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ADSORPTION STUDY OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS ONTO BITUMINOUS COAL BASED ACTIVATED CARBON

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ABSTRACT

Adsorption of methylene blue (MB) on activated carbon developed from bituminous coal (Barapukuria Coal) by physical activation has been investigated. The impacts of numerous variables, including absorbent concentration, contact time, initial dye concentration, and temperature, were explored. The equilibrium adsorption data analysis was performed using the Freundlich, Langmuir, and Temkin adsorption models. The Langmuir isotherm was considered to be the most appropriate. The Langmuir adsorption capacities (Q_o) in 298, 303, 308, 313, 323, and 333K are 80.65, 84.75, 87.72, 90.09, 91.74, and 92.59 mg g^{-1}, respectively. The dye removal percentages at 60 °C decline from 99.84% to 79.38% when dye concentrations are increased from 100 to 350 mgL^{-1}. Increases in adsorbent concentration result in enhanced methylene blue adsorption because of increases in surface area and the number of active centers. From the thermodynamic studies, negative adsorption free energy (ΔG°) implies spontaneous adsorption, while positive enthalpy (ΔH°) reflects endothermic adsorption.

Keywords: *Activated Carbon, Equilibrium Isotherm, Methylene Blue, Thermodynamics Studies*

1. INTRODUCTION

Rapid industrialization, urbanization, and population increase have contributed to the contamination of the major freshwater resources on earth. Wastewater treatment has ended up being one of the most vital environmental concerns today in terms of reducing or preventing pollution of natural water resources such as groundwater, inland surface waters, coastal water, and transitional water, promoting sustainable water reuse, protecting the aquatic environment, and improving the status of aquatic ecosystems. About 80% of the world's inhabitants are facing scarcity of fresh water supply-related problems and water security due to the contamination of the available water resources by industrial and urbanization activities (Vorosmarty et al., 2010). Dyes are influential compounds and are commonly used in textile, printing, cosmetic, food processing, dying, and paper-making industries. Approximately 15% of yearly dye production is released as contaminants into the prevailing water resources (Hussain et al., 2019). Discharge of these colour pigments generates a prime environmental issue for growing countries due to their carcinogenic and toxic effects on residing beings (Yaseen & Scholz, 2018). Powdered or crystalline methylene blue has a dark green colour. It has several biological applications in addition to its common usage as a stain. Similar to electrolytes, it forms the methylene blue cation and the chloride ion when dissolved in water. Multiple adsorbents show strong preferential adsorption for the coloured cation. Methylene blue was therefore chosen as the adsorbate in this study. Due to its numerous detrimental effects on human health, its removal from wastewater is of paramount importance. In addition, it serves as a valuable indication for the evaluation of active carbons. Different techniques, such as ion exchange, chemical coagulation, electrolysis, biological treatments, and activated carbon sorption, have been introduced for the purpose of putting off dye pollution from wastewater. Activated carbon adsorption is very effective at removing pigments and dyes, as well as other organic and inorganic pollutants (Gupta et al., 2006; Yeow et al., 2021). Carbonaceous resources including wood, coal, and nutshells are used to produce activated carbon. It can be activated in one of two ways: physically or chemically. Acidic reagents, $ZnCl_2$, H_3PO_4 (Gupta et al., 2006), HCl (Granda et al., 2007), and H_2SO_4 (Guo & Lua, 2007) or basic reagents, KOH (Guo & Lua, 2007), NaOH (Gupta et al., 2006), and Na_2CO_3 have been used in the chemical activation process.

The most common methods of physical activation are carbonization and oxidation, which are used alone or in combination. Carbonization entails the pyrolysis of materials containing carbon at temperatures between 600 and 900 °C in an inert environment, often composed of gases like nitrogen or argon. Carbonized material or the raw material is subjected to oxidizing atmospheres containing oxygen, carbon dioxide, or steam at temperatures above 250 °C during the oxidation process. Pollutants bind to activated carbon via the Van der Waals force in an adsorption mechanism. Activated carbon does not possess the characteristics of binding well to some specific

