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Adsorption of Methylene Blue onto Acid Modified *Raphia Taedigera* Seed Activated Carbon



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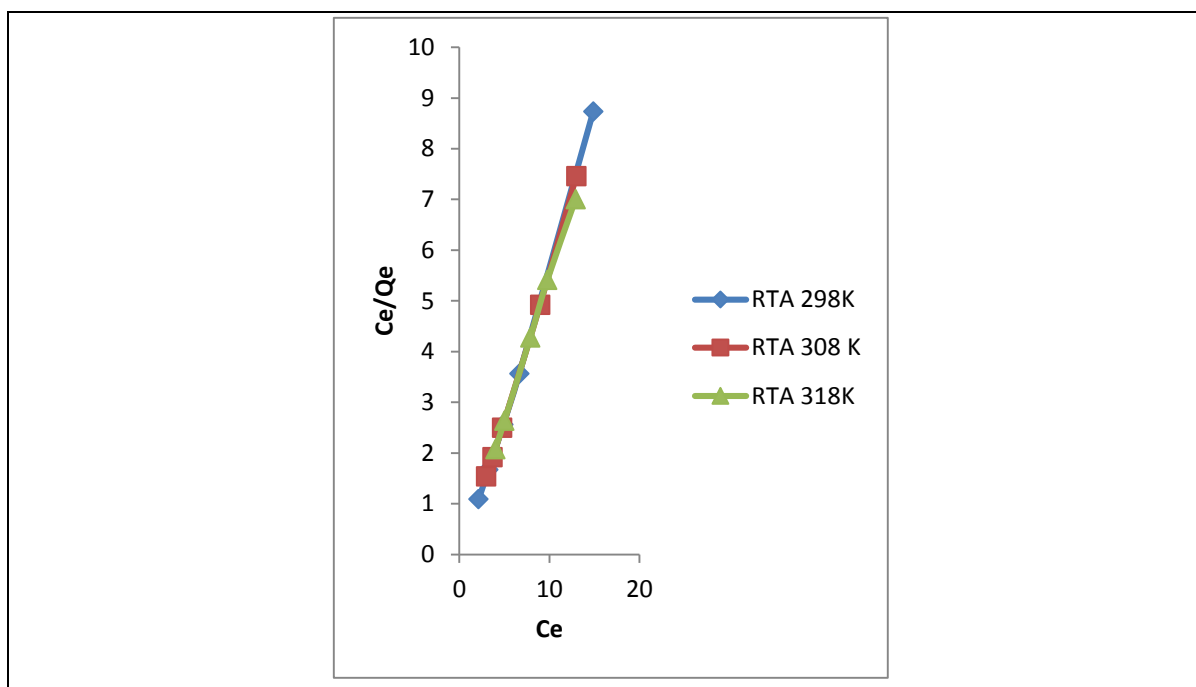
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Methylene blue
Adsorption isotherm
Kinetics

ABSTRACT

In this work, the possibility of using *Raphia taedigera* seed as a low-cost adsorbent to remove methylene blue (MB) dye from aqueous solutions was investigated. The activated carbon was prepared by carbonization and chemical treatment of the seed with sulphuric acid to produce acid-modified *Raphia taedigera* seed activated carbon (RTAC). The surface morphology and bond arrangement of the RTAC were evaluated using the scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR), respectively. The SEM analysis results revealed that the prepared adsorbent had aggregated and rough surface structure with pores and FTIR revealed the presence of several functional groups such as $-C=O$, $-OH$, $-C=C-$, $-N=O$ and $-C=N-$. The adsorption efficiency of the RTAC for the removal of the MB dye was assessed under different experimental conditions including, contact time, temperature, pH, adsorbent dosage, and dye initial concentration. The results gave the performances of 99.611% after 15 min, 99.635% at 303 K, 99.894% at pH 9, 99.256% with 0.9 g, and 99.743% for 40 mg/L for evaluating the effect of the contact time, temperature, pH, adsorbent dosage, and dye solutions initial concentration, respectively. The adsorption of the MB dye onto the RTAC conformed to Langmuir isotherm and fit best to pseudo-second-order kinetic models. Thermodynamic studies indicated a spontaneous, endothermic, feasible, and physisorption nature of the RTAC and MB dye interactions. The present study found the acid-modified *Raphia taedigera* seed activated carbon to be a promising low-cost adsorbent for the removal of MB dye from aqueous solution.

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GRAPHICAL ABSTRACT



Introduction

Recently, bio-environment has suffered from the indiscriminate release of industrial and agricultural wastes, damaging the lives, water bodies, atmosphere, and agriculture land. Textile industries play a major role in the release of dangerous pollutants such as dyes and heavy metals. Methylene blue dye is a cationic dye commonly employed for materials colouring. Uncontrolled release of the methylene blue dye effluent to the environment can lead to eye burns in humans and animals, cyanosis, tachycardia, convulsions, irritation to the skin, and cause gastrointestinal tract irritation, vomiting, nausea, and diarrhoea if ingested [1]. The dye contaminations in water bodies prevent the light penetration which affects the photosynthesis to a large extent [2-5] and poses a great danger on aquatic animals and plants, hence; there is a necessity for removing the dye contaminant.

Several methods have been employed for removing the colour from the industrial wastes. These include the membrane

separation, various microbial aerobic and anaerobic methods, coagulation and flocculation, nano-filtration, chemical oxidation, ozonation, cloud point extraction, ion exchange, ultra-filtration and reverse osmosis [6-12]. Some of these methods proved to be effective; however, they demonstrated some limitations such as high cost of production, a large quantity of chemicals required, and disposal problems due to the accumulation of the bulk of sludge [13,7,8,14,15]. Among these techniques, adsorption, whose principle is based on the pollutant migration from the bulk of the solution to the solid phase, is considered as one of the most efficient for wastewater treatment.

Adsorption process has been a well-known method for the both organic and inorganic contaminants removal from the wastewaters. The technique is popular owing to its simplicity, efficiency, cheap and renewability [13]. Activated carbon has been widely used for various applications: as an adsorbent in chromatography separations, removal of colour and odour from sugar, treatment of

effluents such as dyes and heavy metals removal, among others.

Recently, Scientists have found it economical to prepare adsorbent from agricultural wastes because they are cost-effective, safe, efficient, and readily available. Several agricultural waste products have been employed for this purpose, including *Raphia taedigera* seed [13], bamboo [16], cereal by-product [6], acorn shells [17], cow bone powder [18], groundnut shells [19], palm oil stones [20], coconut shells [21], tobacco residues [22], apricot stones [23], olive stones [24], nutshells [25], walnut shells [24], cherry stones [26], and pine cones [27].

