



COCONUT SHELL-BASED ACTIVATED CARBON AS ADSORBENT FOR THE REMOVAL OF DYE FROM AQUEOUS SOLUTION: EQUILIBRIUM, KINETICS, AND THERMODYNAMIC STUDIES

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ABSTRACT

The need to develop more efficient adsorbent, comparable to commercially available adsorbent, is attracting significant interest as promising adsorbent for waste water treatment. In this study, the potential of activated carbon prepared from waste coconut shell (CSAC) for the removal of methylene blue (Mb) from aqueous solution was reported. Batch experiments were conducted to determine the adsorption isotherm and kinetics of Mb on CSAC. Langmuir, Freundlich and Temkin isotherm models were employed to fit and analyze the adsorption equilibrium data. The result shows Langmuir isotherm model gave the best fit and an adsorption capacity of 320.5 mg/g was obtained for Mb at pH value of 7, 0.02 g adsorbent dosage and contact time of 4.5 hour. The experimental kinetic data at different initial Mb concentrations was also analyzed with pseudo-first order, pseudo-second order and intraparticle diffusion models. The obtained results showed that the pseudo-second order model fits the adsorption kinetic data with R² range of 0.9985-0.9996. Finally, the thermodynamic parameters show that the adsorption of Mb on CSAC was spontaneous and endothermic in nature. This therefore suggests that (CSAC) is a viable adsorbent for effective removal of dye from wastewater effluent.

Keywords: Activated carbon, Adsorption isotherms, Coconut shells, Methylene blue, kinetics.

1. INTRODUCTION

Dye effluent discharge into the environment from textile, plastic, paper and leather industries is a source of water pollution which is harmful to aquatic life and has deleterious effects on human health [1, 2]. For instance, acute exposure to dye such as methylene blue, a commonly used pigment for dyeing wool, leather, cotton and as temporary hair colorant has negative and harmful effect on humans if swallowed or inhaled. It causes irritation in the gastrointestinal tract if swallowed with symptoms such as nausea, vomiting, diarrhea, and increase in human heart rate [3 – 5]. If inhaled, it can result to convulsions, cyanosis and jaundice [6]. Therefore, the treatment of wastewater effluent prior to its final discharge to the environment, to remove dye and

pigment is of great environmental importance. To address this challenge, various methods such as electrochemical treatment, microbial degradation, membrane separation, adsorption and biological techniques have been employed to remove pollutant from industrial wastewater effluent. Among this method, the use of adsorption is particularly promising and attractive because the technique is efficient and economical in terms of cost-effectiveness and process simplicity.

The cost effectiveness of preparing activated carbon from agricultural waste and the possibility of tailoring its structure and properties makes it desirable for adsorption process. They could possess tunable functionality, large specific surface area, and well-defined porosity. Generally, it is visible to prepare

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activated carbon via physical or chemical activation or a combination of both. It has been the most popular adsorbent in removal of pigments and in wastewater treatment owing to its inherent abilities to adsorb pollutants. However, commercially available activated carbons are relatively expensive due to complicated production processes and expensive precursors, which could make them less attractive for use as an adsorbent [7].

In recent years, studies have focused on a growing research interest for preparing activated carbons from cheaper precursors such as agricultural waste by-products. El-sayed *et al.* [8] prepared three different activated carbons from corncob via chemical activation with phosphoric acid. The prepared adsorbent was used to remove methylene blue from aqueous solution and the kinetic and equilibrium data from the batch adsorption studies, were employed to understand the adsorption process. Theydan *et al.* [9] investigated the utilization of ferric chloride as an activator for the preparation of activated carbon from an agricultural date pit. Equilibrium adsorption data of methylene blue onto the prepared ferric chloride activated carbon was reported to be well described by Sips isotherm model, with R^2 value of 0.9995. Pseudo second order model describe the adsorption kinetic data and the obtained thermodynamic data indicated the spontaneous and endothermic nature of methylene blue adsorption on the adsorbent. Their conclusions suggest that the adsorbent may find practical applications for removal of dye pollutants from industrial water effluent.

Alam *et al.* [10] investigated the possibility of utilizing rice husk activated carbon as an adsorbent for the removal of methylene blue dye from aqueous solutions. The effects of various experimental parameters, like initial dye concentration, pH, adsorbent dosage and adsorbent particle size were investigated. The methylene blue maximum uptake from the aqueous solution by the activated rice husk carbon at optimized conditions was 97.15 %. Their results indicate that activated carbon from agricultural rice husk waste has favourable surface properties and could be employed as low-cost alternatives to commercial activated carbon in the removal of basic dyes in waste water treatment.

