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Adsorptive elimination of methylene blue dye from aquatic system using biochar produced from cocoa shell

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ABSTRACT

The present research aims to investigate the potential of new biochar prepared from cocoa shell (CS), through the chemical modification method [sulfuric acid-modified CS (SMCS)]. The prepared material was found to possess an excellent adsorption capacity for the elimination of Methylene blue (MB) dye from a polluted environment by experimenting the several operating parameters which include initial dye concentration, contact time, solution pH, temperature and adsorbent dose. SMCS was characterized using scanning electron microscopy-energy dispersive analysis of X-rays, thermo-gravimetric analysis, Fourier transform infrared, and Brunauer–Emmett–Teller analysis. The equilibrium data were best discussed by the Freundlich model. Langmuir model capacity was estimated at 163.5 mg/g for MB dye removal. The feasibility and spontaneous activities of the adsorption process were observed because of the negative values of Gibbs free energy obtained for SMCS-MB dye adsorption system. Pseudo-first-order, pseudo-second-order, and Elovich kinetic models have been tested for kinetic data of SMCS-MB dye system. Pseudo-first-order model showed good results for SMCS-MB dye system. Through obtained results, it was concluded that the SMCS can act as a potential low cost, environmental friendly, and effective adsorbents and which can be employed as an alternative to various commercial adsorbents.

Keywords: Adsorption; Biochar; MB dye; Equilibrium; Thermodynamics; Kinetics

1. Introduction

Rapid urbanization and industrial growth lead to the most critical issue of water contamination because water is the most essential nutrient to all living life on the earth. Natural wastes and activities done by humans are principal sources of water contaminants. Dyes were used from a long time in many industries, such as pharmaceuticals, food, dyestuffs, cosmetics, textile, plastics, and paper. These industries generate large amount of colored wastewater which is identified as a prime contaminant in the wastewater [1,2]. It is known that more than 8,000 products are associated with the dyeing industry alone, and over 100,000 commercially available dyes exist with over 7×10^5 metric tons of dye stuff produced on annual basis globally [3].

Many dyes are toxic and carcinogenic even at very small quantities available in water (less than 1 mg/L for some dyes) and pose a serious hazard to aquatic living organisms which are highly visible and undesirable. These dyes interfere with the light transmission and disturb the natural

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metabolism processes causing devastation to the marine community in the ecosystem. A cationic dye, Methylene blue (MB), which commonly used for dying silk, wood, and cotton causes problems of breathing, burning sensation, nausea, etc., and eye burning in humans and animals [4,5].

Moreover these pollutants are highly toxic and carcinogenic towards the human health [6]. There is a great need to build up a successful and fitting handling practice to remove these dyes from wastewater streams before its discharge in the natural environment. There exist numerous difficulties in treating this colored wastewater due to its properties such as its stability to heat, light, and oxidizing agents, and its resistance to aerobic digestion [7]. Numerous predictable methods include coagulation precipitation, adsorption, oxidation, and filtration and are not very effective, economical, and environmental friendly to obstinate toxic dyes [8–10]. However, adsorption procedure is prominently used for removing the different coloring compounds [11–13]. In the adsorption process, the pollutant is transferred from wastewater to the adsorbent surface due to the concentration gradient which thereby avoids the exposure of pollutants to the living organisms [14,15]. After treatment by adsorption, the treated effluents can be released into the environment which can be reused by industries that required lower or moderate purity water. The spent adsorbents can be regenerated and reused after completion of the adsorption process [16,17]. The high porous form of material particularly activated carbon holds higher adsorption characteristics [18,19]. The capability of activated carbon primarily depends on the type of organic stuff used in the synthesis of activated carbon from physical and chemical activation procedures [19,20]. Chemical activation employs the chemicals which include H_2SO_4, H_3PO_4, K_2CO_3, KOH, $ZnCl_2$, and NaOH [21].

Cocoa shell (*Theobroma cacao*) (CS) is a low-cost agriculture waste material that can be used as a raw material for preparing biochar. According to available literature, a study on the removal of dyes from wastewater using biochar prepared from cocoa shells has been not reported. In this research, the surface-modified cocoa shell (SMCS) biochar has been prepared by using sulfuric acid activation procedure and the prepared biochar was used to remove Methylene blue (MB) dye from aqueous solution. The effect of different operating parameters like initial dye concentration, pH, contact time, temperature, and adsorbent dose have been studied. The effectiveness of this material was characterized by Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET), and scanning electron microscopy-energy dispersive analysis of X-ray (SEM-EDAX) analyses. The removal of MB dye by SMCS has been analyzed through isotherm, kinetic, and thermodynamic approach.

2. Materials and methods

2.1. Preparation of SMCS biochar

The biochar was prepared by treating raw cocoa shell powder with concentrated H_2SO_4 of 1:2 ratio by weight and the reaction was left for 1 d. The dehydrated cocoa shell powder was removed by washing it completely with double distilled water to maintain the pH of supernatants constant at 7.0. After drying for 3 h at 80°C, it was crushed and sieved to 0.354 mm size named as sulphuric acid-modified cocoa shell (SMCS) biochar. This obtained adsorbent material was kept in a container used for the removal of MB dye from the aqueous solutions.

2.2. Preparation of Methylene blue dye solutions

MB dye powder (CI 52015, molecular formula: $C_{16}H_{18}N_3SCl{\cdot}3H_2O$, molecular weight: 373.9, λ_{max} = 664 nm) supplied by E. Merck (India) was used in the present investigation. The stock solution (500 mg/L) was prepared by dissolving the required quantity of MB dye powder in double distilled water. Stock solutions are diluted with double distilled water to obtain solutions of various desired concentrations (100–500 mg/L) and pH of each of these working solutions were adjusted by using 0.1 M NaOH or 0.1 M HCl.

2.3. Cocoa-shell characterization

The surface area of cocoa shell (CS) was calculated by using BET method by adsorption of nitrogen at 77.15 K (model: Tristar II; Make: M/s Micrometrics, Norcross, GA, USA) and degassing at 423 K in a nitrogen atmosphere for 1 h. The morphology characteristics for both raw CS and SMCS were obtained using SEM (Make: Zeiss, Model: Sigma, Jena, Germany). EDX (Make: Zeiss, Model: Sigma, Germany) analysis was done to know the elemental composition of the prepared adsorbent. FT-IR spectrophotometer analysis (Perkin Elmer FTIRC 100566, UK) was performed to determine the various functional groups present in the adsorbent. The calibration curve was prepared by measuring the absorbance of various concentrations of MB dye solutions at λ_{max} = 664 nm using a UV-vis spectrophotometer (Shimadzu, Japan) which was used to measure solution concentration of MB dye. Thermogravimetric analysis (TGA, make: Netzsch, Model: STA449F3A00 Jupiter, Wittelsbacherstr 42, 95100 Selb, Germany) was performed to investigate the characteristics of the material such as bound moisture and material thermal degradation with temperature. The measured quantity of ten milligrams of CS adsorbents sample was kept in platinum crucibles. Next under 40 mL/min N_2 flow, the sample was subjected to heating by 10°C/min at a constant rate to 600°C.