Raphia taedigera is a caespitous, monoecious and monocarpic species [28,29]. The plant is native to Nigeria, Nicaragua, Brazil, Costa Rica, Cameroon and Panama [29-32]. The tree produces fruits of 5-7 cm long with a diameter of 3-4 cm, covered with imbricate glossy reddish-brown scales containing only one seed. A well-dried seed has a size of a chicken egg, hard, white and shiny on the inside and brown on the outside.

Experimental

Material and methods

Raphia taedigera seed collection and treatment

The seeds were obtained locally, washed and dried in an oven at 60 °C for 10 days. The dried sample was crushed and stored in an airtight plastic container for further use.

Adsorbent preparation

*Carbonization and activation of *Raphia taedigera* seed*

The carbonization was conducted as reported by [2,13]. 100 g of the crushed *R. taedigera* seed was carbonized in a muffle furnace at 350 °C for 2 h. The carbonized material was cooled to room temperature, washed with distilled water to attain the pH of

7 and dried at 105 °C in an oven to constant weight. The material was sieved using 100-mm mesh Tyler sieve and stored in an airtight plastic container.

Surface modification and activation

Acid activation was performed as reported by [13]. 20 g of the carbonized seed was weighed and transferred into a clean 500 mL beaker. 200 mL 0.1 M sulphuric acid solution was added, stirred thoroughly and allowed to stand for 24 h. The impregnated material was diluted with 200 mL distilled water to wash off the sulphuric acid residue used as activating agents until the pH of 7.0 was attained. The activated material was transferred into an oven and dried at 105 °C to constant weight. The dried material was sieved to obtain a fine powder of *Raphia taedigera* activated carbon (RTAC) and stored in an airtight plastic container for further use.

Material characterization

Scanning electron microscopy (SEM)

Morphology of the samples was assessed using the scanning electron microscopy (SEM, model Phenom ProX) at HV value of 15 KV and magnification of 500.

Fourier-Transform infrared spectroscopy (FTIR)

The Fourier-transform infrared spectrophotometry was carried out using Agilent Cary 630 FTIR instrument with scanning range 4000-650 cm⁻¹.

Preparation of methylene blue (MB) Dye

0.1 g MB dye was dissolved in distilled water in a volumetric flask of 1,000 mL capacity and made up to the mark with distilled water. This gave 100 mg/L methylene blue (MB) dye and labelled appropriately as a stock solution. The maximum absorption wavelength was

determined by UV spectrophotometer. Furthermore, 0.1 M of HCl solution and 0.1 M NaOH solution were also prepared to control solution pH.

Effects of adsorption conditions

The effects of adsorbent-adsorbate contact time, adsorbent mass, solution pH, working temperature, and initial solution concentration of the adsorption MB dye onto RTAC were investigated. These parameters are important tools used to evaluate the efficiency and feasibility of a potential adsorbent. All parameters, except the one under investigation, were set as constant.

Contact time effect

The contact time effect was evaluated with an adsorbent dosage of 0.5 g, 10 mL of MB dye solution with an initial concentration of 100 mg/L at room temperature and at time as in 5, 10, 15, 20, and 25 min. 10 mL of 100 mg/L solution of MB solution was transferred into a conical flask containing 0.5 g RTAC. The contents of each beaker were agitated and filtered after 5, 10, 15, 20, and 25 min, respectively. The concentrations of the resulting filtrates were determined using UV spectrophotometer. The concentration of MB adsorbed by the adsorbent and the percentage efficiency were quantified by Equation 1 and 2, respectively.

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

$$\text{Adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where, q_e is the amount of MB adsorbed per unit mass in mg/g, C_0 is the initial MB dye concentration in mg/L, C_e is the MB dye concentration at equilibrium in mg/L, V is the volume of MB dye solution in millilitres and W is the mass of the adsorbent in grams.

Experimental temperature effect

10 mL of 100 mg/L of MB dye, 0.5 g RTAC, contact time of 15 min at 300, 305, 310, 315 and 320 K were used for the evaluation of the temperature effect. 10 mL of 100 mg/l MB dye was introduced into different conical flask containing 0.5 g RTAC set at different temperature and allowed to stand for 15 min with continuous agitation. After 15 min, the content was filtered, and the concentration of the resulting solution was determined using a UV spectrophotometer. Amount of MB dye adsorbed by the adsorbent and the percentage adsorbed were evaluated using the expressions stated as Equation 1 and 2, respectively.

pH effect

10 mL of 100 mg/L solution of MB dye was transferred into a conical flask containing 0.5 g of RTAC. The pH of each of the solutions was adjusted to 1, 3, 5, 7, and 9, respectively using 0.1 M HCl and/or 0.1 M NaOH. The set up was allowed to stand for 15 min with continuous agitation at room temperature, filtered, and concentration of the filtrate was determined using a UV spectrophotometer. Amount of MB dye adsorbed by the adsorbent and the percentage adsorbed were evaluated using the expressions stated as Eq. 1 and 2, respectively.

Initial solution concentration effect

The effect of initial concentrations of MB dye was determined with different concentrations: 20, 40, 60, 80, and 100 mg/L. 0.5 g of the RTAC was introduced into a conical flask containing 10 mL of each of the solutions, stirred, and allowed to stand for 15 min at room temperature. The content was filtered, and the concentrations of the filtrates were determined using UV Spectrophotometer. Amount of MB dye adsorbed by the adsorbent and the

percentage adsorbed were evaluated using the expressions stated as Equation 1 and 2, respectively.

Adsorbent dosage effect

The effect of adsorbent doses was investigated using different adsorbent dosages: 0.1 g, 0.3 g, 0.5 g, 0.7 g, and 0.9 g. 10 mL of stock solution (100 mg/L MB dye) was transferred into a beaker containing each of the adsorbent doses. The mixture was agitated at 150-rpm at room temperature for 15 min. The solution was filtered, and the concentrations of the filtrates were determined. The Amount of MB dye adsorbed by the adsorbent and the percentage adsorbed were evaluated using the expressions stated as Equation 1 and 2, respectively.

Adsorption isotherms

Relationship between adsorbent and adsorbate can be described by adsorption isotherms [11]. Isotherms explain how adsorbing materials interact with pollutants and hence, they are important in optimizing the use of biosorbents. Equilibrium parameters provide important hints for the design of adsorption system for dye removal from solutions [33]. Therefore, it is necessary for establishment of the most appropriate correlation for the equilibrium curve. The isotherm models employed in this present study are Langmuir and Freundlich adsorption isotherms. The experiment was carried out at 298, 303, and 318 K.