In this study, coconut shell based activated carbon was prepared via chemical activation, using waste coconut shell precursor from agricultural waste due to its abundance. Its abundant supply as a waste-

product from the coconut oil and desiccated coconut industry, may make producing activated carbon from this material financially viable. Also, it is an amorphous form of carbon with high density, high purity and dust free nature advantage. Herein, coconut shell-based activated carbon was prepared via chemical activation with $ZnCl_2$ for the removal of methylene blue dye from aqueous solution. The equilibrium, kinetics and thermodynamics data on batch adsorption studies of methylene blue dye onto the prepared coconut shell-based activated carbon (CSAC) adsorbent were carried out, to understand its adsorption process and determine the spontaneity, endothermic or exothermic nature of the process. The properties and performance of the coconut shell based activated carbon in relation to adsorption were also investigated.

2. MATERIALS AND METHODS

2.1 Materials

Activated carbon used in this study was prepared from waste coconut shells. The impurities in the waste coconut shells were removed via washing with distilled water and subsequently dried at 60 °C for 5 h. The obtained coconut shell was then crushed using electric pulverize and sieved with mesh sieve. All the chemicals used were of analytical grade, purchased from Shanghai Chemical Reagents Co. Ltd. China and used as received. These include Zinc chloride (99.9 %), hydrochloric acid (99.9 %) and Methylene blue (Mb) (99.9%). Distilled water from laboratory water distiller was used in this study.

2.2 Preparation of activated carbon

The sieved coconut shell precursor was carbonized in a muffle furnace (BST/MF/1800, Bionics Scientific, Delhi) at a temperature of 600 °C for 3 h and allowed to cool. The carbonized coconut shell (150 g) was soaked in a 150 ml of $ZnCl_2$ solution for 8h at activation weight ratio of 1:1 g activator to precursor. The impregnated samples, coconut shell activated carbon (CSAC) was then washed with distilled water several times to obtain activated carbon of almost neutral pH (6.5-7.0) and subsequently dried in an electric oven (MINO/100, Genlab, UK), at 80 °C for 2 h. Finally, the sample was stored in a tightly closed container. The activated carbon yield, which is defined as the ratio of final weight of the product obtained after washing and drying to the weight of the initially dried precursor used was determined by,

$$\text{Yield (\%)} = \frac{W_f}{W_o} \times 100 \quad (1)$$

where W_f and W_o are the weight of final activated carbon product (g) and the weight of dried coconut shells precursor (g), respectively.

2.3 Characterizations

The surface morphology of the pristine coconut shell carbon (CSC) and the coconut shell activated carbon (CSAC) was studied using a scanning electron microscopy (Quanta 200 FEG, FEI Company, USA). The adsorbent was sputtered with gold before observation under SEM.

2.4 Adsorption isotherms

The equilibrium isotherm of Mb adsorption on CSAC, adsorption tests were carried out using 100 ml conical flasks in which 50 ml of Mb solutions with different initial concentrations (50–450 mg/l) was placed in each flask. The solutions pH was adjusted to pH of 7 by adding 0.1 M HCl solution gradually. Activated carbon (0.02 g) was added to each flask and placed in a shaker at 115 rpm, 303 K for 4.5 h to attain equilibrium. The samples were filtered and the concentrations of the residue of Mb in the filtrate were analyzed by a UV–Visible Spectrophotometer. UV–Vis spectrophotometer (LAMBDA 750, PERKIN ELMER®) was employed to analyze the residue concentration of the Mb in the filtrate at 664 nm wave length. The adsorbed amount of Mb at equilibrium, q_e (mg/g) was calculated by the expression,

$$q_e = \frac{(C_o - C_e) V}{w} \quad (2)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of MB solution, respectively, W (g) is the weight of activated carbon used and V is the volume of the solution in liter. Langmuir [11, 12], Freundlich [11, 12], and Temkin [12, 13] isotherm models were used to fit the experimental isotherm data of Mb adsorption onto CSAC. The isotherms are as follows:

