the correlation coefficients are listed in Table-4. It can be observed from Table-4 that the values of the correlation coefficients (R^2) are small and the values of the calculated q_e are not in agreement with the experimental values of q_e for both adsorbents and at both concentrations. This indicates that the adsorptions of methylene blue on activated carbon fiber and granulated activated carbons do not follow the pseudo-first order kinetic model. Similar results were observed by Tan *et al.*[5] and Liu *et al.*[34].

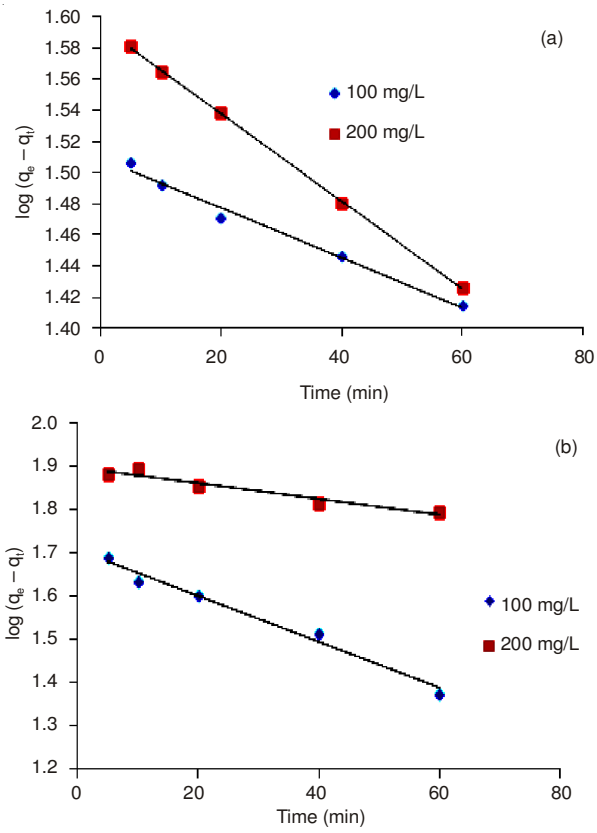

Fig. 9. Pseudo-first-order kinetic for the adsorption of methylene blue on (a) activated carbon fiber and (b) granulated activated carbons at 30 ± 1 °C

TABLE-4
COMPARISON OF PSEUDO-FIRST AND PSEUDO-SECOND ORDER MODELS FOR THE ADSORPTION OF METHYLENE BLUE ONTO ACTIVATED CARBON FIBER AND GRANULATED ACTIVATED CARBONS AT TWO INITIAL DYE CONCENTRATIONS AND 30 ± 1 °C

Adsorbent	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
			$q_{e,cal}$ (mg/g)	K_1 (h^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg min)	R^2	Rate
Activated carbon fiber	100	41.533	32.33	0.004	0.987	42.19	0.0143	0.999	0.603
	200	61.381	39.26	0.006	0.999	62.89	0.0067	0,998	0.421
Granulated activated carbon	100	59.287	50.99	0.012	0.984	62.89	0.0024	0.984	0.151
	200	71.247	78.74	0.004	0.938	74.07	0.0046	0.998	0.341

The values of pseudo-second-order constants such as q_e and K_2 were calculated from the slopes and intercepts of the plots of t/q_t *versus* t, which are demonstrated in Fig. 10 for activated carbon fiber and granulated activated carbons. These values with the corresponding values of the correlation coefficients are also presented in Table-4. It can be seen that the values of R^2 of the pseudo-second-order kinetic model are over 0.98 for both adsorbents. Moreover, it can be observed that there is a conformance between the experimental and the calculated q_e (Table-4) for both activated carbons. The results obtained here confirm the applicability of the pseudo-second order kinetic model for describing the adsorption of methylene blue onto these adsorbents. The adsorption of methylene blue on oil palm fiber activated carbon[5] and grapheme[34] also follows pseudo-second order kinetic model.