Langmuir isotherm model

Langmuir isotherm model assumes that the uptake occurs on a homogeneous surface and that adsorption can only take place on a fixed active site and can only hold one adsorbate molecule at a time (monolayer) without interaction between adsorbed molecules. The model assumes uniform and

equal energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [34]. The Langmuir adsorption isotherm can be represented by Equation 3.

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

An important parameter of Langmuir isotherm equation can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ' R_L '. The R_L value determines the shape of the isotherm to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). R_L is defined by the following Equation 4.

$$R_L = \frac{1}{1 + KL C_0} \quad (4)$$

Where, q_e is the amount of MB adsorbed per unit mass in mg/g, C_e is the MB concentration at equilibrium in mg/L, q_m is the maximum amount of adsorbate adsorbed per unit weight of adsorbent, K_L (L/mg) is Langmuir constant and C_0 is the initial MB dye concentration in mg/L.

Freundlich isotherm model

Freundlich isotherm is known as the earliest relation that describes the adsorption isotherm [35]. It assumes adsorption takes place on a heterogeneous surface with a non-uniform distribution of heat of biosorption through a multilayer adsorption mechanism. The Freundlich isotherm is expressed using the Equation 5.

$$q_e = K_F C_e^{1/n} \quad (5)$$

The linearized form of Equation 6 is given as.

$$\log q_e = \log K + 1/n \log C_e \quad (6)$$

Where q_e is the amount of MB adsorbed per unit mass, C_e is the MB concentration at

equilibrium, K_F and n are Freundlich constants.

Adsorption kinetics

To investigate the mechanism of adsorption of MB dye onto RTAC and the potential rate determining steps, such as mass transport and chemical reactions, pseudo-first-order and the pseudo-second-order can be used to stimulate the experimental adsorption data. Their empirical mathematical models which describe laboratory batch adsorption data are proven useful as tools for scale up process optimization [1]. The kinetic models used for the study are pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-first-order kinetic model

The pseudo-first-order kinetic model assumes that the rate of adsorption on adsorbent is proportional to the number of available active sites on the adsorbent. The rate constant for the adsorption for this study was determined using the linearized form of the pseudo-first-order rate (Equation 7).

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1 t}{2.303} \quad (7)$$

Where q_{eq} is the amount of MB dye adsorbed at equilibrium (mg/g), q_t is the amount of MB dye adsorbed at time t (mg/g); k_1 is the equilibrium rate constant of pseudo-first sorption (min^{-1}).

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model assumes that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electron between methylene blue dye molecule and adsorbent. The linearized form of pseudo-

second order kinetic model equation is expressed as Equation 8.

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (8)$$

Where, q_t is the amount of MB dye adsorbed at time t (mg/g), k_2 is the equilibrium rate constant for the pseudo-second-order adsorption (g/mg/min).

Thermodynamic studies

Temperature is a major determinant in biosorption process. The values of thermodynamic parameters are the real indicators for practical application of adsorption process. Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were studied to have a better understanding of the temperature effect on the adsorption process.

Result and discussion

SEM analysis

The SEM image of the RTAC is demonstrated in Figure 1. Figure 1 illustrates a rough surface morphology with numerous pores on the surface. The structural arrangement of the surface can be attributed to the decomposition and volatility as a result of thermal and acid treatment of RTAC. EDX results showed that, the acid activated RTAC has 76.48% of carbon and 23.52% of oxygen with ratio of C to O as 3.25.

FTIR analysis

Figure 2 represents the FTIR spectral of the acid modified RTAC. The result reveals several functional groups such as carboxylic group, hydroxyl group, aldehydes, ketonic group, ester group, alkenes which are capable of aiding adsorption process.

