



Kinetic and Thermodynamic Studies for Methylene Blue Adsorption using Activated Carbon Prepared from Agricultural and Municipal Solid Wastes

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This study aimed to evaluate and optimize the removal of methylene blue onto low cost starting material activated carbon. The effects of pH, contact time, initial concentration on adsorption process were investigated. Results showed that effective adsorption was occurred in the pH range of 5-12. The maximum adsorption capacity (140.03 mg/g) was obtained at contact time 480 min, at initial methylene blue concentration of 150 ppm. Adsorption kinetics of methylene blue was analyzed by pseudo first order, pseudo second order and intraparticle diffusion models. Results showed that methylene blue adsorption onto activated carbon followed second order kinetics models most appropriately. Thermodynamic parameters; ΔG° , ΔH° and ΔS° indicate that the sorption process was spontaneous and endothermic in nature. The magnitude of ΔG° was -6.27 to -12 kJ/mol, the standard enthalpy and the entropy values in the range of 25-50 °C were obtained as 44.13 kJ mol⁻¹ and 158.3 kJ mol⁻¹ K⁻¹.

Key Words: Copyrolysis, Municipal solid waste, Chemical activation, Activated carbon, Adsorption, Kinetic models.

INTRODUCTION

The removal of dyes from waste effluents is considered as an environmental need because they can be visible and highly toxic even at very low concentration levels¹. Dyes contaminate environment from various industries, like textiles, paper, cosmetics, printing and foods. Dyes can destroy aquatic life because they prevent sunlight from reaching water bottom totally. Also dyes may be mutagenic and/or carcinogenic to human². Usually, methylene blue is used for cotton and wood. Methylene blue can cause eye damage for human and animals. On inhalation, it may lead to short periods of rapid or difficult breathing; ingestion may cause nausea and methemoglobinemia³. Many methods are used to remove colour from industrial effluents such as biological biodegradation⁴ and adsorption⁵.

Many previous works studied the removal of methylene blue using different adsorbent such as coffee husks⁶, yellow passion fruit waste⁷, rice husks⁸, banana peel⁹, cereal chaff¹⁰, spent coffee grounds¹¹, orange peel⁹, wheat shells¹², durian peel¹³, etc. The application of untreated agricultural or plant waste as adsorbents, in addition to its low adsorption efficiency, may lead to additional organic load in the treated effluent in the form of chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) due to release

of soluble organic compounds contained in the plant wastes¹⁴. Activated carbon is mostly used for commercial systems^{15,16}, but limitedly used because of its high operating costs^{17,18}. To reduce the production cost, the utilization of renewable and less expensive precursors for the preparation of activated carbon is attracting the interest of researchers all over the world. The precursors of interest are primarily industrial and agricultural byproducts and forest wastes, such as coconut shell¹⁹, sugar beet bagasse²⁰, rice straw²¹, rubber wood sawdust²² and coconut husk²³. Waste plastics and tires, which are organic materials, can also be converted into activated carbon. Several experimental studies^{24,25} have reported the production of char and activated carbon from waste tires. The potential of these products as possible adsorbents of various pollutants has been assessed and found to be very great. Also the disposed solid waste (SW) may be used as precursor in the production of a low cost adsorbent to treat wastewater contaminated with heavy metals and refractory compounds²⁶. The conversion of locally available solid wastes such as biomass, waste cartons, waste news papers, plastics and industrial byproducts into activated carbon for wastewater treatment would improve the economic value by providing an alternative to costly activated carbon^{27,28}. Pyrolysis is one of the ways to take advantage of the energetic and organic value of these waste materials. Many authors have

studied the pyrolysis of biomass and plastic waste and have demonstrated that it is a suitable method of waste processing^{29,30}. The goals of this study were to optimize the adsorption factors affecting removal of methylene blue from aqueous solutions. Our previously prepared activated carbon from mixed wastes (biomass, waste cartons and poly styrene) by chemical activation with ZnCl₂ was used as an adsorbent²⁸. The sorption process was examined in terms of kinetics and thermodynamics. Batch adsorption experiments were conducted to evaluate the sorption process over a wide range of operation conditions for sorbate concentration, pH, contact time and sorbent dose. The adsorption capacity at the optimum condition was compared to other adsorbent from the literature.

EXPERIMENTAL

Raw materials and activated carbon preparation: The precursors used in this study were trunks of palm trees, waste cartons and poly styrene collected from a municipal solid waste station in Riyadh, Saudi Arabia. In this study, the three-stage process was used for the preparation of activated carbon from mixed wastes. In this process, the precursors are carbonized, impregnated with ZnCl₂ and then activated for a specific period of time as described in our previous work²⁸.