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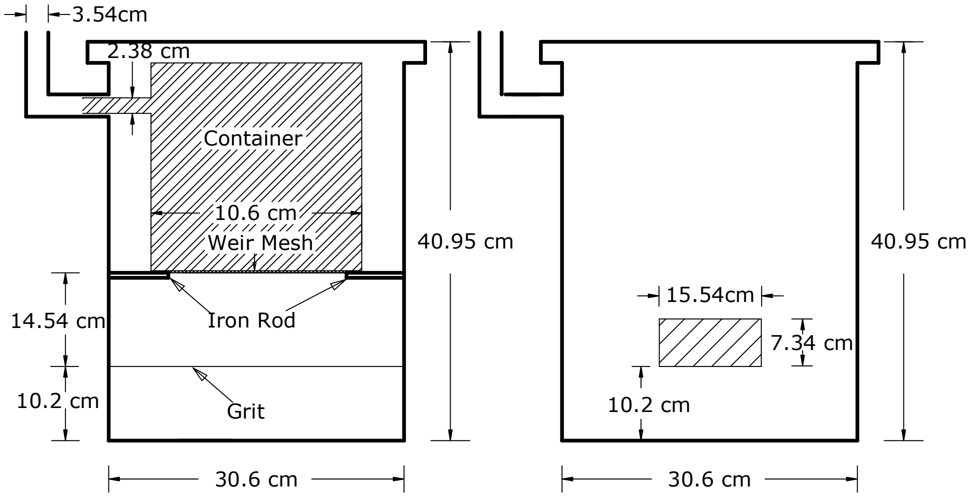
chemicals, including alcohols, bases, strong acids, and metals such as iron, sodium, fluorine, lithium, boric acid, and arsenic. Coconut tree sawdust, maize cob, banana pith, rattan sawdust, silk cotton hull (Hameed et al., 2007), date pits, rice bran, rice husk (Gupta et al., 2006), mango seed, kernel powder, coconut coir dust, and pine have all been employed as carbon sources for the production of activated carbon for the removal of fabric dye effluents. Coal is a cheap and abundant carbon resource; hence it has been studied for its potential use in the development of activated carbon for industrial applications. The adsorption efficiency of activated carbon derived from coal varies depending on the quality of the coal. Barapukuria coal has a higher quality standard than other bituminous coal.

This article investigates the equilibrium isotherm of methylene blue adsorption on activated carbon produced from bituminous coal. The adsorption of methylene blue onto activated carbon was investigated in relation to the initial dye concentration, temperature, contact time, and adsorbent concentration. An analysis of the thermodynamics of adsorption was performed, and values for the constants describing the isotherms were estimated.

2. METHODOLOGY

2.1 Fabrication of Furnace

A model furnace was fabricated based on the raw material capacity that could be employed in adsorption equilibrium. The optimal conditions for developing activated carbon were determined through a series of three batch tests (compacted, loose, and treated with $ZnCl_2$ solution). The furnace measured 30.6 cm in diameter, 40.95 cm in height, and had a bottom aperture measuring 15.54 cm by 7.34 cm. A grit chamber was installed at the bottom of the fuel hole, and the ash was removed via the furnace's bottom. Another small 3.54 cm diameter hole was used as a smoke vent towards the top of the furnace. The top of the furnace was opened and covered with a separate cover during operation. A container, measuring 10.6 cm in diameter and 12.8 cm in height, was placed into the furnace to carry the coal. The bottom entrance of the container was 6.08 cm x 6.76 cm, while the top entrance was attached to the top side of the furnace. Two wire mesh trays were placed inside the container containing the raw components.



(a) Cross-section (b) Front view

Figure 1: Schematic diagram of the fabricated furnace.

2.2 Development of Activated Carbon

Barapukuria Coal Mining Company Limited, in the district of Dinajpur, was the source of the coal that was investigated. Initially, the coal was crushed into smaller pieces, then sieved through a 30-40 mesh screen, and finally washed multiple times in distilled water to get rid of dust and other contaminants. Then the washed coal was dried in an oven at 60 °C for 24 hours to remove moisture. At first, the small container was filled with raw material under different conditions. The pot was positioned inside the furnace, which was then covered and sealed with clay. Coal was deposited on the grit as a fuel source, and the gas was ignited. While the procedure was in progress, the smoke from the furnace entered the pot through the bottom aperture and exited through the top hole, which was linked to the smoke outlet. A digital thermometer was used to measure the temperature. The furnace was fired until the furnace temperature reached above 800 °C and maintained that temperature above 800 °C for about 2 hours. Initially, the smoke was black, and after it turned white, all of the holes were covered with clay. After 24 hours, the sealed furnace was opened to take out the activated carbon that had been produced. The sample was allowed to settle down after activation and later washed several times with deionized water and 0.5 M HCl. The optimal conditions for developing activated carbon were investigated through three separate batch experiments. Most volatile components are extracted during the physical activation process by carbonizing raw material at 400-500 °C and then exposing the carbon to oxidizing gases, typically steam and carbon dioxide, at 800-900 °C (Arshad et al., 2022).