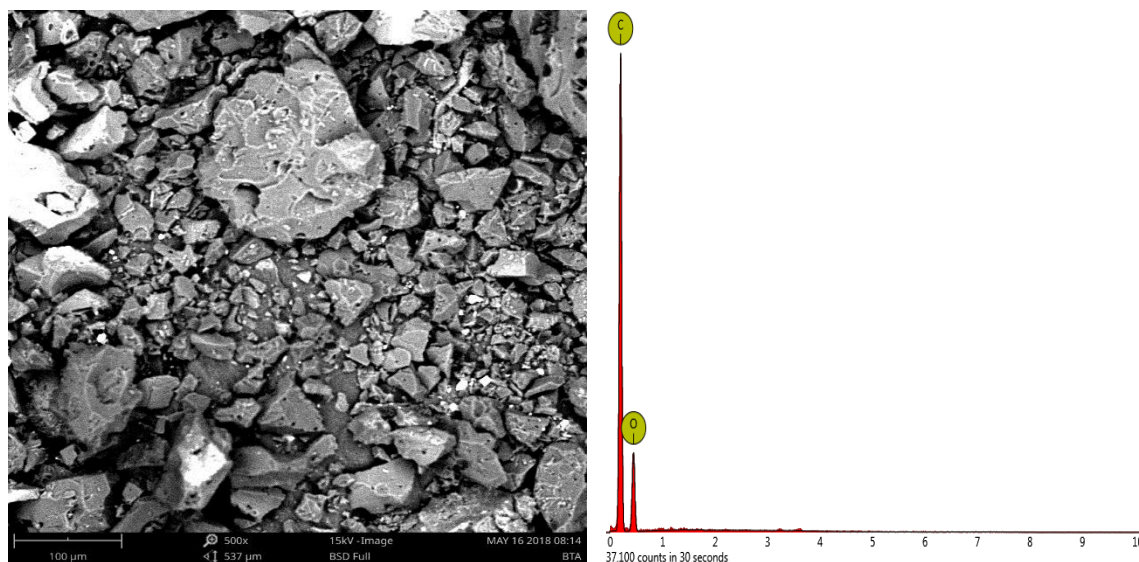


Figure 1. SEM with EDX image of RTAC at 500x

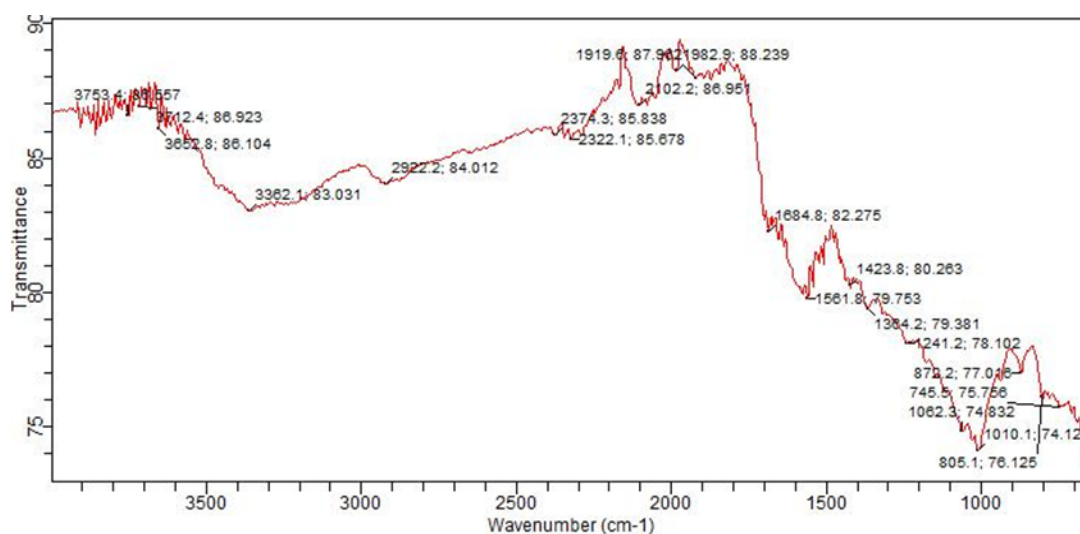


Figure 2. FTIR Spectra of RTAC

There is presence of strong and sharp bands at around 3700- 3500 cm^{-1} due to the free OH group, a broad band at 3600-3200 cm^{-1} representing bonded OH group, a band at about 3000-2850 cm^{-1} corresponding to aliphatic C-H group, band at 2374 cm^{-1} indicating CN stretch of nitrile, a band at around 1820-1670 cm^{-1} indicating C=O stretch, a band at about 1600-1400 cm^{-1} corresponding to C=C of aromatic, a band in about 1385-1345 cm^{-1} indicating N-O stretch of nitro molecule, a band at about 1354 cm^{-1} corresponding to C-N stretching

of amine, a strong band at about 800-600 cm^{-1} indicating C-Cl of alkyl halide. The presence of several spectral bands may be due to the introduction of activating agents for surface modifications [2,13,36] in RTAC.

Maximum absorption wavelength (λ_{max}) determination

The scanning for the maximum absorption wavelength of the MB dye stock solution was determined using the UV-1800 series spectrophotometer at 200-900 nm. The λ_{max} was found to be 659 nm. The

maximum absorption wavelength was later used for the subsequent determinations.

Verification of the Beer-Lambert law

The Beer-Lambert law was verified using a calibration curve obtained from a plot of absorbance against concentration of the diluted solutions of methylene blue and the plot presented in Figure 3. Figure 3 reveals that, the plot is a straight line passing through the origin and a regression coefficient of 0.9966 which is very close to 1. That is absorbance is proportional to the concentration. Hence, there is a possibility to use the law to determine the residual concentration. The concentration used were within the range 0 mg/L and 10 mg/L of methylene blue with higher concentrations diluted to remain within the detention limit of the UV spectrophotometer. However, the actual values were obtained by multiplying the machine readings with the dilution factors.

Effect of contact time

Evaluating the effect of contact time was done for the adsorption of MB dye onto RTAC at the timing range of 5, 10, 15, 20, and 25 min on 0.5 g adsorbent, constant pH and room temperature. The plot of adsorbent efficiency

against time is presented in Figure 4. The percentage efficiency increased with increase in time. Adsorption of the MB dye onto RTAC was rapid within the first 5 min of the evaluation, with 99.611% (96.611 mg/L of MB dye removed) efficiency. This could be as a result of the initial availability of abundant vacant sites on the surface of the adsorbent [37,38]. The curve also revealed that the adsorption increased with increase in time until after 10 min, when efficiency remains almost constant. This may be due to the decrease in driving force owing to the sites on the adsorbent surface being almost filled up by molecules of the adsorbate. The response of the RTAC to time was in accordance with previous reports by [1,18].

Effect of temperature

The effect of temperature on methylene blue dye adsorption onto RTAC was determined using temperature range 298, 303, 308, 313 and 318 K on 0.5 g adsorbent at room temperature for 15 min. The plot of adsorbent efficiency against temperature is presented in Figure 5. The best adsorption efficiency of 99.635% (99.635 mg/L of 100 mg/L MB removal) was attained at 303 K while the least of 97.618% (97.618 mg/L of 100 mg/L MB removal) at 313 K.

Figure 3. Calibration Curve of the Absorption of MB in Aqueous solution at 25 °C

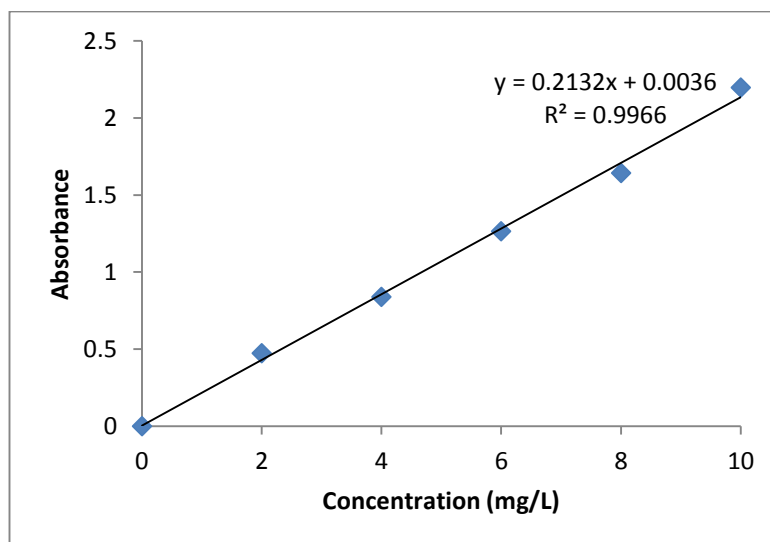
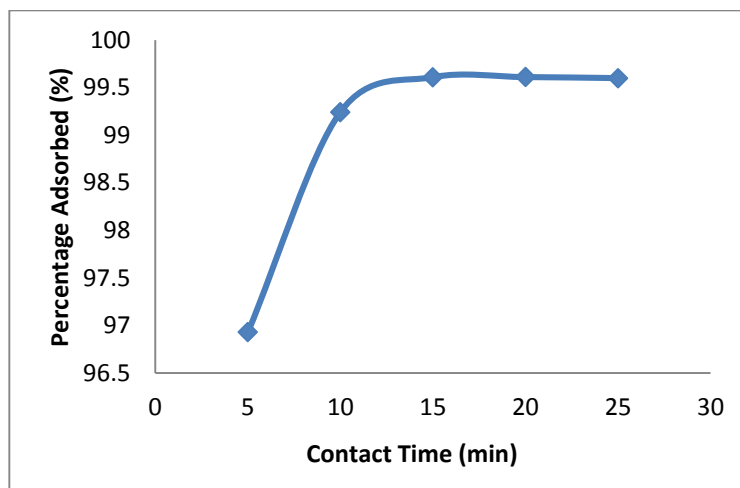