Langmuir isotherm,

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

Freundlich isotherm,

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

Temkin isotherm,

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (5)$$

Linearize form of Temkin isotherm is expressed as,

$$q_e = \beta \ln K_T + \beta \ln C_e \quad (6)$$

where

$$\beta = \frac{RT}{b} \quad (7)$$

The essential equilibrium parameter for the Langmuir isotherm (R_L), can be expressed as,

$$R_L = \frac{1}{k_L + C_o} \quad (8)$$

Where k_L (L/mg) is the Langmuir constant related to rate of adsorption, q_L (mg/g) is the Langmuir maximum uptake of Mb per unit mass of CSAC, n is Freundlich constant which indicate adsorption intensity, K_F ((mg/g) (L/mg)^{1/n}) is Freundlich constants which gives a measure of adsorption capacity. T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), and b is the Temkin constant related to heat of sorption (J/mg). The Temkin constants K_T and b are calculated from the slope and intercept of q_e versus $\log C_e$. C_o is the highest initial solute concentration, and R_L indicates the type of isotherm [reversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$)]. From the plots, the parameters from the equations can be used to establish the accord between experimental observation and theory in terms of the R^2 correlation coefficient value.

2.5 Adsorption kinetics

The procedure used for adsorption equilibrium experiments was repeated here at different time intervals (0.25-5.5 h). A temperature of 303 K and a pH of 7 was maintained for the various solutions. The adsorbent (0.02 g) was put into each conical flask containing Mb solutions and the flasks were shaken at 110 rpm. At the end of each of the contact time, the samples were filtered and the residual concentrations in the filtrate were analyzed by a UV–Visible Spectrophotometer. The amount of Mb adsorbed at time t , q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t) V}{w} \quad (9)$$

where C_t (mg/L) is the liquid-phase concentration of Mb solution at time t (min). Three models namely; Pseudo-first order model, pseudo-second order model, and intraparticle diffusion model were used to analyze the kinetic data. These models are:

Pseudo-first order model,

$$\ln(q_t - q_e) = \ln(q_e) - k_1 t \quad (10)$$

Pseudo-second order model,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (11)$$

Intraparticle diffusion model,

$$q_t = K_3 t^{1/2} + C \quad (12)$$

where q_e is and q_t (mg/g) are the uptake of Mb at equilibrium and at time t (min), respectively. K_1 (min^{-1}) is the adsorption rate constant, K_2 (g/mg.min) is the rate constant of second-order equation, K_3 (mg/g $\text{min}^{1/2}$) is the intraparticle diffusion rate constant, and C (mg/g) is a constant that shows the boundary layer thickness. Δq (%) is the normalized standard deviation which validates the applicability of the kinetic models in describing the adsorption process value, defined as:

$$\Delta q (\%) = 100 \sqrt{\frac{\sum (q_{\text{exp}} - q_{\text{cal}}/q_{\text{exp}})^2}{N - 1}} \quad (13)$$

where N is the number of data points, q_{cal} and q_{exp} (mg/g) are the calculated and experimental adsorption capacities, respectively.

2.6 Adsorption thermodynamics

The effect of temperature to the adsorption capacity of the adsorbent was carried out at 30, 40 and 50 °C in a constant water bath using pH 7, 115 rpm and 0.02 g of adsorbent for 4.5 h to achieve equilibrium. At the end of 4.5 h, the samples were filtered and the residual concentrations of methylene blue in the filtrate was analyzed by a UV-Visible Spectrophotometer. The adsorbed amount of Mb at equilibrium, q_e (mg/g) was calculated and the

thermodynamic behavior of Mb adsorption onto CSAC was evaluated using thermodynamic parameters, which include the change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). These parameters were derived using the following equations [9]:

$$K_d = \frac{q_e \left(\frac{W}{V}\right)}{C_e} \quad (14)$$

$$\Delta G = -RT \ln(K_d) \quad (15)$$

$$\ln(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$$

where R is the universal gas constant (8.314 (J/mole) K), T is temperature (K), and K_d is the distribution coefficient for the adsorption.

3 RESULTS AND DISCUSSION

3.1 Yield and characteristics

Figure 1 shows the Scanning Electron Microscope images for the coconut shells and prepared activated carbon. As shown in Figure 1a, the surface of un-activated coconut shells is very smooth compared to Figure 1b with rougher surface. After ZnCl_2 impregnation and activation at 600 °C activation temperature, it was observed that the homogeneity between the un-activated coconut shell carbon and its matrix decreases in comparison to coconut shell activated carbon (CSAC). The surface of CSAC became rougher and its surface topology differed as shown in Figure 1 b.