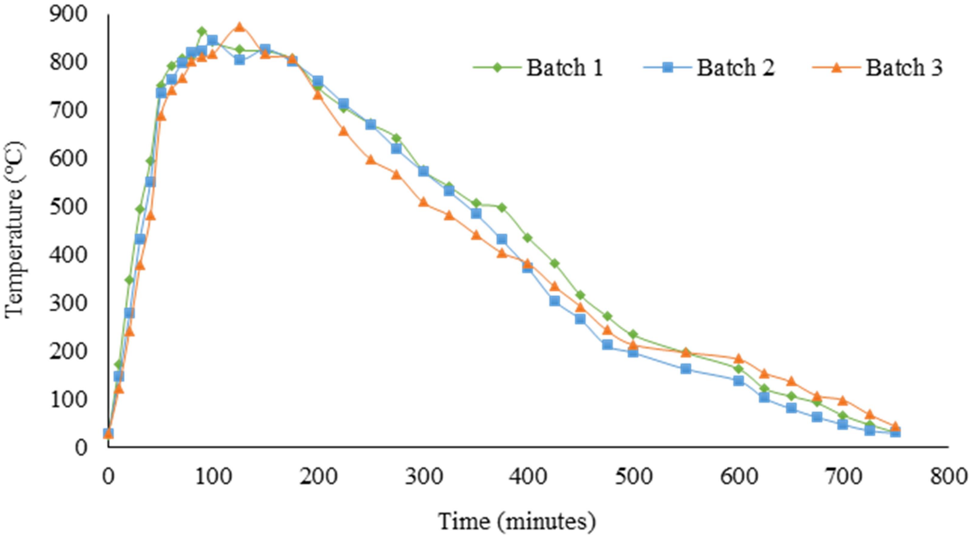


Figure 2: Temperature variation with time at different stages of production for different batches.

2.3 Adsorption Studies

The batch technique was used to study adsorption isotherms in a number of 250 mL conical flasks containing dye solutions at pH 6.8 with initial concentrations ranging from 100-350 mgL^{-1}. Each dye solution was supplemented with an equivalent amount (0.3g) of activated carbon. To maintain equilibrium, the flasks were stirred at 100 rpm for 225 minutes in an automatic water batch shaker at various temperatures, including 25, 30, 35, 40, 50, and 60 °C. The dye solutions were kept calm for 30 minutes before collecting samples with a burette from the top surface. Methylene blue concentration was evaluated using a spectrophotometer (Hatch DR 3900) at 455 nm. The percentage of adsorption was computed using the following equation.

$$\%\,\text{Removal} = \frac{X_o - X_t}{X_t} \times 100 \tag{1}$$

Where X_o and X_t (mgL^{-1}) represent, respectively, the initial dye concentration and concentration at time t.

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time

Methylene blue and carbon surfaces interact through induced dipole interactions and Van der Waal forces at their interfaces. Activated carbon graphitic granules change neutral organic molecules into intramolecular dipoles. Because of the attraction and clustering caused by the generated dipoles, the molecules are forced to precipitate out of the solution in the micro pores (or sorption gaps) of the carbon. This is performed by the activated carbon and is known as "premature condensation." At an absorbent concentration of 3 gL^{-1}, the adsorption of methylene blue is plotted as a function of contact time throughout a range of initial concentrations (Figure 3). Dye adsorption is linear with contact time and is constant after equilibrium is reached. The equilibrium proportion of extraction efficiency was reduced from 99.26 to 70.82% when the ambient MB concentration was raised from 100 to 350 mgL^{-1}. At lower doses of 100 and 150 mgL^{-1}, equilibrium was achieved in 105 and 125 minutes, respectively, but it took 210 minutes at higher doses of 200, 250, 300, and 350 mgL^{-1}.