Methylene blue (MB), C₁₆H₁₈ClN₃S·3H₂O (Fig. 1) supplied by Sigma Aldrich was used as an adsorbate. Stock solution was prepared by dissolving 1 g of methylene blue in 2 L distilled water.

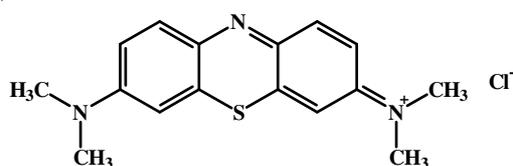


Fig. 1. Structure of methylene blue

Batch adsorption studies: The adsorption capacity of the activated carbon was evaluated using methylene blue as an adsorbate. The adsorption was determined using a batch method, which allows for the convenient evaluation of parameters that influence the adsorption process. A stock solution of methylene blue (1000 mg/L) was prepared in double-distilled water and further diluted to the desired concentrations. The batch adsorption experiments were performed in 250 mL conical flasks by mixing 80 mL of the methylene blue solution with 0.03 g of activated carbon and then equilibrated in a thermostat-cum-shaking assembly (model MSW 275) at 30 °C and 200 rpm. After equilibrating, the concentration of remaining methylene blue in the solution was measured using a UV-visible spectrophotometer (UV-30 LC, Thermo Scientific, England) at λ_{\max} = 665. The amount of methylene blue per unit weight of adsorbent, q_e (mg/g), was calculated using the following equation:

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

where C_0 and C_e are the initial and equilibrium concentrations of methylene blue in solution (mg/L), V is the solution volume (L), W is the weight of the adsorbent (g) and q_e is the adsorption capacity (mg/g).

The effect of the initial pH on the removal of methylene blue was examined over the pH range of 2-12 using 80 mL solutions with a methylene blue concentration of 50 mg/L. The solution pH was adjusted to the desired value by the addition of 0.1 M HCl or NaOH.

The effect of shaking time on the adsorption of methylene blue was examined at three different initial concentrations (40, 80, 120 mg/L) of methylene blue at 30 °C, 0.03 g of adsorbent and the selected pH. At predetermined times; the solution of the specified flask was filtered using Whatman No. 42 filter paper and analyzed using a UV-visible spectrophotometer.

Adsorption kinetic models

Lagergren-first-order equation: Lagergren-first-order equation is the most popular kinetics equation³¹. The form is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively, (mg/g) and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). After integration and applying initial conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of eqn. 2 becomes:

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

The adsorption rate constant k_1 , can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t .

Pseudo-second-order equation: The pseudo-second-order chemisorption kinetic rate equation is expressed as³²:

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

where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively, (mg/g) and k_2 is the rate constant of pseudo-second-order sorption ($\text{g}/(\text{mg min})$). After integration and applying initial conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, the integrated form of eqn. 4 becomes:

$$\frac{t}{dt} = \frac{1}{Kq_e^2} + \frac{1t}{q_e} \quad (5)$$

where t is the contact time (min) and q_e (mg/g) and q^2 (mg/g) are the amount of the solute adsorbed at equilibrium.

Intraparticle diffusion model: The intraparticle diffusion model was tested to identify the diffusion mechanism³³, is expressed as:

$$q_t = k_{id}t^{1/2} + C \quad (6)$$

where k_{id} is the intraparticle diffusion rate constant (mg/g $\text{min}^{1/2}$), C is the intercept (mg/g).

The plot of q_t versus $t^{1/2}$ gave straight line and the values of k_{id} were calculated from the slopes of the plots. Values of C gave an idea about the thickness of boundary layer, *i.e.*, the larger the intercept, greater the contribution of the surface sorption in the rate controlling step.