Figure 4. Effect of contact time on methylene blue dye adsorption by RTAC



The efficiency was in order 303>308>318>298>313 K. The results indicated that, the increased temperature (thermal energy) might be due to the mobility of the methylene blue dye molecules in aqueous solution which could result in desorption. The results demonstrated that, the adsorption was favoured just above the room temperature.

Effect of initial concentration of solution

The effect of initial concentrations was experimented with MB dye concentrations of 20, 40, 60, 80 and 100 mg/L adsorbate on the adsorption onto 0.5 g RTAC at constant pH, room temperature in 15 min was evaluated. Figure 6 depicts the response of RTAC to different initial concentration of MB dye. The results showed that the highest efficiency (99.743% MB removal) was obtained with 40 mg/L. The efficiency, increased from 20 mg/L to 40 mg/L from where adsorption efficiency decreased with increase in initial concentration. As the initial concentration increased, the initial vacant sites on RTAC were completely filled with molecules of MB dye, and the equilibrium was attained. This was in line with earlier reports that pollutant removal through the adsorption process is concentration dependent [36,39,40].

Effect of pH

The effect of pH on the adsorption of MB dye onto RTAC was evaluated using 0.5 g RTAC, at room temperature in 15 min. Figure 7 presents the efficiency of RTAC against pH. The result of the evaluation showed that the efficiency of the adsorbent increased with enhancing the pH (increasing alkalinity). The maximum adsorption capacity was recorded at pH of 9, indicating that the MB adsorption onto the RTAC was favoured at weaker acidic medium.

Low adsorption of MB dye at low pH is probably due to the presence of H⁺ ions competing with the cation groups on the dye for the adsorption sites. Also, the electrostatic repulsion between the surface of the activated carbon and positively charged methylene blue dye is lowered, due to surface charge density decrease with an increase in the solution pH, may result in an increase in the adsorption rate. This further supports the earlier reports that the removal of dyes from aqueous solution by adsorption technique is significantly dependent on the pH of surrounding medium, which affects the adsorbent surface charge and the degree of ionization of the adsorbate [40,36].

Figure 5. Effect of Temperature on methylene blue dye adsorption by RTAC

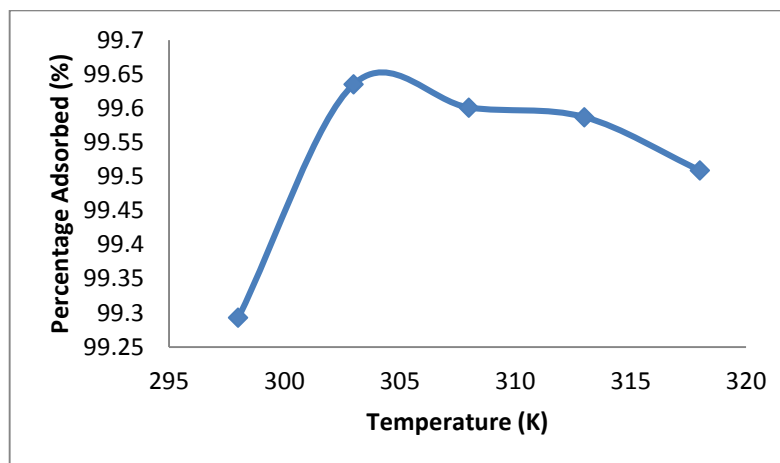
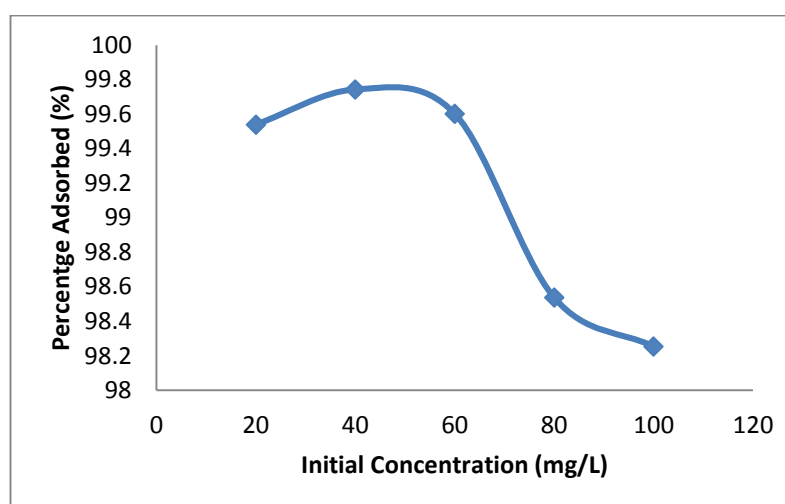


Figure 6. Effect of Initial Concentration on methylene blue dye adsorption by RTAC



Effect of adsorbent dosage

The effect of the adsorbent dose on the adsorption of MB dye onto RTAC was evaluated using adsorbent doses of 0.1, 0.3, 0.5, 0.7 and 0.9 g at room temperature, constant pH and constant time of 15 min. The results are presented as a plot of adsorbent efficiency in percentage against adsorbent dose in Figure 8. The results showed an increased in MB removal with an increase in adsorbent dosage. 0.1 g RTAC removed 86.363 mg/L from, 100 mg/L of MB solution and the maximum adsorption was achieved with 0.9 g (with 99.256% efficient). However, the capacity of the adsorbent was almost constant when adsorbent dose was increased from 0.7 to 0.9 g (99.107 to 99.256 mg/L from 100 mg/L by 0.7 g and 0.9 g respectively). The

increasing in the efficiency could be as a result of the increase in the number of active sites owing to increase in the mass of the adsorbent. Similar results were reported for Sumac Leaves [42] and bamboo [42].