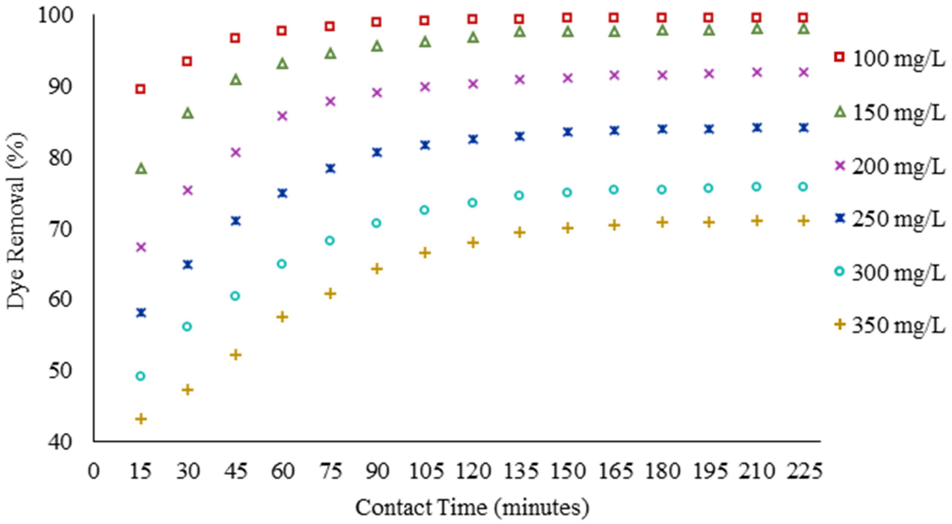


Figure 3: Influence of contact period on the adsorption of MB at various initial concentrations.

3.2 Effect of Adsorbent Dose

The influence of adsorbent concentration on an adsorption experiment was analyzed using physical conditions including 100 rpm stirring speed, a pH value of 6.8, a contact period of 210 minutes, a temperature of 28 °C, an initial dye concentration of 300 mgL^{-1}, and adsorbent doses ranging from 3 gL^{-1} to 12 gL^{-1}. Increases in adsorbent concentration result in a greater proportion of dye removal from solutions, as depicted in Figure 4. The removal percentage of dye increases from 75.60% to 99.64% with the rise in adsorbent concentration from 3 gL^{-1} to 12 gL^{-1}. So, the increased adsorbent concentration increases the surface area as well as the number of operating centres.

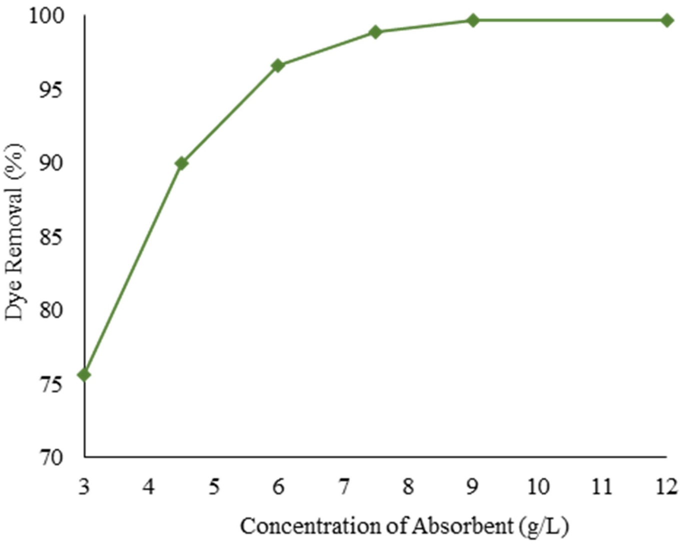


Figure 4: Variation in methylene blue adsorption with adsorbent concentration.

3.3 Effect of Temperature

The influence of temperature on the adsorption of MB was measured at 0.3 g in 100 mL of adsorbent dosage, a contact period of 210 min, a 100 rpm stirring speed, and a pH of 6.8 for a series of dye concentrations (100-350 mgL^{-1}). The percentage removal of dye in relation to temperature is linear between 25 and 60 °C. Increasing temperatures improve adsorption capacity because more molecules diffuse through the outer boundary layer more quickly as the temperature rises (Song et al., 2014). At 60 °C, the maximum dye removal percentages are 99.84, 99.48, 96.94, 90.86, 84.63, and 79.38% for various dye doses of 100, 150, 200, 250, 300, and 350 mgL^{-1}, respectively.