2.4. Batch adsorption

Batch experiments on adsorption were carried out by altering the different parameters like initial MB dye concentration, solution pH, temperature, time, and adsorbent dosage. In each set of investigation, accurately weighed SMCS was mixed with 100 mL of MB dye solution and agitated at 80 rpm in a rotary shaker for about 10–90 min and centrifuged later. The supernatants concentration was determined from the absorbance of its solution at a characteristic wavelength of 664 nm using a double beam UV-vis spectrophotometer. Experiments were performed thrice and average values were noted. These experimental data were used to calculate the percentage removal of MB dye by using Eq. (1):

$$\% \text{ Removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where C_e and C_0 are respective equilibrium and initial concentration (mg/L) of the MB dye solutions.

2.5. Batch equilibrium investigation

Batch equilibrium studies have been experimented by adding SMCS dose of 0.3 g to each conical flask consisting of 100 mL MB dye solution of various initial concentrations (100–500 mg/L) at 30°C. The flasks were agitated at 80 rpm in a rotary shaker for about 1 h. Experiments were conducted thrice and average of the values was noted. The quantity of MB dye adsorbed at equilibrium time, q_e was calculated using the following expression.

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V \quad (2)$$

where q_e is adsorption capacity at equilibrium (mg/g), V is MB dye solution volume, and m is adsorbent mass (g).

2.6. Equilibrium experiments

Langmuir [22], Freundlich [23], Langmuir–Freundlich, and Sips model [24] are four prominent isotherms used for testing adsorption equilibrium data to find the adsorption characteristics of SMCS for MB dye removal. Nonlinear regression analysis has been carried out by using MATLAB R2009a software to calculate the parameters, constants, coefficient of correlation (R^2), and error values. The results of this analysis were used to determine the best adsorption isotherm models for the acquired equilibrium curve.

The Langmuir isotherm model is given as:

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

where K_L is Langmuir constant related to the affinity of MB dye to adsorbent (L/mg) and q_m is maximum monolayer adsorption capacity (mg/g).

The Freundlich model is given as:

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

where K_F is Freundlich constant ((mg/g) (L/mg)$^{1/n}$) used to measure adsorption capacity and n is Freundlich exponent which is used to measure the intensity of adsorption. The outcome of n is given as follows: $n = 1$ (linear); $n < 1$ (physical process); $n > 1$ (chemical process).

Langmuir–Freundlich model is given as:

$$q_e = \frac{q_{m\text{LF}} (K_{\text{LF}} C_e)^{m\text{LF}}}{1 + (K_{\text{LF}} C_e)^{m\text{LF}}} \quad (5)$$

where q_e is adsorbed amount at equilibrium (mg/g), $q_{m\text{LF}}$ is Langmuir–Freundlich maximum adsorption capacity (mg/g), C_e is adsorbate equilibrium concentration (mg/L), K_{LF} is equilibrium constant for a heterogeneous solid, and m_{LF} is heterogeneity parameter which lies between 0 and 1.

Sips model is given as:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + \alpha_S C_e^{1/\beta_S}} \quad (6)$$

where α_S is Sips isotherm constant, K_S is Sips model constant, and β_S is Sips model exponent. The outcome of β_S is given as follows: $\beta_S = 1$ (homogeneous binding sites); $\beta_S > 1$ (heterogeneous adsorption system).

2.6. Kinetics studies

Adsorption kinetic experiments were performed at 30°C with 100 mL MB dye solution of various initial concentrations (100–500 mg/L) and 0.3 g dosage of SMCS in 250 mL conical flasks. The mixture was shaken constantly and the test samples were drawn at set time intervals and filtered for analyzing the residual concentration of MB dye. The experiments were performed thrice and the average values were noted. The amount of MB dye adsorbed at time t, q_t was calculated using the following expression:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (7)$$

where C_t is concentration of MB dye measured at time interval t (mg/L) and q_t is adsorption capacity of adsorbent at any time t (mg/g).

The kinetic data were plotted using pseudo-first-order [25], pseudo-second-order [26], and Elovich kinetic [27] models to examine the removal kinetics of MB dye from aqueous solution using SMCS.

Pseudo-first-order model:

$$q_t = q_e \left(1 - \exp\left(-k_1 t\right)\right) \quad (8)$$

Pseudo-second-order model:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (9)$$

Elovich model:

$$q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \quad (10)$$

where k_1 is pseudo-first-order constant (1/min), k_2 is pseudo-second-order constant (g/mg min), β_E (g/mg) is constant of desorption, and α_E is the rate of adsorption at initial (mg/(g min)).

2.7. Analysis of thermodynamics

Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) are thermodynamic parameters and which can be estimated from the following expressions:

$$K_c = \frac{C_{\text{Ae}}}{C_e} \quad (11)$$

$$\Delta G^\circ = -RT\ln\left(K_c\right) \tag{12}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{14}$$

where K_c is constant of equilibrium, C_{Ae} is the equilibrium quantity of MB dye available on the surface of adsorbent per volume of solution (mg/L), T is the temperature (K), and R is gas constant (8.314 J/mol/K).

3. Results and discussion

3.1. Cocoa-shell characterization

Scanning electron microscopy (SEM) illustrates the structure of the surface and porous morphology of adsorbent material (SMCS). The surface consistency of virgin cocoa shell without pre-treatment was found to be smooth, uneven, and swelling having cracks and pits Fig. 1. The vesicles and spaces within this micrograph show no pores, and large holes with the poorly developed pores [28]. On the other hand, virgin cocoa shell treated with sulfuric acid Fig. 2 (SMCS), shows various pores on its exterior surface with enhanced surface characteristics containing uniform pore size distribution [29]. Fig. 2 shows uneven pores spread of various sizes formed due to sulfuric acid treatment on the raw cocoa shell and indicates SMCS bio-adsorbents has a more sufficient surface morphology for adsorption of MB dye. EDX analysis (Figs. 1 and 2) was reported that the maximum carbon yield of 68.38% was achieved for SMCS biochar which is 16% higher than the carbon in raw CS. Increased carbonaceous content of the adsorbent indicates that it will possess a greater adsorption capacity.