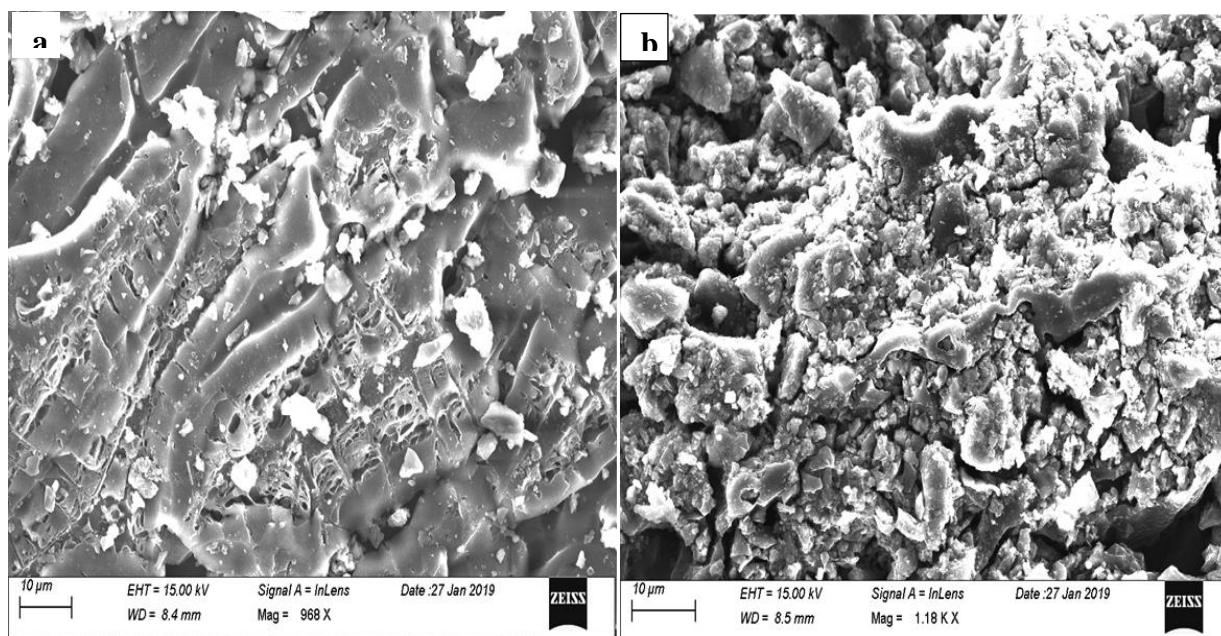


Figure 1: Surface morphologies of pristine coconut shell carbon (CSC) (1a) and coconut shell activated carbon (CSAC) (1b)

3.2 Adsorption isotherm

The equilibrium experimental data for Mb adsorption on CSAC were fitted with Langmuir, Freundlich and Temkin isotherms, using equations (3), (4) and (5). These three isotherm equations constants along with the R^2 values are calculated as shown in Table 1 and the correlated adsorption isotherm are shown in Figures 2b, 3a and 3b. From Table 1, the correlation coefficient, R^2 values for the Langmuir, Freundlich and Temkin isotherms at 303K are 0.9923, and 0.8888, 0.9591 respectively. According to the linear regression method, the Freundlich and Temkin isotherms were poorly suitable to the adsorption of the activated carbon prepared from CSAC in comparison to the Langmuir isotherm which gave the best correlation. This can also be observed in Figure 2a, where the Langmuir isotherm was the best fit to the experimental isotherm and this reflects monolayer adsorption. The validity of the Langmuir model indicated that the dye uptake was due to monolayer coverage of solute particles onto the surface of the activated carbon and adsorption of each molecule had equal activation energy. The same behavior was observed by Hameed *et al.*, [14], Peydayesh and Rahbar-Kelishami [15].

From Table 1, it can be seen that the Langmuir isotherm, values of R_L is 0.139 for adsorption of Mb. This indicated that the adsorption behavior of activated carbon was favourable for the dye ($R_L < 1$). Also, a maximum Mb adsorption capacity of 324.78 mg/g was obtained from the Langmuir isotherm fitting and compared to those obtained in the literature from various agricultural wastes as seen in Table 2. As shown in Table 2, the adsorption capacity of CSAC adsorbent used in this study for the removal of methylene blue in aqueous solution, is comparable to those previously reported in literature. CSAC shows much higher maximum adsorption capacity than some reported adsorbent, such as *platanus orientalis* leaves powder, walnut shell-carbon, oil palm shell-carbon, cotton stalk carbon, ficus carica

bast carbon, rice husk carbon, citrus fruit peel-carbon and Apricot stones-carbon. Furthermore, CSAC adsorption capacity is low when compared with date stones-carbon. However, CSAC adsorbent used in this study is agricultural waste-based at almost cost free, relative to Date stones-carbon adsorbent. This comparison, indicates that CSAC is an efficient and low-cost adsorbent than some existing adsorbent for methylene blue sorption. Therefore, CSAC can be classified as one of the effective adsorbents for wastewater treatment and could be utilized instead of the conventional adsorbent.