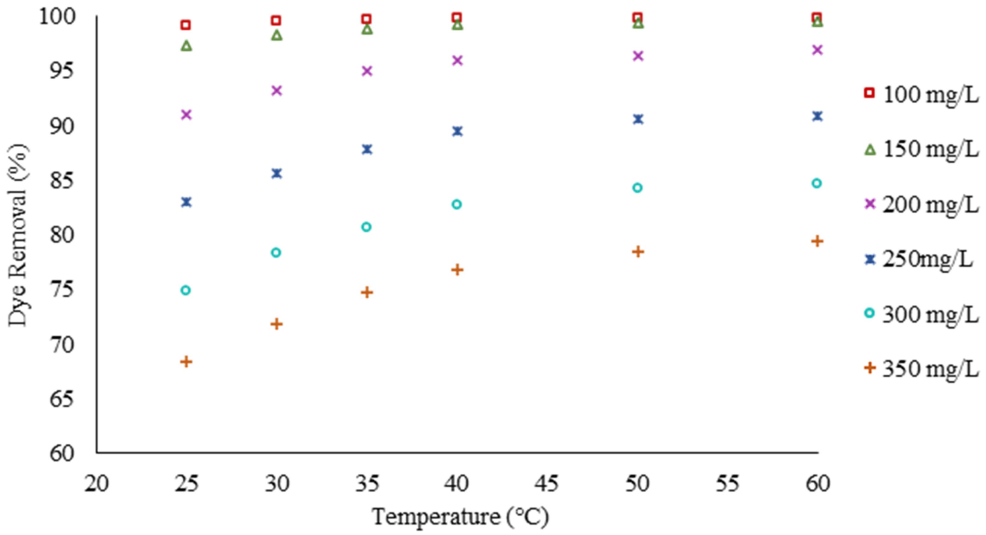


Figure 5: Influence of temperature on the adsorption of MB.

3.4 Adsorption Isotherms

An adsorption isotherm represents the equilibrium concentration of a surfactant adsorbate on a solid of unit mass as a function of the initial concentration of the surfactant at a specific temperature. In this research, the adsorption isotherms for the Langmuir, Freundlich, and Temkin models at a varying range of temperatures are analyzed. The correlation coefficients R^2 have been used to evaluate the relative effectiveness of several isotherm equations.

3.4.1 The Langmuir Isotherm

The Langmuir isotherm, which reconciles the relative rates of surface assimilation and desorption, provides the framework for describing surface coverage. Adsorption is compared to the immaterial portion of the adsorbent's exterior layer that is exposed, whereas desorption is compared to the finite portion of the adsorbent surface that is enclosed (Gupta et al., 2006). The Langmuir isotherm equation is shown in its linear version.

$$\frac{X_e}{q_e} = \frac{1}{Q_o K_L} + \frac{X_e}{Q_o} \tag{2}$$

Where X_e (mgL^{-1}) is the equilibrium concentration of the dye solution, q_e (mg g^{-1}) is the quantity of dye adsorbed per unit mass of adsorbent, and Q_o (mg g^{-1}) is the monolayer adsorption proportions, and K_L (Lmg^{-1}) is the Langmuir constant associated with the selection of the optimal percentage and porousness of the adsorbent, implying that a substantial surface area and pore volume. The characteristics of the Langmuir isotherm can be explained using a non-dimensional equilibrium parameter (R_L). The parameter is defined by,

$$R_L = \frac{1}{1 + K_L X_o} \tag{3}$$

Where K_L represents the Langmuir constant and X_o represents the maximal dye concentration (mgL^{-1}). R_L specifies the nature of the isotherm based on its value. An unfavorable isotherm has R_L larger than 1, a linear isotherm has R_L equal to 1, a favorable isotherm has a value of $0<R_L<1$, and an irreversible isotherm has R_L equal to 0. At 60 °C, the optimal capability for adsorption was calculated to be 92.59 mgg^{-1}, and this value increases with increasing temperature.