Thermogravimetric analysis (TGA) is a thermal analysis that measures the changes in properties of adsorbent materials as a function of temperature increment (heating rate is kept as constant). Otherwise, the changes in material property were observed as a function of time (kept temperature as constant or loss of mass is kept as constant). The degradation levels of SMCS were investigated and the weight loss percentage was measured as 23.72% and it was endure till 870°C. Fig. 3 shows the decomposition of SMCS with an increase in temperature. It is evident that SMCS was more firm under higher temperatures.

The analysis of FT-IR spectra is shown in Fig. 4 for raw and SMCS in a range of 400–4,000 cm^{-1}. The results indicate presence of numerous functional groups on the SMCS before the adsorption process. The peak at 3,287.81 cm^{-1} corresponds to O–H stretching vibration and the presence of alkanes group and aldehydes group are indicated by C–H bond vibration between 2,914.43 and 2,850.67 cm^{-1} [30,31]. This may be due to the stretching of C–H bond in cellulose and hemicellulose. The peak at 1,602.76 cm^{-1} could be of C–C stretch (in–ring) and peak at 1,316.16 cm^{-1} corresponding to C–O stretch. The peak at 1,245.27 cm^{-1} is due to C–N stretch and the peaks at 895.74 cm^{-1} could be assigned to the C–H groups. The peaks at 810.52 cm^{-1} showed the presence of C–H groups which concludes the presence of sufficient functional groups on adsorbent surface SMCS for removal of MB dye from aqueous solution.

Generally, the adsorption capacity of the adsorbent was found to be high because of the larger surface area of the adsorbent [32]. BET analysis provides precise specific surface area assessment of materials yielding important information in studying the effects of surface porosity and particle size by nitrogen multilayer adsorption measured as a function of relative pressure. In the present study, Figs. 5a and b show average monolayer capacity for methylene blue adsorption on SMCS is 163.5 mg/g and cross-sectional area of dye is 0.1620 nm^2, and the specific surface area of the adsorbent was found to be 1.4325 m^2/g. Thus, SMCS has more larger surface area compared to that of the number of other adsorbents, such as *Macor heimulis* (0.3129 m^2/g) [33], egg shell (1.20 m^2/g) [34], but less than that of some others work using activated carbon from *Enteroporpha prolifera* (ACEP) (683 m^2/g) [35] and activated carbon felt (1,112 m^2/g) [36].

3.2. Adsorbent amount influence

The batch experiments on the influence of adsorbent amount on MB dye removal by SMCS are shown in Fig. 6. The elimination of MB dye was increased with increase in SMCS dosage and it was reached the maximum at 3 g/L and after that, the constant removal was observed. Enhancement of dye removal at higher dosage was due to the increase in SMCS surface area and active sites which leads to more adsorption sites [37].

3.3. pH influence

The pH plays an important role in the adsorption process because the adsorption process was highly influenced based on the solution pH. The experiments were carried at different solution pH (2.0–10.0) on the removal of MB dye from its aqueous solution with SMCS and its outcomes are shown in Fig. 7. The increment on the removal of MB dye was observed with an increase in solution pH till 8.0 and remains almost a constant afterwards. The acidic condition of the adsorption system indicates that the hydronium ions in the solution have been adsorbed onto the adsorbent surface which results in acquiring the positive charges on the adsorbent surface. This positive charge on the adsorbent surface avoids the separation of MB dye molecules from aqueous solution by the adsorbent because of the electrostatic repulsion between the adsorbent surface and MB dye molecules. The pH of the solution was increased with an increase in the negatively charged adsorbent surface which leads to an increase in the separation of MB dye molecules by the adsorbent because of the electrostatic attraction between the MB dye and adsorbent surface [37]. A small removal of dye molecules by adsorbent was observed when the pH was increased from 8.0 to 10.0. The pH results observed that the solution pH of 8.0 was identified as a possible solution pH for the SMCS-MB dye system.

3.4. Influence of dye concentration

The different initial concentration (100–500 mg/L) influences on the removal of dye by the adsorbents have been