3.3 Adsorption kinetics

Figure 4a shows the effect of CSAC adsorption capacity on Mb, using different initial concentrations. This figure depicts an increase in the adsorption capacity of Mb with an increase in contact time. It also indicates that the adsorption reached equilibrium in about 4.5 h. The amount of Mb adsorbed at various time interval was obtained using Equation 9 and correlated with the pseudo-first order, pseudo-second order and intraparticle diffusion models, Equations 10 – 12. The constants and R^2 values for these models at different initial concentration of Mb are tabulated in Table 3. It can be observed that R^2 value of pseudo-first order and interparticle diffusion models are of low values compared to pseudo-second order model. This indicates the measure of pseudo-second order model fits the kinetic experimental data. Furthermore, a large difference was observed between the calculated and experimental values of adsorption capacity (Δq (%)), which also confirm the fit of pseudo-second order model in contrast to pseudo-first order model. The pseudo-second order linear plot of t/q_t against t which depict the high R^2 value of good fit as shown in Figure 5a. It is therefore evident that the adsorption kinetics of Mb on CSAC is better represented by second-order kinetics.

Table 1: Adsorption isotherm plot parameters for Mb on CSAC

Models	Isotherm Constant				
Langmuir	Temp (K)	q_L (mg/g)	K_L (l/mg)	R_L	R^2
	303	324.780	0.014	0.139	0.992
Freundlich	Temp (K)	$1/n$	K_F (mg/g)(l/mg) ^{1/n}	N	R^2
	303	0.4631	25.950	2.159	0.889
Temkin	Temp (K)	β	K_T (l/mg)	B	R^2
	303	189.430	0.190	13.300	0.959

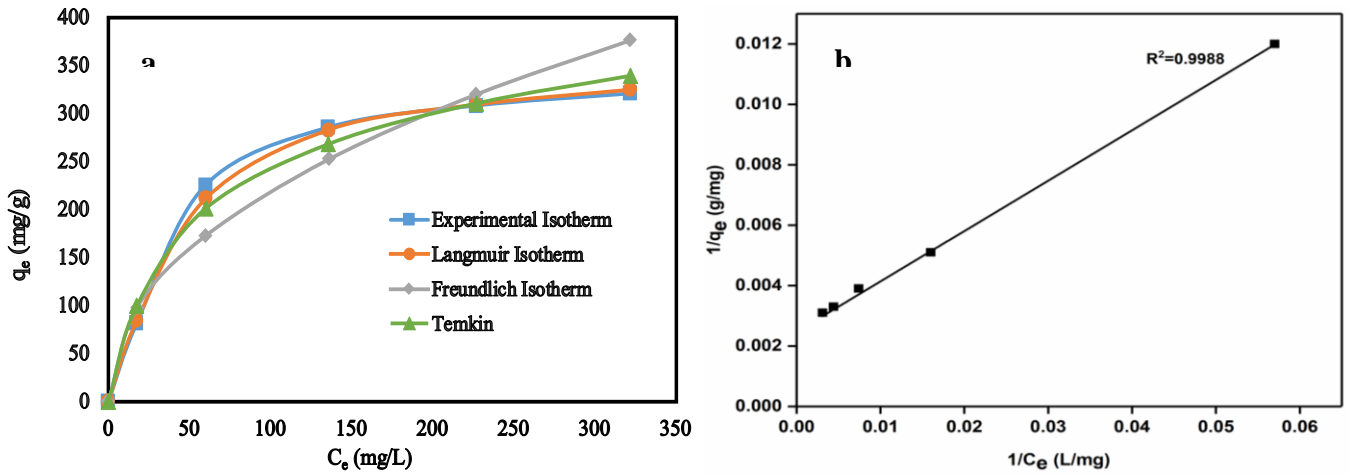


Figure 2: (a) Isotherm models comparison for Mb adsorption on CSAC (b) Langmuir isotherm for Mb adsorption on CSAC. [contact time (4.5hr), pH (7), adsorbent dosage (0.02g)]