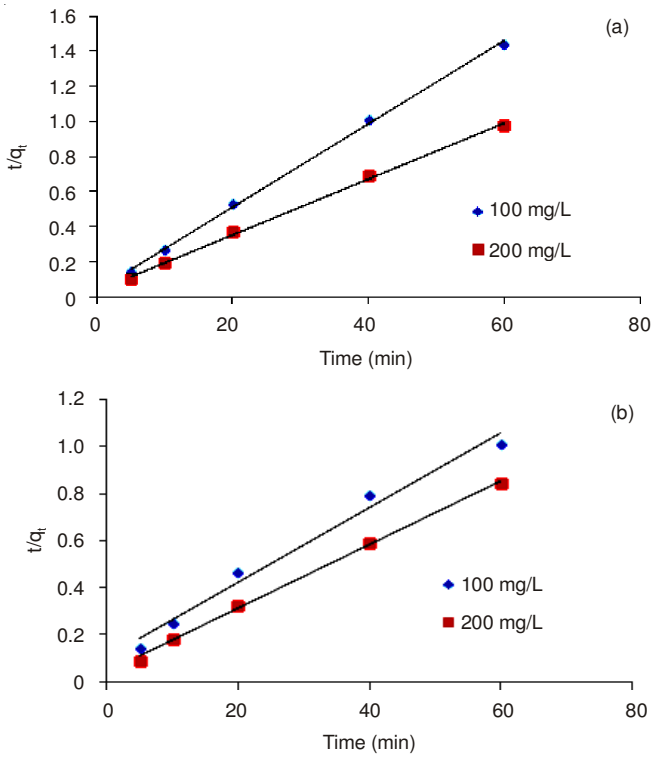

Fig. 10. Pseudo-second-order kinetic for the adsorption of methylene blue on (a) activated carbon fiber and (b) granulated activated carbons at 30 ± 1 °C

The intraparticle diffusion kinetic parameters were determined for activated carbon fiber and granulated activated carbons from the slopes and intercepts of the plots of q_t *versus* $t^{1/2}$ (Fig. 11). The values of the intraparticle diffusion parameters are summarized in Table-5. It can be clearly seen that

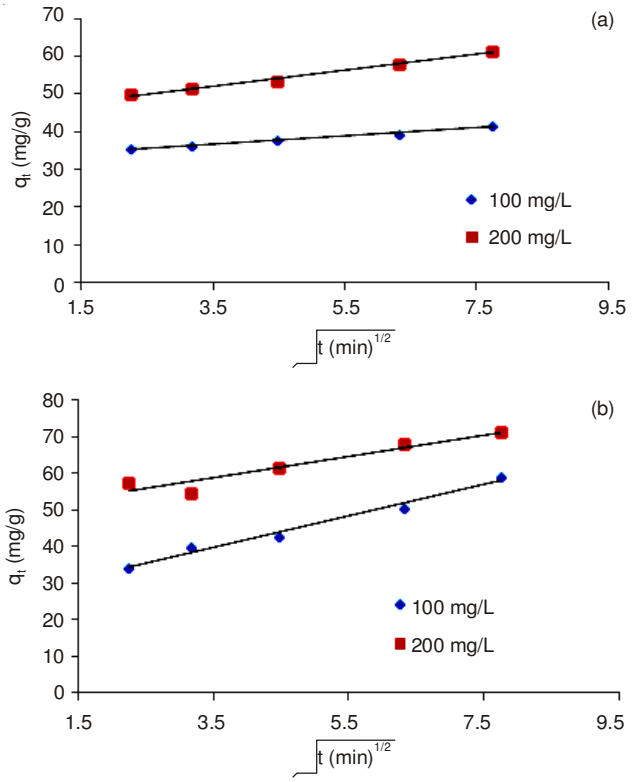

Fig. 11. Intraparticle diffusion model for the adsorption of methylene blue onto (a) activated carbon fiber and (b) granulated activated carbons at 30 ± 1 °C

the regression coefficient (R^2) values of the intraparticle diffusion are relatively high. The obtained results demonstrate that the intraparticle diffusion mechanism was involved in the adsorption of methylene blue by activated carbon fiber and/or granulated activated carbons.

In general, the results obtained in this work are in agreement with results reported in the literature for the adsorption of methylene blue onto titanate nanotubes[35] and lotus leaf[36]. Table-5 illustrates that the adsorption rates of this dye by activated carbon fiber are higher than that of granulated activated carbons.