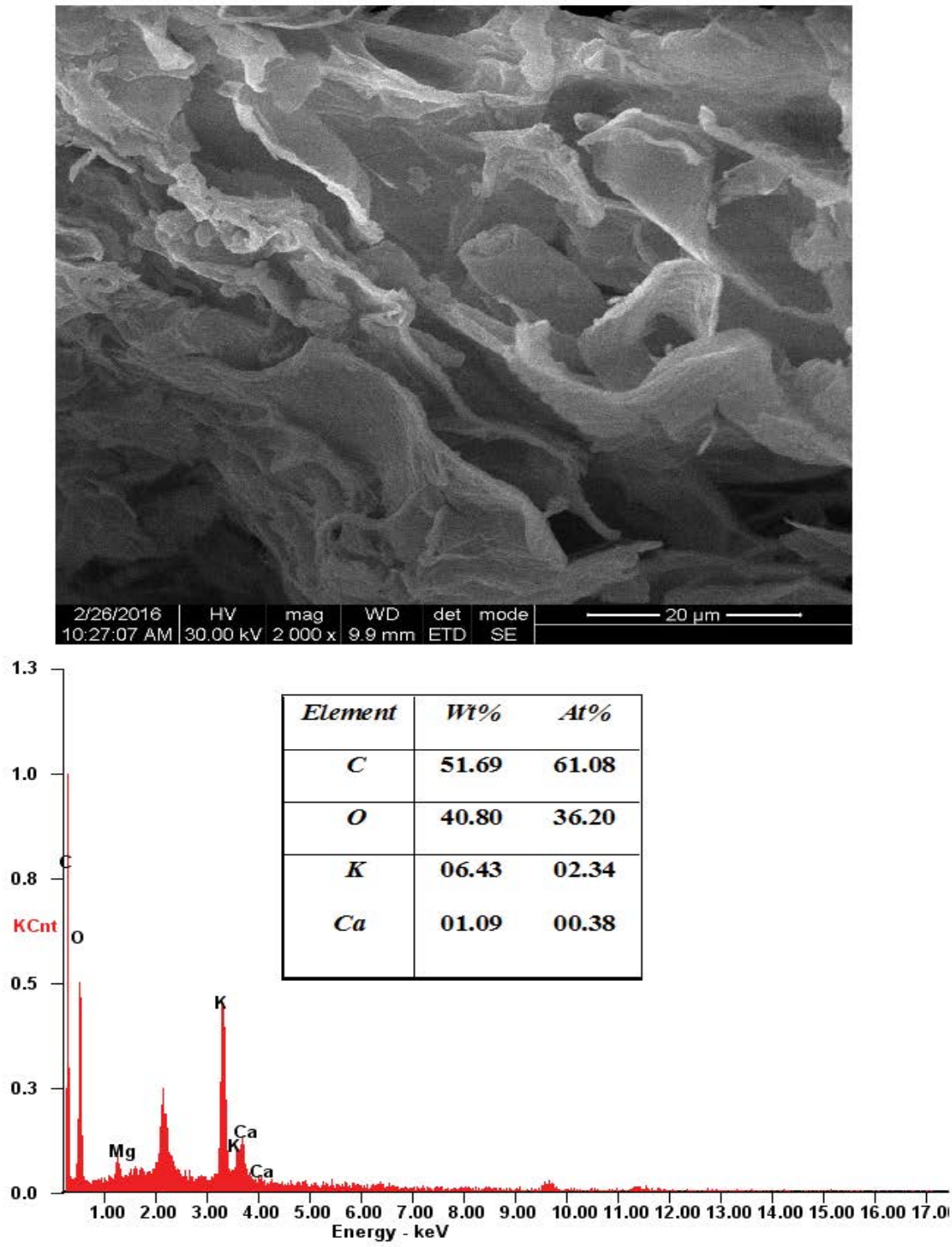
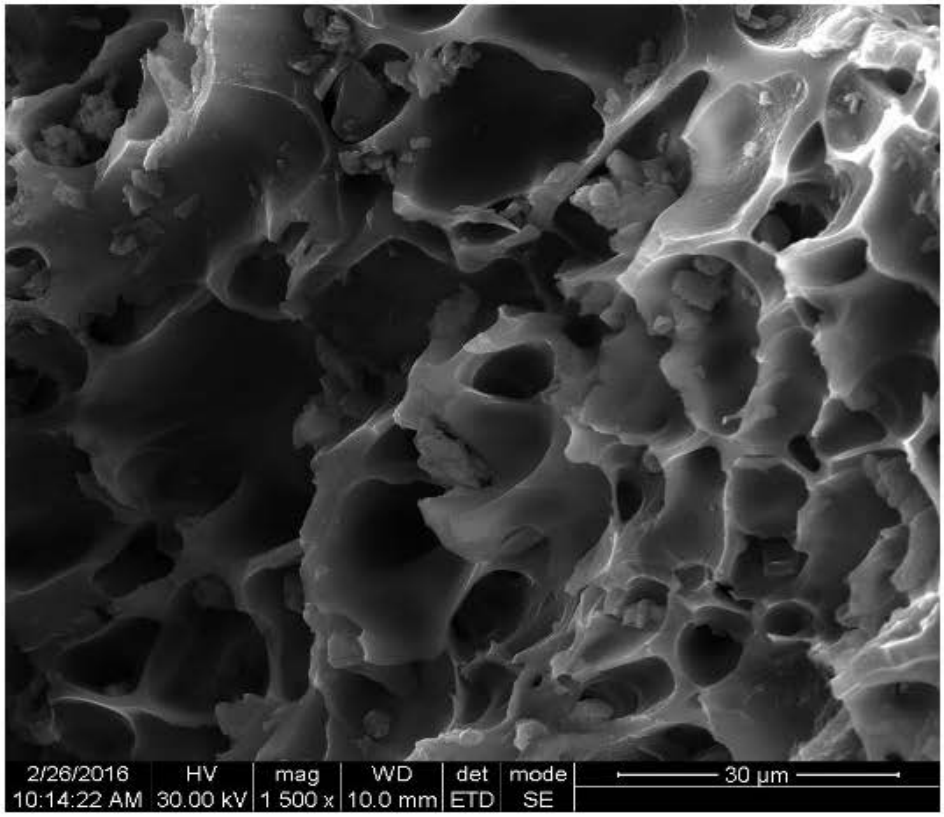
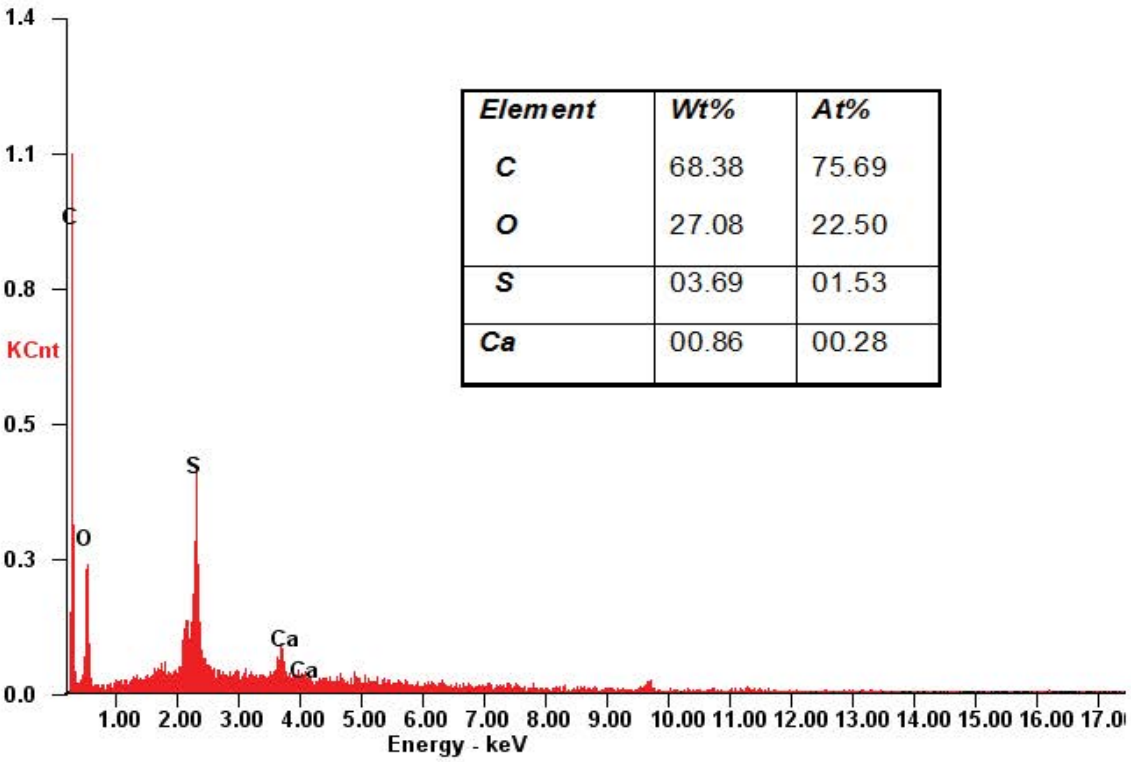


Fig. 1. SEM-EDX image of virgin cocoa shell.

experimented and the results are given in Fig. 8. The importance of this study is to verify the adsorbent ability for the different initial dye concentrations. The results observed that the reduction in the removal of MB dye with increase of MB dye concentration. The highest removal of dye was achieved at lesser dye concentration because of the higher ratio of adsorbent sites to the number of dye molecules and lesser removal of dye was achieved at higher dye concentration because of the lesser ratio of adsorbent sites to the number of dye molecules [38].