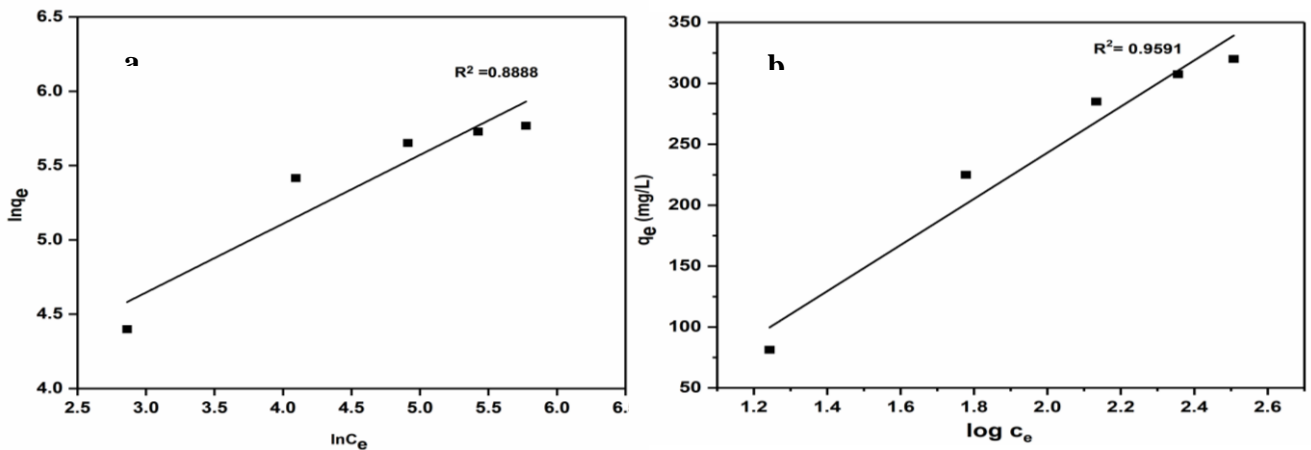


Figure 3: (a) Freundlich, (b) Temkin adsorption isotherm of Mb adsorption unto CSAC. [Contact time (4.5hr), pH (7), adsorbent dosage (0.02g)]

Table 2: Comparison of Methylene blue (Mb) adsorption capacity onto activated carbons (each adsorbate is methylene blue)

Adsorbent	Maximum capacity (mg/g)	Reference
Coconut shell-carbon	320.50	This study
Platanus orientalis leaves powder	114.94	[15]
Date stones-carbon	398.19	[9]
Walnut shell-carbon	315.00	[16]
Oil palm shell-carbon	277.78	[17]
Cotton stalk carbon	193.5	[18]
Ficus carica bast carbon	48.5	[19]
Rice Husk carbon	47	[10]
Citrus fruit peel-carbon	20	[20]
Apricot stones-carbon	4.11	[21]

Intraparticle diffusion model, Equation 12 is widely used to predict the rate controlling step. The values of R^2 for this model is lower in comparison with values obtained from the pseudo- second and pseudo-first order models. A high deviation between

the calculated and experimental values Δq (%) was also observed (Table 3). In concluding that the intraparticle diffusion is the rate controlling step, the plot of q_t versus $t^{1/2}$ should be linear and pass through the origin. As shown in Figure 5b, the plot

did not go through the origin. From these results, it can be concluded that intraparticle diffusion is not the dominating mechanism for the adsorption of Mb from aqueous solution by prepared activated carbon. Accordingly, the optimum adsorption factors obtained were shaking speed of 110 rpm, adsorbent dosage of 0.02 g, initial concentration of 450 mg/L, and contact time of 4.5 hours for 92.39 % removal of methylene blue.

3.4 Adsorption thermodynamics

Applying equation 14, the values of the distribution coefficient for adsorption (K_d) at different temperature were obtained from the adsorption isotherm data. The values of ΔG , ΔH , and ΔS for MB

were then obtained using equation 15 and 16. ΔH and ΔS were obtained from the slope and intercept of the plot of $\ln K_d$ against $1/T$ (Figure 6), and the calculated values are tabulated in Table 4. The obtained values for Gibbs free energy change (ΔG) for the adsorption of Mb on CASC are -1559.35 , -1956.70 , and -2107.78 J/mole at the temperature of 303 K, 313 k, and 323 K respectively. The negative value of the Gibbs free energy is an indication of the thermodynamically spontaneous nature of the Mb adsorption on CSAC. A decrease in the feasibility of adsorption was observed at higher temperatures as indicated by the decrease in ΔG values with increasing temperature.