Effect of pH on adsorption: The effect of pH on the adsorption of methylene blue onto activated carbon fiber and granulated activated carbon is shown in Fig. 12. It is evident that the amounts of methylene blue adsorbed at equilibrium shows a slight increase as pH is increased within the range under study (pH = 2-11). The pH_{ZPC} values for activated carbon fiber and granulated activated carbons were found to be 7.6 and 6.4. Upon dissolution, methylene blue is ionized and thus releasing positively charged ions into the solution[3]. The adsorption of these cations onto the adsorbent surface is primarily

TABLE-5
PARAMETER VALUES OF INTRA-PARTICLE DIFFUSION MODEL FOR THE ADSORPTION OF METHYLENE BLUE ON ACTIVATED CARBON FIBER AND GRANULATED ACTIVATED CARBONS AT TWO INITIAL DYE CONCENTRATIONS AND 30 ± 1 °C

Adsorbent	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Intra-particle diffusion kinetic model		
			K_{dif} (mg/h$^{1/2}$g)	C	R^2
ACF-16	100	41.533	1.081	32.979	0.995
	200	61.381	2.086	44.839	0.992
ACG	100	59.287	4.284	24.815	0.980
	200	71.247	2.956	48.483	0.922

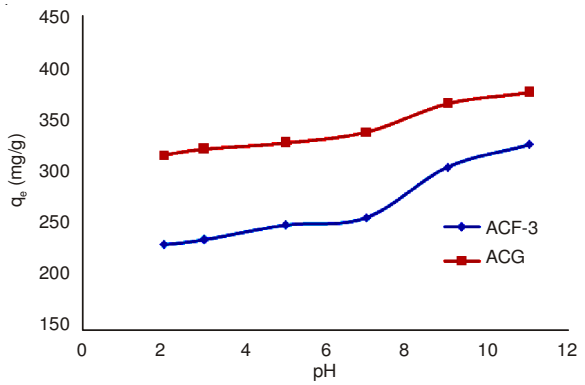

Fig. 12. Effect of initial pH on the adsorption of methylene blue on activated carbon fiber-3 and granular activated carbon

affected by the adsorbent surface charge, which in turn is affected by the solution pH[3]. The adsorbent surface charge is positive at pH < pH_{ZPC} and negative when the solution pH > pH_{ZPC}. When the solution pH increased from the starting pH to pH_{ZPC}, the coulombic repulsions between the positively charged methylene blue and the surface of the adsorbents are lowered due to decreasing the number of the positive charge on the adsorbent surface as the solution pH is increased. This explains the slight increase in the adsorption of this dye on both adsorbents. While the sharp increase in the amounts of methylene blue adsorbed onto these adsorbents at pH > pH_{ZPC} is due to the electrostatic attractions between the positively charged dye and the negative adsorbent surface. Similar trends were reported previously for the adsorption of methylene blue onto activated carbon prepared from coconut husk fiber by Al-Aoh *et al.*[22]. It can also be observed from Fig. 12 that the maximum methylene blue adsorptions onto both samples are at pH = 11, which is in agreement with the results reported in the literature for the adsorption of this dye on activated carbon prepared from coconut husk fiber[22].

Conclusion

Coconut husk fiber was used as a starting material for the preparation of activated carbon fiber. Adsorption isotherms of methylene blue on the prepared sample of activated carbon fiber and commercial granulated activated carbons were investigated at three different temperature using Langmuir and Freundlich models. It was found that the Langmuir model offers a better fit than the Freundlich model for adsorption of methylene blue on activated carbon fiber. On the other hand, both models satisfactorily fit the adsorption of methylene blue on the commercial granulated activated carbons. It was also observed that the commercial granulated activated carbons has adsorption capacity towards methylene blue higher than that of activated carbon fiber at each temperature. Adsorption kinetics was analyzed by pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The kinetic experimental data followed the pseudo-second order model in the case of activated carbon fiber and granulated activated carbons. Thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ were determined. The values of the parameters confirmed that the adsorption affinity of granulated activated carbons towards methylene blue is more significant than that of activated carbon fiber.