Adsorption isotherm

The Langmuir adsorption isotherm can be represented as Equation 3. Plot of the C_e/q_e against C_e for the adsorption of methylene blue dye onto RTAC at temperatures of 298, 308 and 318 K is presented in Figures 9. From the plots 9 and 10, the correlation coefficients (R^2) of over 0.998 were observed at all the temperatures indicating a strong relationship between adsorption data.

Figure 7. Effect of pH on methylene blue dye adsorption by RTAC

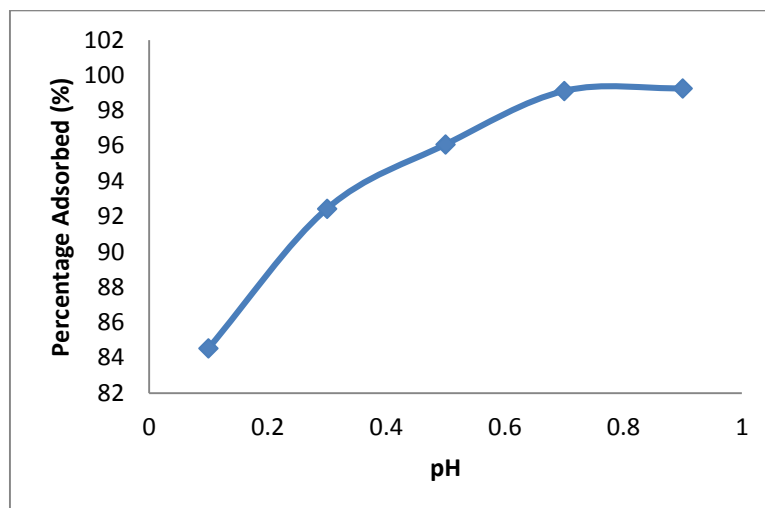
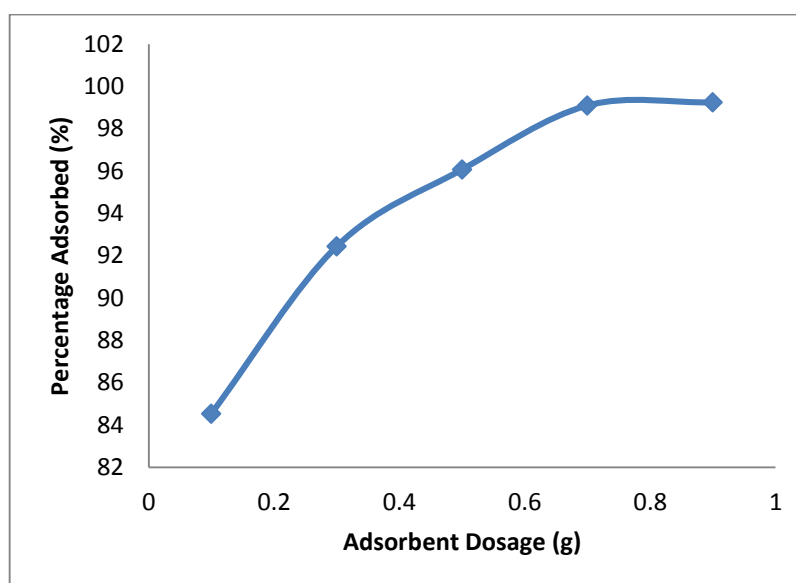


Figure 8. Effect of Adsorbent Dosage on methylene blue dye adsorption by RTAC



The values of q_{\max} and K_L (L/mg) are Langmuir parameters obtained from the slope and intercept of the plot of C_e/q_e against C_e , respectively and are presented in Table 1. From Table 1, the values of q_{\max} are close to experimented values of q_e . Also, the values of K_L showed increased in value with increasing temperature indicating a stronger adsorption taking place [35]. Values of q_{\max} increased with increasing temperature suggesting endothermic reactions. Increase in temperature can increase rate of diffusion of molecules and reduce the viscosity of liquid which facilitates easier migration of adsorbate

molecules towards and through adsorbents pores.

Furthermore, To to ascertain whether the adsorption process is favourable or not, a dimensionless constant known as separation factor (R_L) was evaluated as defined in Equation 4. The R_L value determined the shape of the isotherm to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The values of R_L indicated the adsorption process is favourable.

The Freundlich isotherm was defined using the Equation 5 and the linearized form is presented in Equation 6.

Figure 9. Langmuir isotherm plot for the adsorption of MB dye onto RTAC

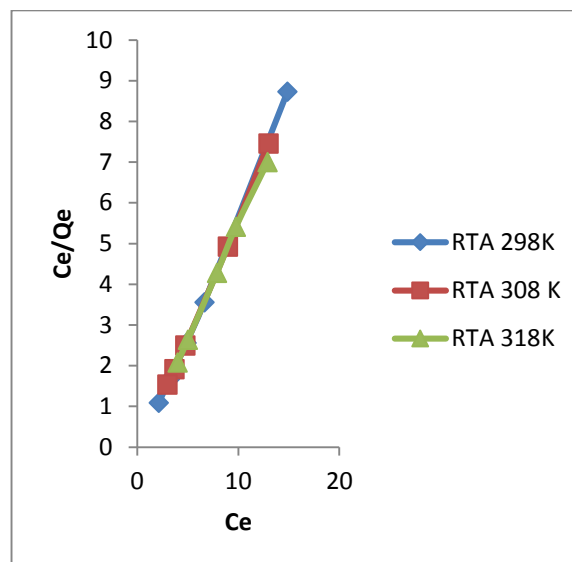
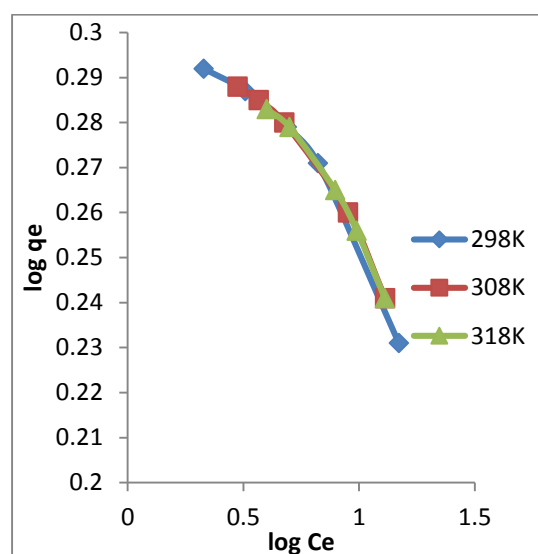


Figure 10. Freundlich isotherm plot for the adsorption of MB dye onto RTAC



The values of K_F and n were obtained from the intercepts and slopes of $\log q_e$ versus $\log C_e$ plot. The slope, $(1/n)$, ranging from 0 to 1 is a measure of intensity of adsorption or surface heterogeneity. The surface becomes more heterogeneous as the value $1/n$ approaches zero and a value of $1/n$ below 1 indicates a normal Langmuir isotherm while value of $1/n$ above 1 is indicative of cooperative adsorption [43,44]. The Freundlich parameters and correlation coefficients (R^2) from the plot are contained in Table 1. As seen in Figure 10, the correlation coefficients (R^2) above 0.916 (close to unity) were observed at all the temperatures indicating a strong relationship between adsorption data. It is also important to note that

the values of n are greater than 1 at all the temperatures and the values of $1/n$ increased slightly with increased temperature while the value of n decreased with increasing temperature. The values of n greater than unity indicated a favourable adsorption taking place while the values of $1/n$ tending towards zero indicate the heterogeneity of the surface. According to Table 1, the values of K_F increased with increasing temperature indicating that adsorption capacity increased slightly at higher temperature.