Table 3: Kinetic Parameters for Adsorption of methylene blue (Mb) on CSAC

	Co(mg/L)	$q_{e, exp}$	$q_{e, cal}$	$K_1(1/min)$	R^2	$\Delta q(\%)$
PSEUDO-FIRST ORDER MODEL	50	81.25	38.11	0.0121	0.9516	26.55
	150	225	59.84	0.0123	0.9365	36.70
	250	285	63.91	0.0169	0.9827	38.79
	350	307.5	86.10	0.0113	0.9798	36.00
	450	320	103.77	0.0113	0.9531	33.79
	Co(mg/L)	$q_{e, exp}$	$q_{e, cal}$	$K_2(g/mgmin)$	R^2	$\Delta q(\%)$
PSEUDO-SECOND ORDER MODEL	50	81.25	85.47	3.34	0.9989	2.597
	150	225	232.56	7.17	0.9994	1.680
	250	285	294.12	11.33	0.9996	1.600
	350	307.5	312.5	8.00	0.9996	0.813
	450	320	333.33	5.00	0.9985	2.083
	Co(mg/L)	$q_{e, exp}$	C(mg/g)	$K_3 (mg/gmin^{1/2})$	R^2	
INTRAPARTICLE DIFFUSION MODEL	50	81.25	39.298	20.194	0.8542	
	150	225	157.510	32.752	0.8103	
	250	285	224.430	29.948	0.7980	
	350	307.5	218.320	41.969	0.9238	
	450	320	215.530	48.683	0.9420	

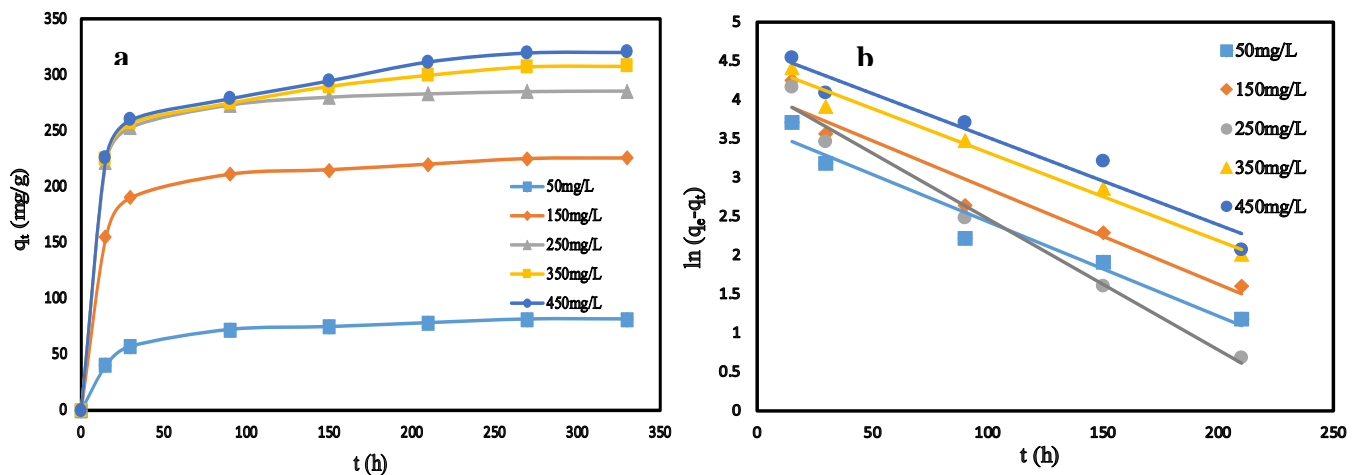


Figure 4: (a) Contact time effect on Mb adsorbed on CSAC at different initial concentration. (b) Pseudo-first order kinetic for Mb adsorption on CSAC at different initial concentration. [pH (7), temperature 303 K, adsorbent dosage (0.02)].