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REFERENCES

1. A.M.M. Vargas, A.L. Cazetta, M.H. Kunita, T.L. Silva and V.C. Almeida, *Chem. Eng. J.*, **168**, 722 (2011).
2. S. Senthilkumaar, P.R. Varadarajan, K. Porkodi and C.V. Subbhuraam, *J. Colloid Interf. Sci.*, **284**, 78 (2005).
3. H. Deng, J. Lu, G. Li, G. Zhang and X. Wang, *Chem. Eng. J.*, **172**, 326 (2011).
4. Y. Liu, Y. Zheng and A. Wang, *J. Environ. Sci. (China)*, **22**, 486 (2010).
5. I.A.W. Tan, B.H. Hameed and A.L. Ahmad, *Chem. Eng. J.*, **127**, 111 (2007).
6. M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim and A. Idris, *Desalination*, **280**, 1 (2011).
7. I.N. Najm, V.L. Snoeyink, B.W.J. Lykins and J.Q. Adams, *J. Am. Water Works Assoc.*, **83**, 65 (1991).
8. A. Kurniawan and S. Ismadji, *J. Taiwan Inst. Chem. E*, **42**, 826 (2011).
9. M. Suzuki, *Carbon*, **32**, 577 (1994).
10. N.H. Phan, S. Rio, C. Faur, L. Le Coq, P. Le Cloirec and T.H. Nguyen, *Carbon*, **44**, 2569 (2006).
11. M.A.A. Zaini, Y. Amano and M. Machida, *J. Hazard. Mater.*, **180**, 552 (2010).
12. A. Castro-Muñiz, F. Suárez-García, A. Martínez-Alonso and J.M.D. Tascón, *J. Colloid Interf. Sci.*, **361**, 307 (2011).
13. M.C. Blanco López, A. Martínez-Alonso and J.M.D. Tascón, *Micropor. Mesopor. Mater.*, **34**, 171 (2000).
14. J.-P. Wang, H.-M. Feng and H.-Q. Yu, *J. Hazard. Mater.*, **144**, 200 (2007).
15. A. Macías-García, E.M. Cuerda-Correa, M. Olivares-Marín, A. Díaz-Paralejo and M.Á. Díaz-Díez, *Ind. Crops Prod.*, **35**, 105 (2012).
16. F.F. Avelar, M.L. Bianchi, M. Gonçalves and E.G. da Mota, *Bioresour. Technol.*, **101**, 4639 (2010).
17. S. Aber, A. Khataee and M. Sheydaei, *Bioresour. Technol.*, **100**, 6586 (2009).
18. K. Li, Z. Zheng and Y. Li, *J. Hazard. Mater.*, **181**, 440 (2010).
19. D. Mohan, K.P. Singh and V.K. Singh, *J. Hazard. Mater.*, **135**, 280 (2006).
20. H.A. Al-Aoh, M.J. Maah, R. Yahya and M.R. Abas, *Asian J. Chem.*, **25**, 9573 (2013).
21. H.A. Al-Aoh, M.J. Maah, R. Yahya and M.R. Abas, *Asian J. Chem.*, **25**, 9582 (2013).
22. H.A. Al-Aoh, R. Yahya, M. Jamil Maah and M. Radzi Bin Abas, *Desalinat. Water Treat.*, **52**, 6720 (2014).
23. H.A. Al-Aoh, Ph.D. Thesis, Preparation, Characterization and Adsorption Studies of Activated Carbon Fiber from Coconut Husk (2013).
24. B.M. Babic, S.K. Milonjic, M.J. Polovina and B.V. Kaludierovic, *Carbon*, **37**, 477 (1999).
25. M.S. Sajab, C.H. Chia, S. Zakaria, S.M. Jani, M.K. Ayob, K.L. Chee, P.S. Khiew and W.S. Chiu, *Bioresour. Technol.*, **102**, 7237 (2011).
26. S. Karagöz, T. Tay, S. Ucar and M. Erdem, *Bioresour. Technol.*, **99**, 6214 (2008).
27. J. Ma, Y. Jia, Y. Jing, Y. Yao and J. Sun, *Dyes Pigments*, **93**, 1441 (2012).
28. A.N. Fernandes, C.A.P. Almeida, N.A. Debacher and M.M.S. Sierra, *J. Mol. Struct.*, **982**, 62 (2010).
29. G. Atun, G. Hisarli, W.S. Sheldrick and M. Muhler, *J. Colloid Interface Sci.*, **261**, 32 (2003).
30. O. Hamdaoui, *J. Hazard. Mater.*, **135**, 264 (2006).
31. B.H. Hameed and A.A. Ahmad, *J. Hazard. Mater.*, **164**, 870 (2009).
32. M. Alkan and M. Dogan, *Fresen. Environ. Bull.*, **12**, 418 (2003).
33. S.K. Theydan and M.J. Ahmed, *J. Anal. Appl. Pyrol.*, **97**, 116 (2012).
34. T. Liu, Y. Li, Q. Du, J. Sun, Y. Jiao, G. Yang, Z. Wang, Y. Xia, W. Zhang, K. Wang, H. Zhu and D. Wu, *Colloid Surf. B*, **90**, 197 (2012).
35. L. Xiong, Y. Yang, J. Mai, W. Sun, C. Zhang, D. Wei, Q. Chen and J. Ni, *Chem. Eng. J.*, **156**, 313 (2010).
36. X. Han, W. Wang and X. Ma, *Chem. Eng. J.*, **171**, 1 (2011).