Effect of methylene blue concentration and Dubinin-Radushkevich (D-R) model: The effect of methylene blue concentration on the adsorption capacity examined at three different initial concentrations (5, 10, 20, 30, 40, 50, 100, 150 mg/L) of methylene blue at 30 °C, 0.03 g of adsorbent and the

selected pH. The adsorption data was also modeled by D-R isotherm to determine the adsorption type (physical or chemical)^{34,35}. The linear form of this model is expressed in eqn. 7

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

where q_e is the amount of the metal adsorbed onto per unit dosage of the adsorbent (mol/L); q_m , the monolayer adsorption capacity (mol/g); β , the activity coefficient related to mean sorption energy (mol^2/J^2) and ϵ is the Polanyi potential ($\epsilon = RT \ln(1 + 1/C_e)$)^{34,35}. The mean sorption energy E (kJ/mol), can be calculated using eqn. 8

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

Thermodynamic studies: Thermodynamic parameters, such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were evaluated using eqns. 9 and 10:

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

where K_d is the equilibrium partition constant calculated as the ratio between sorption capacity (q_e) and equilibrium concentration (C_e), R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin (K). From eqn. 9 a plot of $\log K_d$ versus $1/T$ (Fig. 8) give ΔH° and ΔS° .

RESULTS AND DISCUSSION

Effect of pH: The pH of aqueous solution is one of the most important factors that influence the adsorption of dyes due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the dye molecule³⁶. The adsorption of methylene blue was studied as a function of pH over a pH range of 2-12 onto the activated carbon at initial concentration of 100 ppm, as shown in Fig. 2. It is clear that the adsorption capacity presented a slight increase with increasing the pH, but there is no significant change in the percentage removal of methylene blue over the whole pH range. After 24 h, the adsorption capacity was 56.02 % at pH = 2 and presented an average of 66.37 % in the pH range of 4-12. This may be due to the formation of more functional groups on the surface of activated carbon which increase their surface complexation capability.

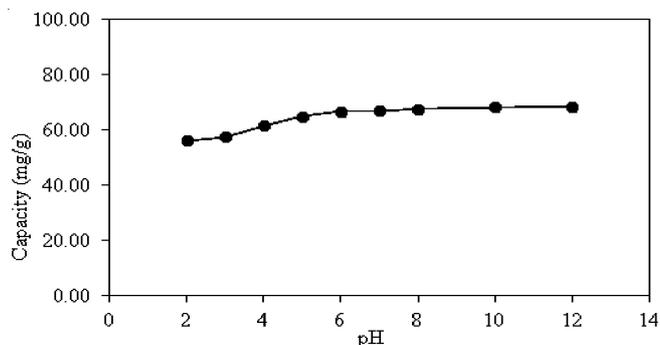


Fig. 2. Effect of pH on methylene blue adsorption onto activated carbon prepared from mixed wastes at low carbonization temperature of 200 °C, followed by activation with 2 M ZnCl_2 solution

Effect of contact time: The amount of methylene blue adsorbed onto activated carbon was studied as a function of the shaking time at different initial concentrations at 30 °C and desired pH. The effect of contact time for three different concentrations (40, 80, 120 ppm) of methylene blue adsorption by activated carbon is given in Fig. 3. It is evident from the figure that the amount of methylene blue adsorbed increases with increasing contact time. Further, the adsorption was rapid in the early stages and then gradually decreased to become constant after the equilibrium point. The saturation point is almost reached at 480 min. At this point, the amount of dye desorbing from the activated carbon is in a state of dynamic equilibrium with the amount of the dye being adsorbed on the activated carbon. The amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent. The removal of methylene blue was found to be dependent upon the initial concentration. The amount of methylene blue adsorbed, q_e (mg/g), increased with an increase in the initial concentration. In this study, the amount of methylene blue adsorbed at equilibrium increased from 70.15-122.23 mg/g with the increase in the initial dye concentration from 40-120 ppm. The mass transfer driving force becomes larger when the initial concentration increased and hence resulting in higher adsorption of methylene blue. At low concentrations, the ratio of available surface to initial methylene blue concentration is larger, so the removal becomes independent of the initial concentration. However, in the case of higher concentrations, this ratio is low and the percentage removal depends upon the initial concentration.

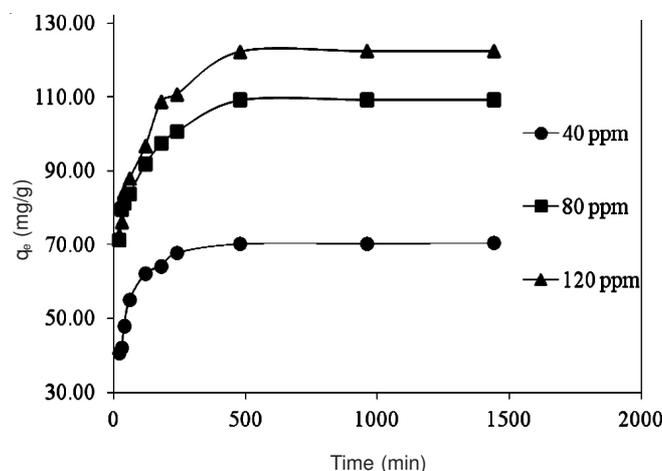


Fig. 3. Effect of contact time on methylene blue adsorption onto activated carbon prepared from mixed wastes at low carbonization temperature of 200 °C, followed by activation with 2 M ZnCl_2 solution