As can be seen in Table 1, the values of the solute-adsorbent complex dissociation coefficient, K_L , demonstrated that a stronger

adsorption took place between the adsorbate and adsorbent as the values of the K_L increased

by enhancing the temperatures.

Table 1. Results of Adsorption isotherm at temperature 298, 308, and 318 K

Isotherms equation	Parameters	RTAC		
		298 K	308 K	318 K
Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	Exp. q_m	1.6551	1.6906	1.7921
	Cal. q_e	1.7030	1.7400	1.7420
	K_L	1.9216	2.1035	4.1035
	R_L	0.0052	0.0047	0.0024
	R^2	0.9988	0.9993	0.9992
Freundlich $\log q_e = \log K_f + \frac{1}{n} \log C_e$	$1/n$	0.0723	0.0732	0.0810
	n	13.8312	13.6612	12.3457
	K_f	2.1033	2.1193	2.1602
	R^2	0.9169	0.9687	0.9707

In addition, the value of R_L was less than one at all temperatures, indicating that the adsorption system was favourable. The values of the maximum adsorption capacity, q_{max} , obtained from the Langmuir plot increased with enhancing the temperature which predicts the endothermic nature of the adsorption. As seen in Table 1, that the values of the calculated maximum adsorption capacity per unit weight of adsorbent and experimental adsorption capacity have nearly the same values. Furthermore, it can also be observed that the values of R^2 at all temperature are closer to unity than that of other isotherm models. From these data, it can be inferred that the adsorption of MB dye onto RTAC fitted well into Langmuir isotherm model and best be represented by the isotherm.

Adsorption kinetics

The kinetic models used for this study include the pseudo-first-order and pseudo-second-order kinetic models. The rate constant for the adsorption for this study was determined using the pseudo-first-order-order rate Equation 7. A plot of $1/q_t$ against $1/t$ is presented in Figure 11. The values of the q_e and k_1 were obtained from the intercept and slope of the plot respectively. From Figure 11, the values of R^2 at all temperatures range from 0.8502 to

0.9483. As seen in Table 1, the calculated values of q_e are 0.0427, 0.0500 and 0.0530 at 298, 308, and 318 K, respectively. Also, the values of the pseudo-first-order rate constant, k_1 are 0.021, 0.026 and 0.026 at 298, 308, and 318 K, respectively. Based on these data, though R^2 values were high but the calculated values of q_e were far below the corresponding experimental values. Therefore, the pseudo-first-order kinetic model was not proved to be the best fit in representing the experimental kinetic data in this research study.

The pseudo-second order linearized equation is expressed in Equation 8. A plot of t/q_t against t was presented in Figure 12. The pseudo-second-order parameters: q_e , k_2 and R^2 were calculated and presented in Table 2. The values of q_e and k_2 were obtained from the intercept and slope of plot in Figure 12, respectively. From Figure 12, the values of R^2 are greater than 0.999 at all temperatures. Also, as contained in Table 2, the calculated values of q_e are 2.028, 2.006 and 1.977 at temperature 298, 308 and 318 K, respectively.

Comparing the data with those obtained from the pseudo-first-order kinetic model showed that the values of the correlation coefficients are greater at all the temperature and attained correlation coefficient of 1 (unity) at 298 K.

Figure 11. Plot of Pseudo-first-order kinetic model for the adsorption of MB dye onto RTAC

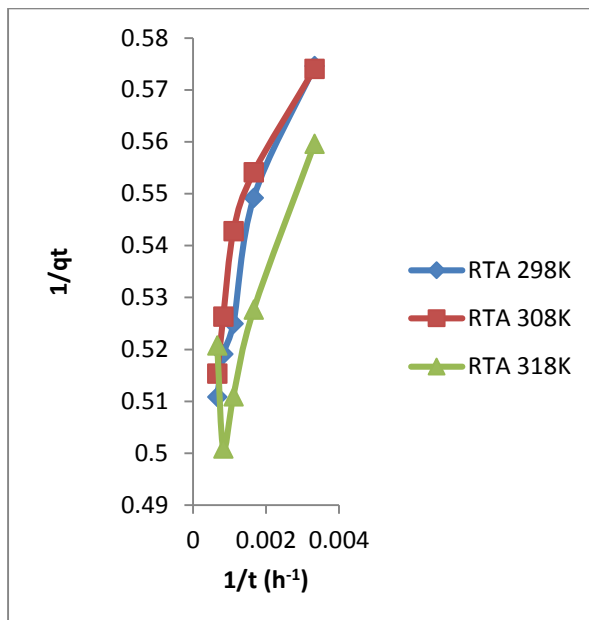


Figure 12. Plot of Pseudo-second-order kinetic model for the adsorption of MB dye onto RTAC