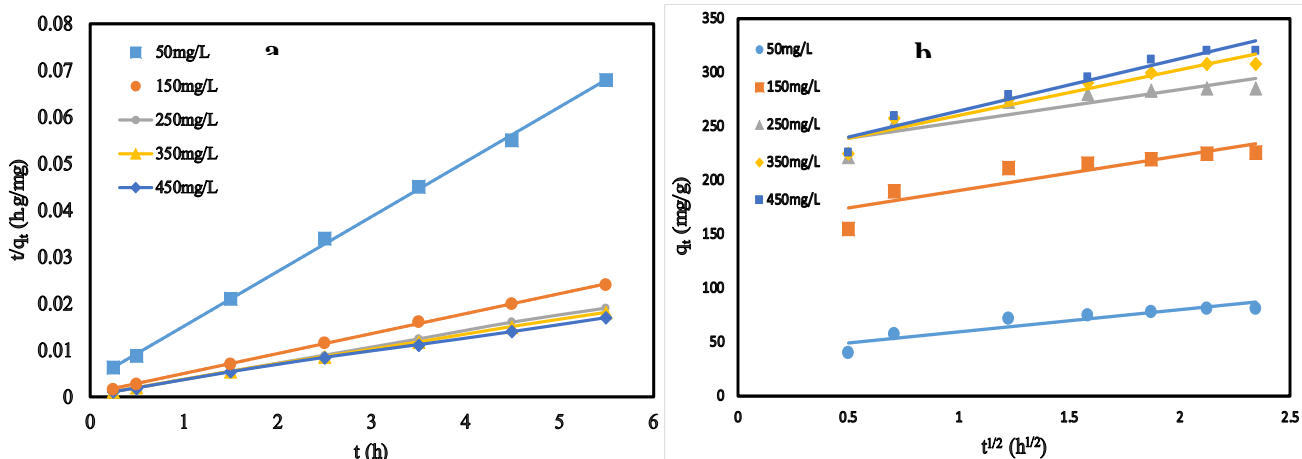


Figure 5: (a) Pseudo-second order kinetic for Mb adsorption on CSAC at different concentration, (b) Intraparticle diffusion model for Mb adsorption on CSAC at different initial concentration [temperature (303 K), pH (7), adsorbent dosage (0.02 g)].

Table 4: Thermodynamics adsorption parameters for Mb on CSAC.

$\Delta H(\text{J/mole})$	$\Delta S(\text{J}/(\text{mole})(\text{K}))$	$-\Delta G(\text{J/mole})$		
		303K	313K	323K
7015.76	26.15	1559.35	1956.70	2107.78

The ΔH value is 7015.76 J/mole for Mb adsorption on CSAC and this positive value indicate the endothermic nature of the adsorption. Adsorption enthalpy ranging from 2.1 to 20.9 kJ/mol correspond to physical adsorption and this indicate that the adsorption of Mb on CASC is physisorption [9, 22]. Also, the positive value of ΔS (26.15 J/mole) indicates that during the adsorption process there is an increase in the randomness at adsorbate-solution interface which enhance the process.

4 CONCLUSIONS

In conclusion, the preparation of activated carbon from waste coconut shell with zinc chloride activation and its ability to remove methylene blue (Mb) from aqueous solutions was reported in this study. The maximum adsorption capacity of Mb on CASC was 320.5 mg/g at a pH value of 7, 0.02 g adsorbent dose and 4.5 h contact time. Langmuir isotherm fits the equilibrium adsorption data for Mb adsorption with a correlation coefficient (R^2) value of 0.9923. The pseudo-second order model describes the adsorption kinetics data. The calculated thermodynamic parameters namely ΔG , ΔH and ΔS indicates the spontaneous and endothermic nature of Mb adsorption onto CSAC under the examined conditions. This study indicates

its potential as effective adsorbent for removal of dye from wastewater effluent.

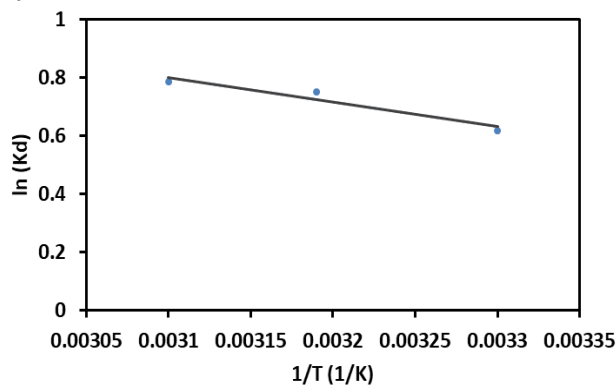


Figure 6: Plot of $\ln (K_d)$ versus $1/T$ for Mb adsorption on CSAC ($C_o = 50 \text{ mg/L}$, time = 4.5h, pH = 7, adsorbate dosage= 0.02 g).

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