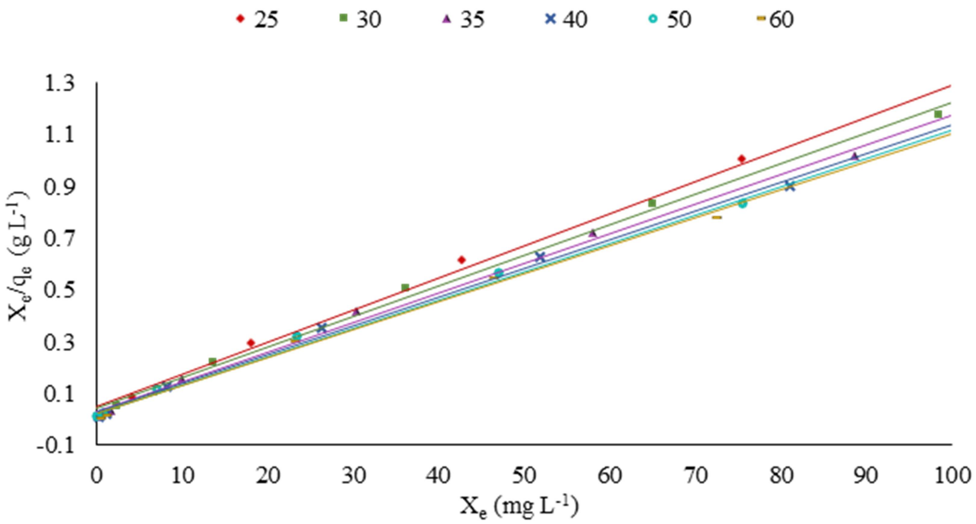


Figure 6: Plots of the Langmuir isotherm at various temperatures.

3.4.2 The Freundlich Isotherm

The Freundlich isotherm features a mathematical expression for the exponential distribution of adsorption sites and their energy, as well as the heterogeneity of the surface (Ayawei et al., 2015). The following is a simplified form of the Freundlich equation.

$$\log q_e = \log K_F + \frac{1}{n}\log X_e \tag{4}$$

Adsorption capacity is denoted by the Freundlich constant K_F, and adsorption intensity is proportional to the reciprocal of the number of adsorbed molecules, 1/n. The surface grows increasingly heterogeneous as its value approaches zero. For a standard Langmuir isotherm, the value of 1/n is less than one, whereas a value of 1/n greater than one suggests cooperative adsorption (Liu et al., 2010). For the current systems, as indicated in Table 1, the value of the Freundlich constant 1/n obtained from Figure 6 is between 0 and 1, suggesting favourable adsorption.

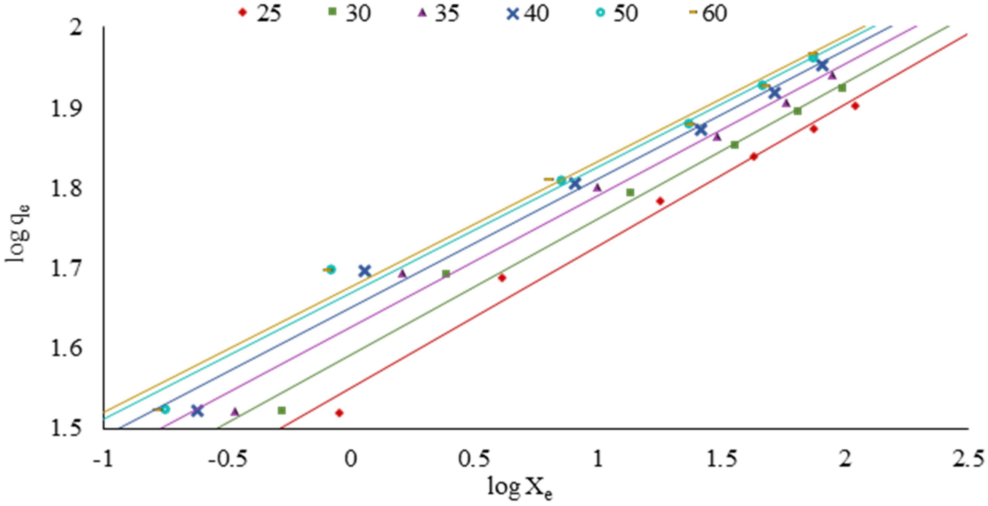


Figure 7: Plots of the Freundlich isotherm at various temperatures.

3.4.3 The Temkin Isotherm

The Temkin isotherm model makes assumptions about the impact of implicit adsorbent engagement on the adsorption process. The heat of adsorption for all molecules in the layer is likewise assumed to decrease linearly with increasing surface coverage. The following is the linear equation for the Temkin isotherm model.

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln X_e \tag{5}$$

Where b ($Jmol^{-1}$) is the Temkin constant, which is related to the heat of adsorption, and K_T (Lg^{-1}) is the Temkin isotherm constant.