Element	Wt%	At%
C	68.38	75.69
O	27.08	22.50
S	03.69	01.53
Ca	00.86	00.28

Fig. 2. SEM-EDX image of sulfuric acid modified cocoa shell (SMCS).

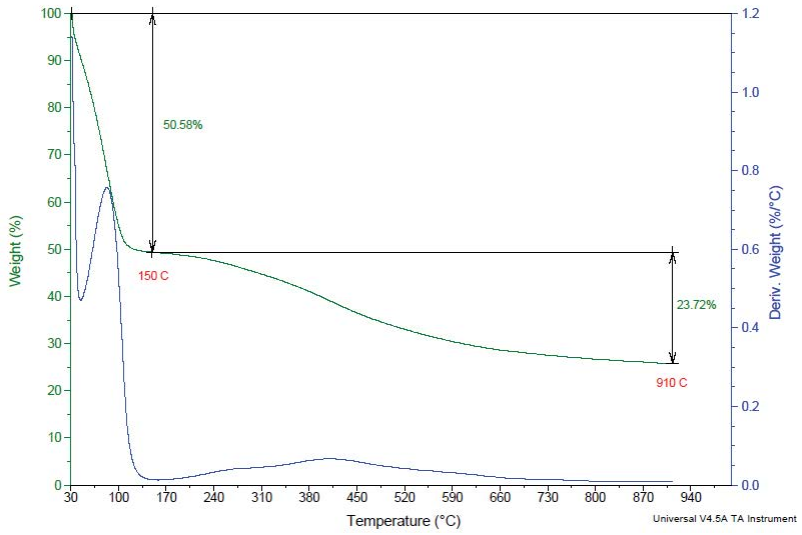


Fig. 3. TGA curve of SMCS.

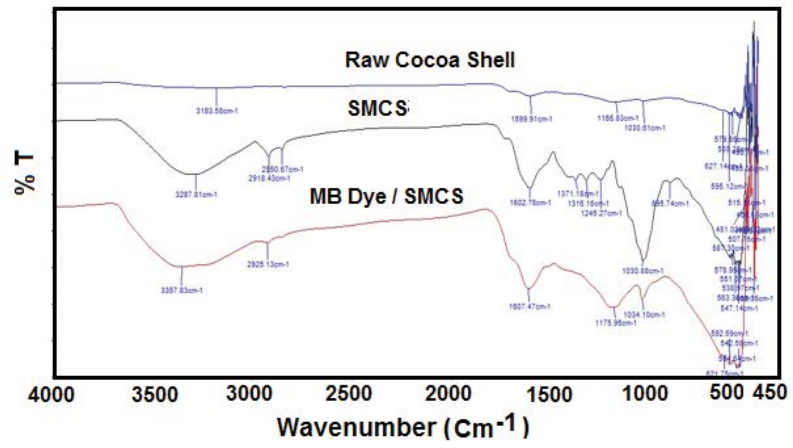


Fig. 4. FT-IR spectrum of cocoa shell.

3.5. Contact time influence

Fig. 9 shows the influence of contact time on the separation of MB dye from the aquatic system by SMCS. The contact time plays an essential role in the adsorption of dye molecules because it decides the proper residential time required between the adsorbent and adsorbate in an adsorption system. The results explain that the dye removal was increased with an increase in time of contact and it reaches almost maximum removal at 60 min. Lower residential time leads to lower adsorption and higher residential time leads to maximum adsorption [39].

3.6. Temperature influence

The temperature influence on the adsorption process is important because the adsorption capacity may increase or decrease due to the nature of the adsorption process. Fig. 10 shows the influence of temperature on the separation of dye molecules of different initial MB dye concentrations (100–500 mg/L) by SMCS. The result explains that the decrease in the elimination of dye was achieved with an increase in temperature and adsorption phenomena followed the exothermic process. This may be because of the decline in activity of the adsorbent with temperature increment [40,41]. The highest dye elimination was achieved at 30°C.

3.7. Equilibrium analysis

Adsorption isotherms are vital for adsorber design. It explains the concept of the distribution of dye molecules between the adsorbent surface (q_e) and in the aqueous solution (C_e) at an equilibrium condition. Adsorption equilibrium studies have been experimented to explain the adsorption behavior, predicting the possible removal mechanism and to estimate the adsorption capacity. The isotherm explains that the equilibrium adsorption capacity of the adsorbent was increased with an increase in equilibrium concentration of dye in solution. The adsorption equilibrium data was applied with Langmuir, Freundlich, Langmuir–Freundlich, and Sips models, and the outcomes are presented in Fig. 11.

BET Surface Area Report

BET Surface Area: 1.4325 ± 0.0841 m²/g
Slope: 3.071538 ± 0.177401 g/cm³ STP
Y-Intercept: -0.032683 ± 0.018606 g/cm³ STP
C: -92.980606
Qm: 0.3291 cm³/g STP
Correlation Coefficient: 0.9966808
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.058118977	0.4006	0.154042
0.082192640	0.4196	0.213447
0.113157736	0.4184	0.304996
0.145119830	0.4032	0.421066