Batch kinetic studies: Adsorption kinetics provides valuable information about the reaction pathways and mechanism of the reactions. In order to examine the controlling mechanism of the adsorption process, the pseudo first-order, pseudo second-order and intraparticle diffusion models³¹⁻³³ were applied to analyze the experimental data of adsorption of methylene blue on the prepared activated carbon. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

Pseudo-first order kinetic model: The linearized-integral form of the pseudo first-order model³¹, is generally expressed as:

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

where q_e and q_t are the amounts of adsorbed of methylene blue (mg/g) at equilibrium and at time t , respectively and k_1 is the rate constant of first order adsorption (min^{-1}). Straight lines were obtained by plotting $\log(q_e - q_t)$ against t , as shown in Fig. 4. The values of the rate constant k_1 and q_e at three different initial concentrations were obtained from the slopes and intercepts of the plots, respectively and presented in Table-1. Results showed that there are differences between the experimental q_e (70.15, 109.16 and 122.23 mg/g) and the calculated q_e (65.8, 52.5 and 59.2 mg/g) in case of initial methylene blue dye concentration of 40, 80 and 120 ppm, respectively.

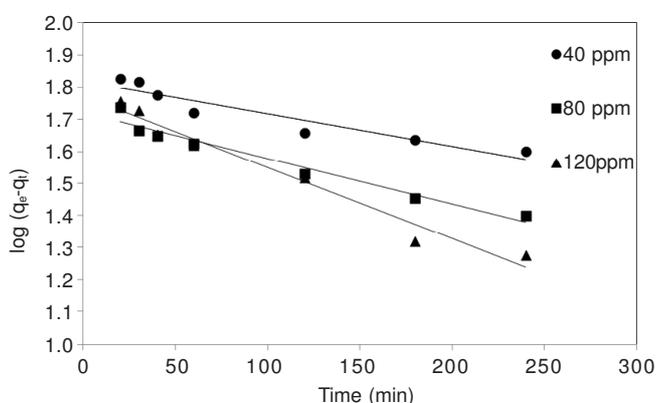


Fig. 4. Lagergren first order plot for methylene blue adsorption onto activated carbon prepared from mixed wastes at low carbonization temperature of 200 °C, followed by activation with 2 M ZnCl₂ solution

Pseudo second-order kinetic model: The parameters of pseudo second-order adsorption kinetic model can be determined from eqn. 5

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

The plots of t/q_t versus t of eqn. 6 gave linear plots Fig. 5. The values of q_e and k_2 were determined from the slopes and intercepts of the plots, respectively and are listed in Table-1. Good agreement are obtained between the experimental q_e (70.15, 109.16 and 122.23 mg/g) and the calculated q_e (71.4, 111.1 and 125 mg/g) in case of initial methylene blue dye concentration of 40, 80 and 120 ppm respectively.

Intraparticle diffusion model: The intraparticle diffusion model was tested to identify the diffusion mechanism, is expressed as in eqn. 6:

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

where k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$), C is the intercept (mg/g).

The plot of q_t versus $t^{1/2}$ gave straight line and the values of k_{id} were calculated from the slopes of the plots. Values of C gave an idea about the thickness of boundary layer, *i.e.*, the larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The data for methylene blue adsorption onto activated carbons applied to intraparticle diffusion model is shown in Fig. 6 and the results are given in Table-1.

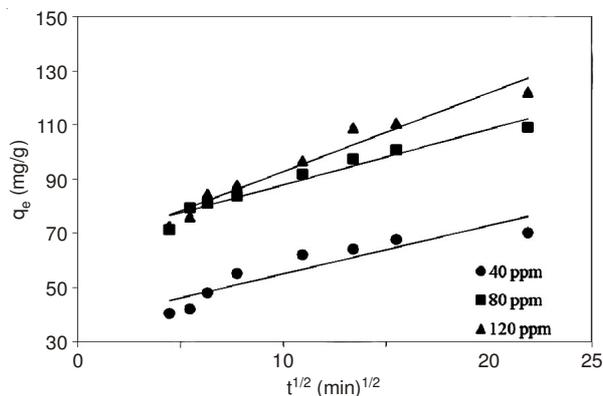


Fig. 6. Intraparticle diffusion model plot for methylene blue adsorption onto activated carbon prepared from mixed wastes at low carbonization temperature of 200 °C, followed by activation with 2 M ZnCl₂ solution