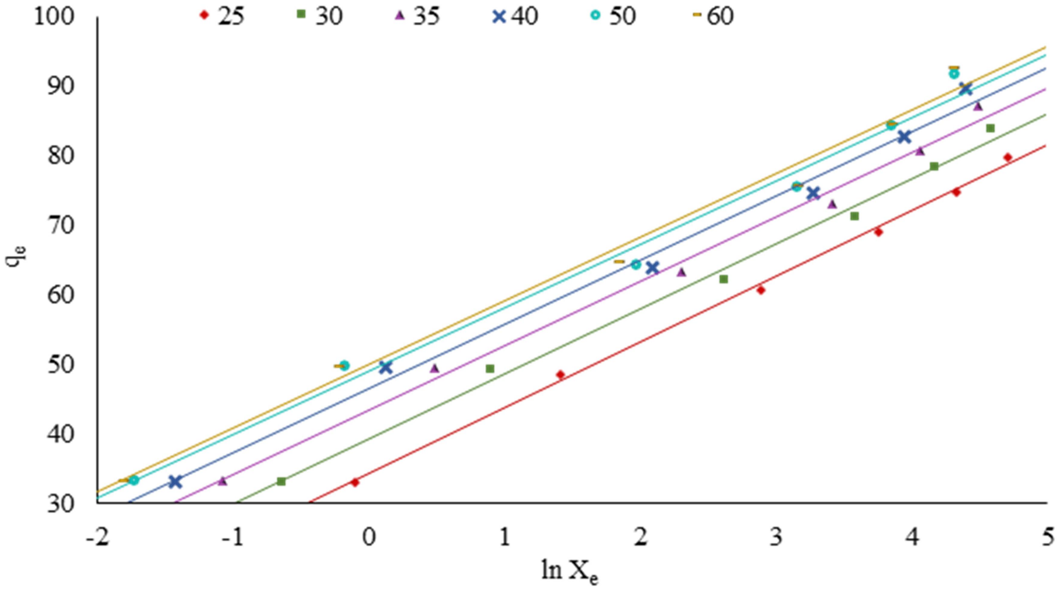


Figure 8: Plots of the Temkin isotherm at various temperatures.

Figure 8 shows that the value of the Temkin isotherm constant increases with an increase in temperature. This implies that an increase in the isotherm constant is associated with an increase in surface area and pore volume.

The properties of the three isotherms and their corresponding interaction factors at different temperatures are recorded in Table 1. When comparing the correlation coefficients (R^2) of all equations, the Langmuir model provides the best fit to the equilibrium adsorption data.

3.5 Specific Surface Area

Specific surface area is the ratio of the reactive surface area accessible for the adsorption of solute to the total mineral mass. Both the physical and chemical properties of activated carbon are heavily dependent on its specific surface area. The conventional approach for calculating surface area is the Brunauer-Emmett-Teller (BET) method, which is based on the amount of gas absorbed. Although the BET method is the most commonly used technique for calculating surface area, other approaches have been reported using ethylene glycol monoethyl ether (EGME) (Fahmi et al., 2019). Based on the adsorption of methylene blue, the Langmuir model was used to figure out the specific surface area of activated carbon. The equilibrium time, the adsorption isotherms according to the Langmuir model, and the maximum adsorption capacity Q_o were estimated to establish the specific surface area associated with MB adsorption. The following formula could be used to determine the specific surface area:

$$\text{Specific surface area, } S_M = \frac{Q_o N_a A_m}{M} \tag{6}$$

Where S_M is the specific surface area (m^2/g), Q_o is the maximum adsorption capacity (mol/g), A_m is the surface area occupied by the adsorbent in the form of molecules (m^2) (methylene blue cross sectional area = 130 $Å^2$), N_a is the Avogadro Number (mol^{-1}), and M is the molecular mass of MB ($gmol^{-1}$). At 60 °C, 203.713 m^2/g was found to be the specific surface area of activated carbon as shown in Table 1.

Table 1: Related constants for the adsorption of MB on activated carbon at various temperatures.

Adsorption isotherm constants	Temperature (°C)					
	25	30	35	40	50	60
The Langmuir isotherm constants						
Q_o (mg g^{-1})	80.645	84.746	87.719	90.090	91.743	92.593
K_L (Lmg^{-1})	0.2451	0.2965	0.3608	0.4111	0.4467	0.4737
R^2	0.9964	0.9957	0.9955	0.9953	0.9951	0.9944
R_L	0.01152	0.00954	0.00786	0.00690	0.00635	0.00599
The Freundlich isotherm constants						
K_F (mg g^{-1}) (Lmg^{-1})$^{1/n}$	35.506	39.120	42.237	44.687	46.590	47.453
1/n	0.1767	0.1694	0.1641	0.1605	0.1571	0.1564
R^2	0.9843	0.9836	0.9825	0.9820	0.9816	0.9814
The Temkin isotherm constants						
K_T (Lmg^{-1})	37.3472	66.783	108.573	156.638	215.519	240.333
b ($Jmol^{-1}$)	21.971	26.699	31.430	36.092	45.584	54.618
R^2	0.9976	0.9946	0.9939	0.9919	0.9886	0.9885
Specific surface area						
S_M (m^2/g)	177.426	186.449	192.897	198.206	201.842	203.713