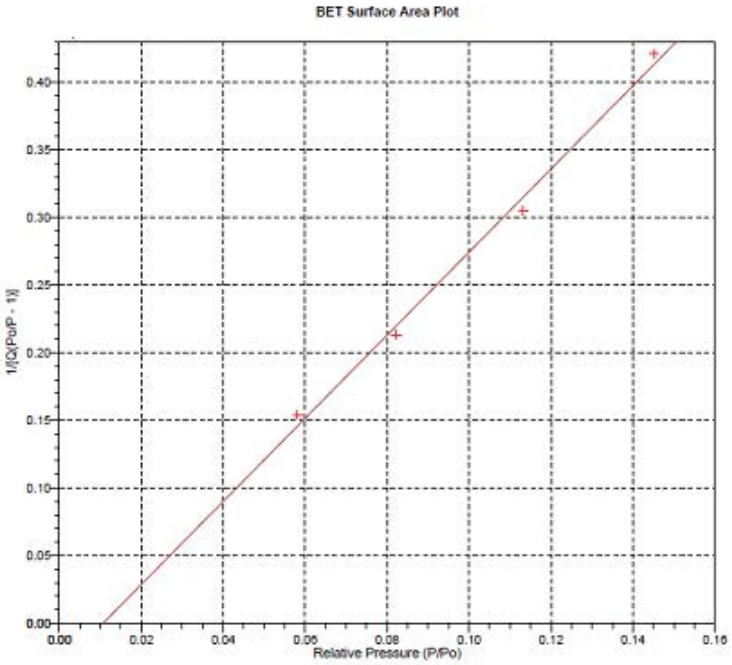


Fig. 5. BET surface area report of SMCS.

The monolayer adsorption capacity (q_m), Langmuir constant (K_L), Freundlich constants, (K_L and n), Langmuir–Freundlich constants (K_{LF}, m_{LF}, q_{LF}), and Sips model constant (K_S and a_S and b_S) have been estimated from the non-linear isotherm plot of C_e vs. q_e. Table 1 showed the estimated parameters of isotherm models, correlation coefficient (R^2), root mean squared error (RMSE), and sum of squared error (SSE) values from the isotherm plots (Fig. 11). Langmuir model informs that the interaction between the dye and the adsorbent was due to monolayer adsorption behavior. Freundlich model showed higher R^2 value as compared to other isotherm models which inform that the adsorbent possessed the heterogeneous adsorbent surface and the interaction between the dye and adsorbent was of multilayer adsorption [42,43]. Table 1 showed that the Freundlich model is a suitable model to demonstrate the adsorption equilibrium for SMCS for the different initial dye concentrations. The Freundlich model provides a high value of R^2 (0.9857) and error values (SSE = 130.7 and RMSE = 6.6) for SMCS was found to be low as compared to other model error values.

3.8. Kinetics and removal mechanism

The removal rate of dye molecules from aquatic system and its removal mechanism was explained with adsorption kinetics. The removal kinetics was best addressed with

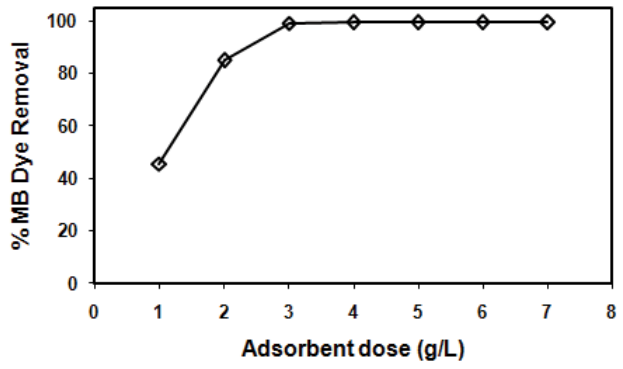


Fig. 6. Effect of adsorbent dose on MB dye adsorption by SMCS (MB dye concentration = 100 mg/L, solution pH = 8.0, equilibrium time = 60 min, and temperature = 30°C).

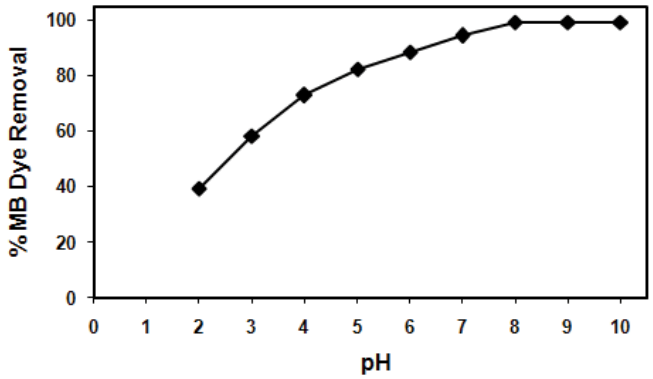


Fig. 7. Effect of pH on MB dye removal by SMCS (initial MB dye concentration = 100 mg/L, SMCS dose = 3 g/L, time = 60 min for SMCS, volume = 100 mL, and temperature = 30°C).

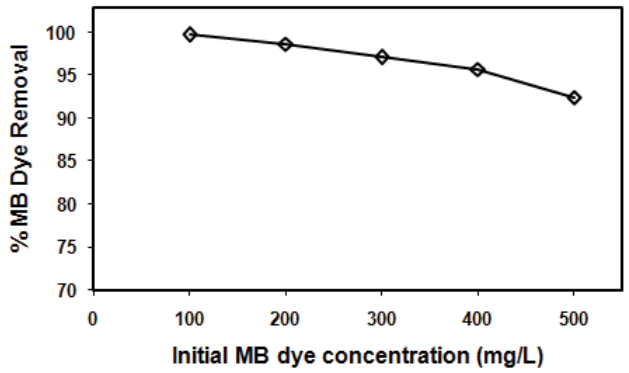


Fig. 8. Effect of initial MB dye concentration on MB dye removal by SMCS (pH = 8.0, SMCS dose = 3 g/L, time = 60 min for SMCS, volume = 100 mL, and temperature = 30°C).

pseudo-first-order, pseudo-second-order, and Elovich kinetic models. The results on the removal kinetics for SMCS-MB dye systems have been displayed in Fig. 12. Table 2 shows the estimated parameters of kinetics models, R^2, RMSE, and SSE values from the kinetics plots (Fig. 12). The equilibrium adsorption capacity was estimated from experimental

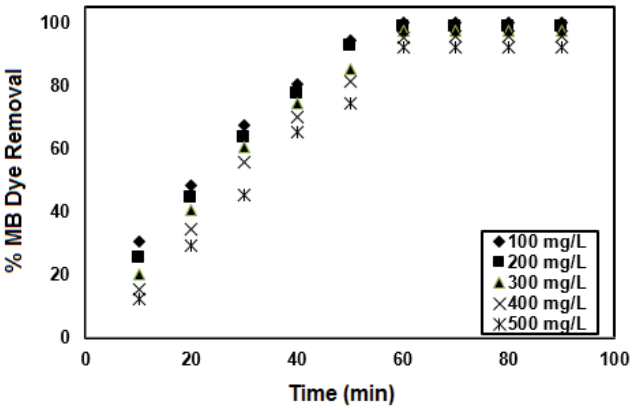


Fig. 9. Effect of contact time on MB dye removal by SMCS (initial MB dye concentration = 100–500 mg/L, pH = 8.0, SMCS dose = 3 g/L, volume = 100 mL, and temperature = 30°C).