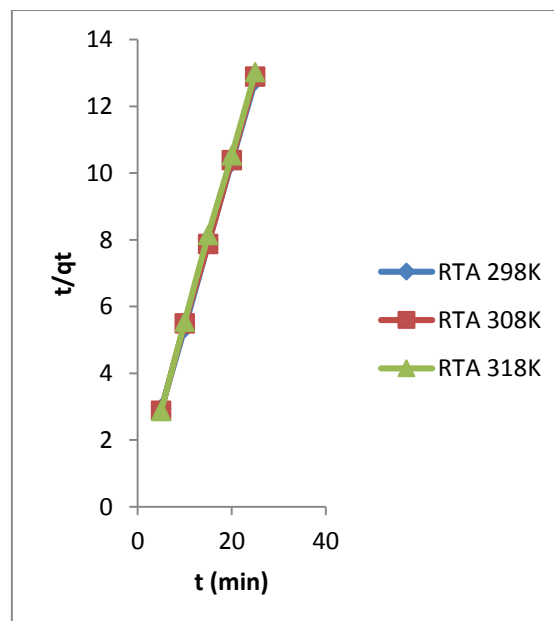


Table 2. Results of adsorption kinetics at temperature 298, 308, and 318 K

Kinetic model	Parameters	RTAC		
		298 K	308 K	318 K
Pseudo-first-order $\frac{1}{qt} = \frac{K_1}{q_{et}} + \frac{1}{q_e}$	q_e	0.0427	0.050	0.053
	K_1	0.021	0.026	0.026
	R^2	0.9483	0.8704	0.8502
Pseudo- second-order $\frac{t}{qt} = \frac{1}{K_2q_2e} + \frac{1}{q_e}t$	q_e	2.028	2.006	1.977
	K_2	0.529	0.530	0.560
	R^2	1.0000	0.9998	0.9995

Also, the values of calculated adsorption capacity q_e gave a better agreement with corresponding experimental value q_e . It can be said that adsorption process follows pseudo-second order kinetic model for the concentration of the dye at all temperature. The results of similar findings have been reported for the adsorption of MB dye on biosorbents [8,45].

Thermodynamic studies

Thermodynamic parameters such as the Gibbs free energy change (ΔG), enthalpy changes (ΔH) and entropy changes (ΔS) were studied to have a better understanding of the temperature effect on the adsorption process. The thermodynamic parameters were calculated using the Equation 9.

$$K_c = \frac{C_s}{C_e} \quad (9)$$

Where C_s is the MB dye concentration on the adsorbent at equilibrium in mg/L, C_e is

the equilibrium concentration of the MB dye is solution in mg/L and K_c is the thermodynamic equilibrium constant. The Gibbs free energy, ΔG^0 (kJ/mol) for the adsorption MB dye onto the adsorbents can be calculated using Eq. 10:

$$\Delta G^0 = -RT \ln K_c \quad (10)$$

Where T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol/k). Enthalpy and entropy are obtained using Van't Hoff's equation [35]. The change in free energy is related to other thermodynamic properties through Equation 11 and 12:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)$$

$$\ln K_c = \Delta S^0/R - \Delta H^0/RT \quad (12)$$

Where ΔH^0 is change in enthalpy and ΔS^0 is the degree of disorderliness of a reaction. The plots of $\ln K_c$ against $1/T$ are presented in Figure 13. ΔH^0 and ΔS^0 were obtained from plots in Figure 13.

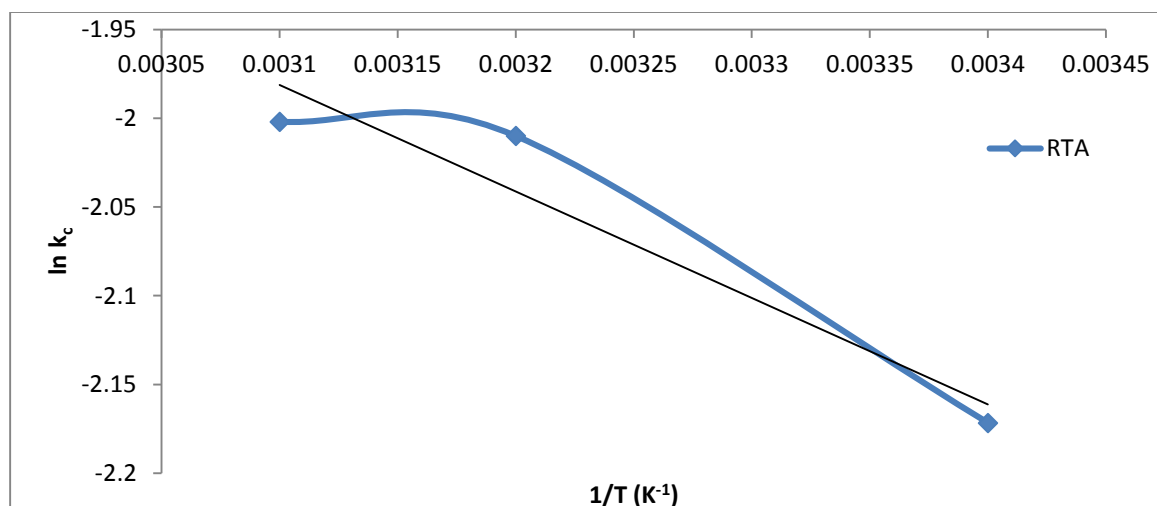


Figure 13. Plot of $\ln K_c$ against $1/T$ for the adsorption of MB dye onto RTAC

Table 3. Results of thermodynamic studies

Activated carbon	Temperature	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol/K)
RTA	298 K	-3.42	-7.72	11.47
	308 K	-3.65		
	318 K	-3.65		

As seen in Table 3, the negative values were observed for the ΔG^0 at all the working temperature. The negative values of the ΔG^0 for the MB dye adsorption onto RTAC implied that the adsorption processes were spontaneous and feasible at all temperatures. The negative value of the ΔG^0 increased with enhancing the temperature, indicating that, the spontaneity is proportional to temperature. The positive value of the ΔH^0 confirmed that the adsorption of the MB dye onto the RTAC is endothermic. The low enthalpy value of the processes also predicted that the adsorption is physisorption. Positive value of the ΔS^0 was indicating that the degrees of the disorderliness increased at the RTAC-MB interface during the adsorption of the MB dye onto RTAC predicting low energy of attraction between the adsorbent and methylene blue dye molecules. The result of the present study was in agreement with report presented in [46].

Conclusion

In this present study, an acid modified activated carbon was prepared from the *R. taedigera* seed. The results of the SEM and FTIR analysis revealed that, the activated carbon can effectively remove the MB dye from the aqueous solutions. The results also depicted that, the presence of the pores in the structure and adsorption favourably bond arrangement. Furthermore, the performance evaluation carried out at different adsorption conditions on the RTAC gave the efficiencies ranging from 84.542% to 99.894%. The results of the adsorption modelling showed that the adsorption data can best be represented by the Langmuir adsorption isotherm while the results of adsorption kinetic isotherm revealed that the adsorption of MB dye onto RTAC conformed to pseudo-second-order kinetic. Thermodynamic studies predicted a feasible, favoured, reversible, exothermic, and physisorption nature of the adsorption process. Satisfactorily, the use of

the RTAC for the removal of dyes is considered to be effective with great potential for practical applications.

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Disclosure statement

No potential conflict of interest was reported by the author.

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