It is clear from Table-1 that among these three models, pseudo-second order kinetic equations had high R^2 values and also the experimental q_e is in accordance with calculated q_e . The low values of R^2 for pseudo-first order and intra particle diffusion models indicated apparently that these models did not fit the data well. Furthermore, for pseudo-first order kinetic

TABLE-1
KINETIC CONSTANT PARAMETERS OBTAINED FOR MB ADSORPTION ON ACTIVATED CARBON PREPARED FROM MIXED WASTES AT LOW CARBONIZATION TEMPERATURE OF 200 °C, FOLLOWED BY ACTIVATION WITH 2 M ZnCl₂ SOLUTION

C_i (ppm)	Pseudo-first order				Pseudo-second order				Intraparticle diffusion model		
	$q_{e,exp}$ (mg/g)	K_1 (10^{-3}) (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (10^{-4}) (g/mg min)	$q_{e,cal}$ (mg/g)	h (mg/g min)	R^2	k_{id} (mg/g.min)	C (mg/g)	R^2
40	70.15	2.303	65.856	0.892	8.292	71.428	4.081	0.999	1.784	37.110	0.842
80	109.16	3.224	52.505	0.962	5.291	111.11	6.173	0.999	2.065	67.185	0.953
120	122.23	5.066	59.265	0.968	3.585	125.00	5.594	0.999	2.895	63.882	0.952

model the experimental q_e are not in good agreement with calculated q_e . In the view of these results, it can be said that the pseudo second order kinetic model provided a good correlation for the description of the mechanism of sorption of methylene blue in contrast to the other models.

Effect of initial methylene blue concentration and D-R model: Results presented in Table-2 shows the effect of initial methylene blue concentration on the adsorption capacity by mixed waste activated carbon. The adsorption capacity increases from 10 to 141.03 mg/g with increasing initial methylene blue concentration from 5-150 ppm, at 30 °C, contact time 480 min. The increase in the adsorption capacity may be due to enhanced driving force, *i.e.*, the concentration gradient. These results are in agreement with that reported by Oliveira *et al.*⁶.

Initial methylene blue conc. (ppm)	Adsorption capacity q_e (mg/g)	Initial methylene blue conc. (ppm)	Adsorption capacity q_e (mg/g)
5	10	50	87.02
10	20	80	114.50
20	40	100	121.50
30	51.08	150	141.03
40	69.30	—	—

The adsorption data were also applied to the D-R isotherm model based on the heterogeneous surface of the adsorbate to differentiate between physical and chemical adsorption. Fig. 7 shows the D-R isotherm plot for the adsorption of methylene blue onto mixed waste activated carbon. The correlation coefficient R^2 is 0.971. The β constant and q_m were calculated from the slopes and intercept of the plot. The β constant and the q_m value were found to be $8.8 \times 10^{-3} \text{ mol}^2/\text{kJ}^2$ and 0.403 mol/g, respectively. The mean free energy of adsorption E gives information about adsorption mechanism as chemical ion-exchange or physical adsorption. If E value is between 8 and 16 kJ/mol, the adsorption process follows by chemical ion exchange and if $E < 8 \text{ kJ/mol}$, the adsorption is physical in nature^{34,35}. From eqn. 8, the numerical value of E was calculated as 5.33 kJ/mol indicating the adsorption process may be carried out *via* physical interaction including van der waals forces.

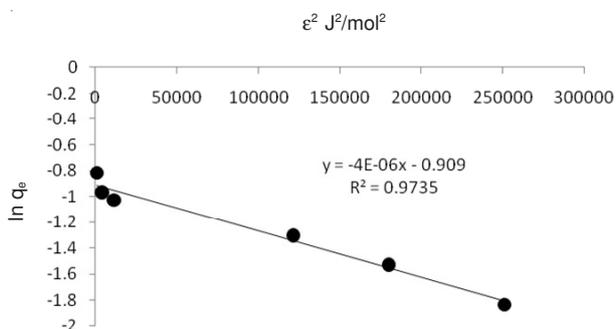


Fig. 7. Shows the D-R isotherm plot for the adsorption of methylene blue onto mixed waste activated carbon

Thermodynamic studies: Thermodynamic parameters, such as change in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were evaluated using eqns. 8 and 9:

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

where K_d is the equilibrium partition constant calculated as the ratio between sorption capacity (q_e) and equilibrium concentration (C_e), R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin (K). From eqn. 8 a plot of $\log K_d$ versus $1/T$ (Fig. 8) give ΔH° and ΔS° , the calculated thermodynamic parameters are given in Table-3.