3.6 Thermodynamic Studies

Thermodynamic parameters such as the Gibbs free energy (ΔG°), the enthalpy (ΔH°), and the entropy (ΔS°) for the adsorption of methylene blue were calculated from the subsequent equations.

$$\Delta G^{o} = -RT \ln K_L \tag{7}$$

$$\ln K_L = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT} \tag{8}$$

Where K_L is the equilibrium constant, R is the universal gas constant and T is the absolute temperature (K). All of the thermodynamic parameters were calculated using the value of K_L since the Langmuir adsorption isotherm provides a strong correlation.

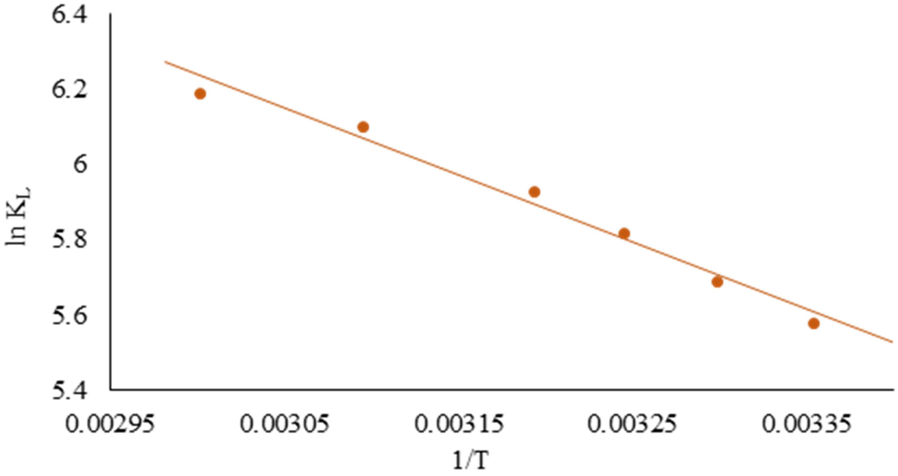


Figure 9: Plot of ln K_L vs 1/T for thermodynamic studies.

Table 2: Thermodynamic parameters for the adsorption of MB on activated carbon.

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	R^2
298	-13.83	14.77	0.096	0.9794
303	-14.35			
308	-14.91			
313	-15.44			
323	-16.40			
333	-17.15			

The values of the standard ΔH° and the standard ΔS° were determined by analyzing the slope and intercept of the ln K_L against the 1/T graph. ΔG° depends on ΔH°, and ΔS° which is the adsorption driving force. Adsorption processes were shown to be favourable and spontaneous when ΔG° was negative. Adsorption was facilitated by the higher temperature, as seen by the steady drop in ΔG° values with increasing temperature. A higher value for ΔH° implies an endothermic activity in the adsorption reaction. During adsorption, the interface between the solid solution and the adsorption medium expands in response to a positive value of ΔS°.

4. CONCLUSIONS

The adsorption of MB from an aqueous solution onto activated carbon produced from bituminous coal was evaluated. Physical activation was accomplished using a model furnace after granular coal was crushed to a size of 30-40 mesh. The contact time, initial dye concentration, adsorbent dose, and effect of temperature are all factors that influence methylene blue adsorption. The efficiency of removing methylene blue decreases with increasing initial dry concentration and improves with increasing absorbent concentration. As the temperature climbs from 25 to 60 °C, a greater amount of methylene blue is absorbed. When the concentration of MB is enhanced from 100 to 350 mgL^{-1}, the equilibrium proportion of dye absorption drops from 99.26% to 70.82%. The percentage of dye removed improves from 75.60% to 99.64% with a 3 g to 12 g upsurge in adsorbent concentration. The Langmuir adsorption model provided the best description of the equilibrium data, with a maximum adsorption capacity of 92.59 mg g^{-1} at 60 °C. The specific surface area of activated carbon was found to be 203.713 m^2/g at 60 °C. The values of ΔG° and ΔH° suggest that the adsorption process is instinctive and endothermic, respectively. Activated carbon derived from Barapukuria coal is a potent adsorbent for removing methylene blue from water.

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