Table 1
Evaluated adsorption isotherm parameters for MB dye removal by SMCS

Adsorption isotherm model	Parameters	Values	R^2
Langmuir	q_m (mg/g)	163.5	
	K_L (L/mg)	0.2275	0.8719
	SSE	1,170	
	RMSE	19.75	
Freundlich	K_F ((mg/g) (L/mg)$^{(1/n)}$)	56.95	
	n (g/L)	3.721	0.9857
	SSE	130.7	
	RMSE	6.6	
Langmuir-Freundlich	K_{LF}	9.605	
	m_{LF}	0.2684	
	q_{LF}	2,472	0.9837
	SSE	149.2	
	RMSE	7.053	
Sips	α_S	12.12	
	β_S	1.136	
	k_S	722.6	0.9441
	SSE	510.3	
	RMSE	13.04	

data using the mass balance equation and it is reported in Table 2. The removal kinetic data was applied to the kinetic models and the model predicted equilibrium adsorption capacities of SMCS have been reported in Table 2. While comparing these two equilibrium adsorption capacity values, the pseudo-first-order model showed the closest values as compared to the pseudo-second-order model. This showed the pseudo-first-order model is a most preferable model for SMCS-MB dye system. This was further confirms that the larger R^2 values and least error values have been observed for the pseudo-first-order model as compared to other kinetic models. The chemical adsorption principles can

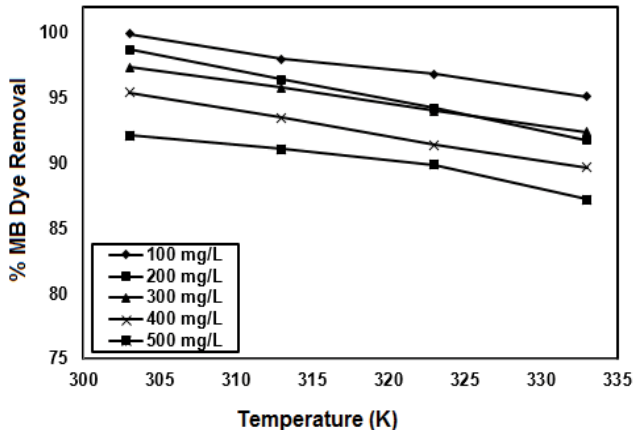


Fig. 10. Effect of temperature on MB dye removal by SMCS (initial MB dye concentration = 100–500 mg/L, pH = 8.0, SMCS dose = 3 g/L, and time = 60 min).

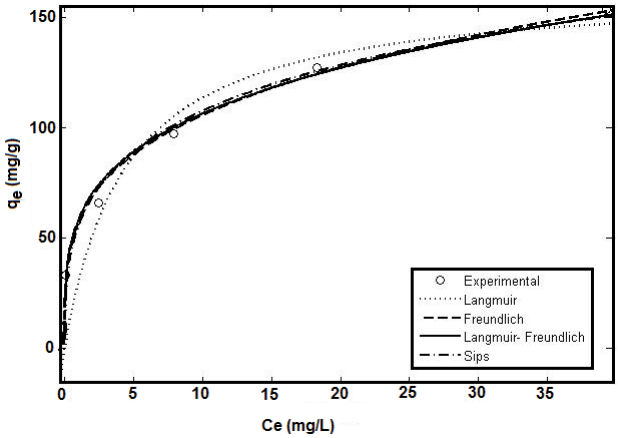


Fig. 11. Adsorption isotherm for the removal of MB dye by SMCS.

be best explained by the Elovich model and which informs that the adsorbent possessed heterogeneous surface [44]. The Elovich model parameters and other related values have been given in Table 2. For the SMCS-MB dye system, the Elovich model doesn't fit well as compared to other models based on errors and R^2 values. Overall, the kinetic results confirm that the elimination of MB dye by SMCS was followed pseudo-first-order model.

3.9. Thermodynamic analysis

The thermodynamic parameters for the SMCS-MB dye system have been evaluated from the logK_c vs. 1/T plots (Fig. 13) and the obtained results are given in Table 3. The Gibbs free energy values for the studied system were estimated as negative and which informs that the adsorption process was feasible. The negative values of changes in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) indicate that adsorption was exothermic and enthalpy driven indicating its phenomenon as the effect of physical adsorption through electrostatic interaction [45,46]. The predicted adsorption thermodynamic parameters indicate that the adsorption is more favorable at 30°C.

4. Conclusion

The biochar was produced from the raw cocoa shell by treating it with sulphuric acid which leads to receiving the greater adsorption capacity toward the MB dye. The best possible operating conditions on the maximum removal of MB dye by adsorbent were observed as (i) optimum adsorbent dose of 3 g/L, (ii) contact time of 60 min, (iii) optimum pH of 8.0, and (iv) temperature at 30°C. Adsorption isotherm and kinetic models have been tested for the adsorption data using non-linear method of approach. Isotherm results showed that the Freundlich model explained the adsorption system well and confirms that the adsorbent possessed heterogeneous adsorbent surface. Langmuir adsorption capacity of the SMCS for MB dye was estimated as 163.5 mg/g at optimum conditions. Kinetic results showed that pseudo-first-order provided good results for SMCS-MB dye adsorption process. Exothermic nature of adsorption was identified for the SMCS-MB dye system because of the decrease of dye

Table 2
Evaluated kinetic parameters for MB dye removal by SMCS

Kinetic models	Parameters	Concentration of MB dye Solution (mg/L)				
		100	200	300	400	500
$q_e$exp (mg/g)		33.33	65.87	97.55	127.41	160.75
Pseudo-first-order	k_1 (1/min)	0.0376	0.02887	0.02501	0.02094	0.0194
	$q_e$cal (mg/g)	36.75	75.02	115.4	160.8	175.3
	R^2	0.9799	0.9745	0.9745	0.9642	0.985
Pseudo-second-order	k_2 (g/mg/min)	0.0005721	0.0002226	0.0001129	0.000005	0.000125
	$q_e$cal (mg/g)	49.52	104.6	167.1	243.8	234
	R^2	0.965	0.9603	0.9631	0.955	0.9735
Elovich kinetic model	α (mg/g min)	0.02215	0.006441	0.002656	0.001152	0.00453
	β (g/mg)	5.387	13.41	23.52	37.44	28.54
	R^2	0.9421	0.9453	0.9515	0.9461	0.9604