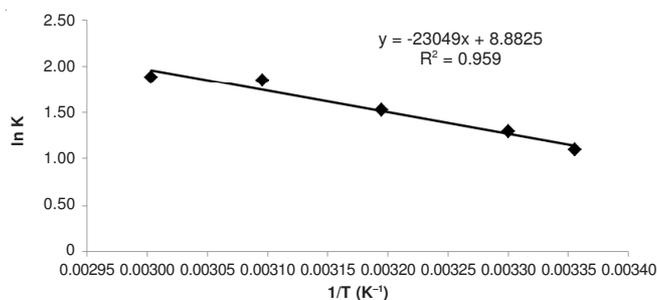


Fig. 8. Thermodynamic study of adsorption of methylene blue onto mixed waste activated carbon

Temperature T (K)	Thermodynamic parameters		
	ΔG° (kJ/mol)	ΔS° (J/mol/K)	ΔH° (kJ/mol)
298	-6.27		
303	-7.53		
313	-9.12	158.3	44.13
323	-11.4		
333	-12		

The negative value of ΔG° indicates the spontaneous nature of adsorption of methylene blue onto mixed waste activated carbon. Generally, a value of ΔG° in between 0 and -20 kJ/mol is consistent with electrostatic interaction between adsorption sites and the adsorbing ion (physical adsorption) while a more negative ΔG° value ranging from -80 to -400 kJ/mol indicates that the adsorption involves charge sharing or transferring from the adsorbent surface to the adsorbing ion to form a coordinate bond (chemisorption)³⁷⁻⁴¹. As shown, the magnitude of ΔG° (-6.27 to -12 kJ/mol) which indicate a typical physical process. According to the van't Hoff equation, the standard enthalpy and the entropy values in the range of 25-50 °C were obtained as 44.13 kJ mol⁻¹ and 158.3 kJ mol⁻¹ K⁻¹ at initial pH 5 and initial methylene blue concentration 50 ppm, respectively. As can be deduced from Fig. 8, the positive value of ΔH° suggests the endothermic nature of adsorption while the positive values of ΔS° indicates an increase in the degree of freedom (or disorder) of the adsorbed species. In general, the thermodynamic parameters indicate that the adsorption is spontaneous and endothermic.

Comparison of adsorption capacity of various modified adsorbant for methylene blue: It is clear from Table-4 that by comparing maximum adsorption capacities (q_{max}) of mixed waste activated carbon and other adsorbents from literature, mixed waste activated carbon have a large capacity in the removal of methylene blue from aqueous solutions.

TABLE-4
COMPARISON OF ADSORPTION CAPACITY OF VARIOUS
MODIFIED ADSORBANT FOR METHYLENE BLUE

Adsorbent	q _{max} (mg/g) (temperature °C)	Reference
Activated carbon from mixed wastes	140.03 (30)	This study
Coffee husks	90.1 (30)	6
Yellow passion fruit waste	44.7 (25)	7
Rice husks	40.6 (32)	8
Banana peel	20.8 (30)	9
Cereal chaff	20.3 (25)	10
Spent coffee grounds	18.7 (25)	11
Orange peel	18.6 (30)	9
Wheat shells	16.6 (30)	12
<i>Posidonia oceanica</i> (L.) fibres	5.6 (30)	13

Conclusion

Activated carbon which is prepared by the coprolysis of mixed solid wastes (biomass, cartons and polystyrene) and by chemical activation with ZnCl₂ at low carbonization temperature showed high efficiency in removal of methylene blue from aqueous solutions. By optimizing the adsorption process, results showed that pH had no considerable effect on the adsorption of methylene blue. Effective adsorption was occurred in the pH range of 5-12. The kinetics of methylene blue adsorption followed pseudo-second order rate expressions. The adsorption of methylene blue was found to be dependent on the initial concentration. The amount methylene blue adsorbed at equilibrium increased from 10-141.03 mg/g with the increase in the initial dye concentration from 5-150 ppm. Thermodynamic parameters; ΔG° , ΔH° and ΔS° showed that the sorption process was spontaneous and endothermic in nature. Also D-R model confirm the physical adsorption of methylene blue onto mixed waste activated carbon.

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