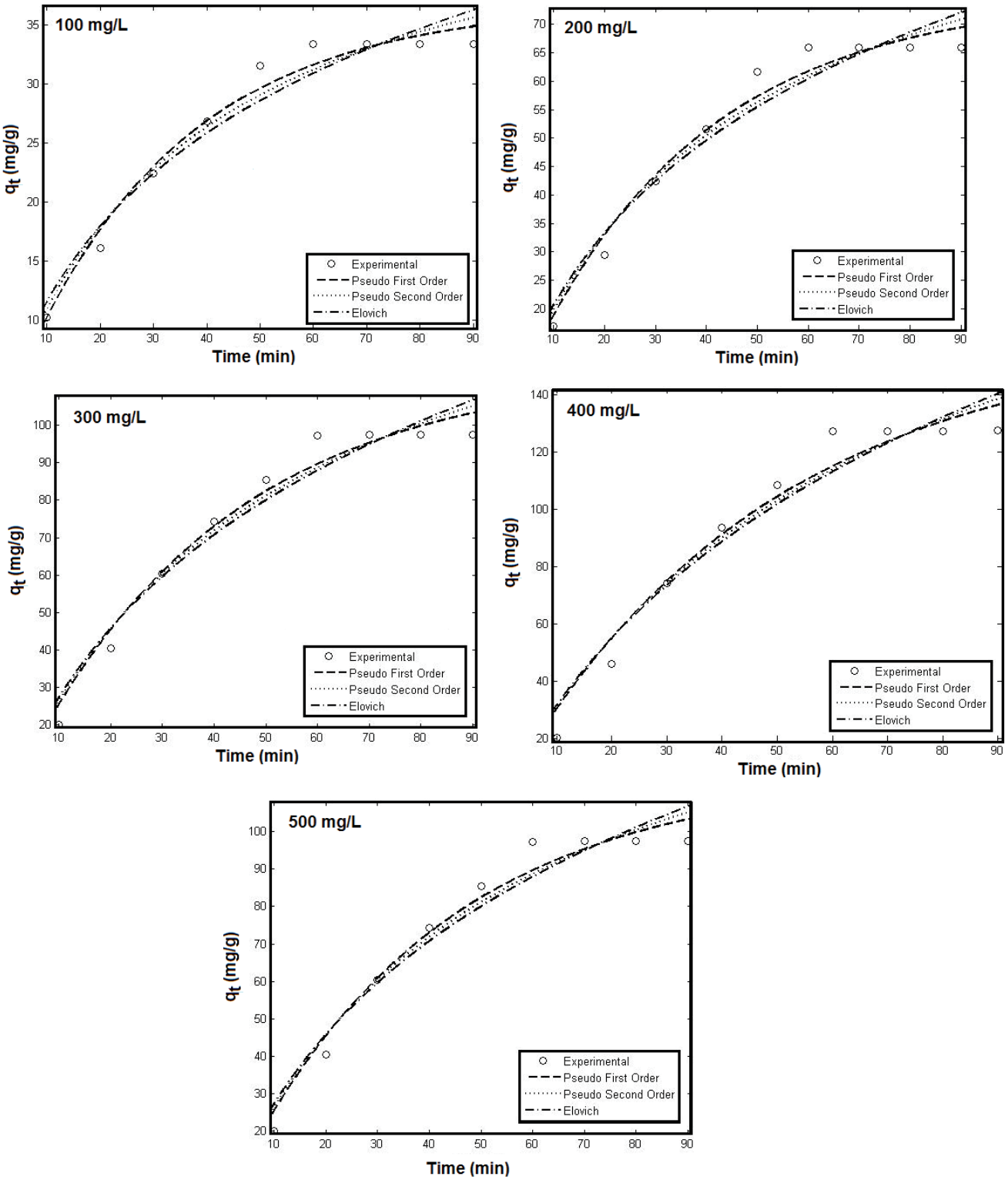


Fig. 12. Adsorption kinetics for the removal of MB dye by SMCS (MB dye concentration = 100–500 mg/L, volume of sample = 100 mL, and adsorbent dose = 3 g/L).

Table 3
Evaluated thermodynamic parameters for MB dye removal by SMCS

Initial MB dye Conc. (mg/L)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/mol/K)	$\Delta G°$ (J/mol)			
			30°C	40°C	50°C	60°C
100	–124,322.4	–354.05	–19,356.6	–10,143.6	–9,206.66	–8,219.04
200	–53,914.52	–142.97	–11,023.6	–8,574	–7,511.45	–6,681.52
300	–31,112.19	–73.00	–9,093.05	–8,154.01	–7,413.89	–6,925.68
400	–24,611.47	–56.21	–7,651.32	–6,948.39	–6,335.5	–3,989.68
500	–14,651.58	–27.64	–6,201.62	–6,047.85	–5,870.18	–5,323.38

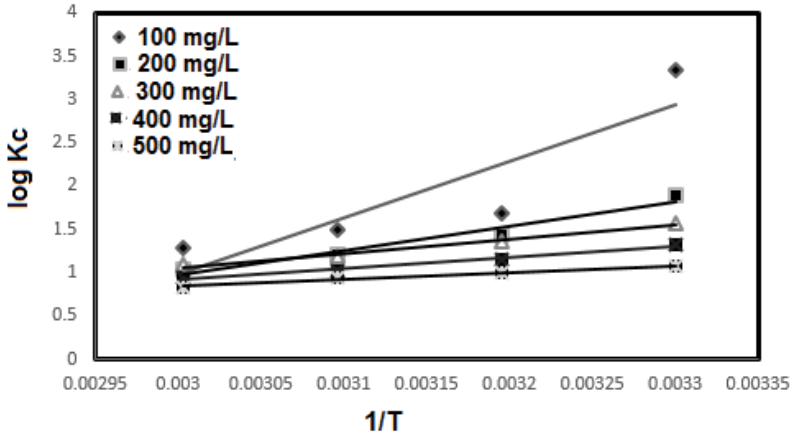


Fig. 13. Thermodynamic analysis of the removal of MB by SMCS.

removal with an increase in temperature. This was further confirmed with a negative value of enthalpy change. The dye removal was identified as a feasible and enthalpy driven process. From these observations, it can be concluded that SMCS is very effective and economical adsorbent for the elimination of dye from water and wastewater.

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