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Sorption dynamics and isotherm studies of methylene blue uptake on to palm kernel fibre

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Abstract

The effect of temperature on the sorption of methylene blue from aqueous solution onto palm kernel fibre has been studied. Batch kinetics and isotherm studies were performed at temperatures ranging from 299 to 339 K. The kinetic data were studied in terms of the pseudo-first-order and pseudo-second-order kinetic models and the Bangham and intraparticle diffusion models. The pseudo-second-order model best described the sorption process and was employed in predicting the rate constant, equilibrium sorption capacity and the initial sorption rate with effect of temperature. In addition activation energy of sorption has also been determined based on the pseudo-second-order rate constant. The isotherm data was analyzed by the Langmuir and Freundlich isotherms. Palm kernel fibre was found to have a Langmuir monolayer capacity of 233.41 mg g^{-1} at 299 K. The adsorption is endothermic at ambient temperature and the computation of the thermodynamic parameters, ΔH°, ΔS° and ΔG° indicates that the sorption was favourable at all temperatures.

Keywords: Palm kernel fibre; Solution temperature; Pseudo-second-order; Langmuir isotherm; Methylene blue

1. Introduction

Knowledge of the interaction at a solid–liquid interface at varying temperatures is very important in applied surface science. It is known that adsorption depends to a large extent on the surface energy interaction involved between solute and sorbent [1], therefore the equilibrium relationship between solute molecules in solution and solute molecules on the adsorbent surface will depend on solution temperature. An area of practical interest of this field is in the separation of colored substances from textile effluents. Textile effluents containing dyes are usually discharged into receiving water bodies at relatively high temperatures (50–60 °C); therefore temperature will be an important design parameter affecting the sorption of dye molecules and sorption capacity of sorbents in real application [2–4].

Basic dyes although organic, carry a positive charge on their structure and are water-soluble. They have maximum adsorption capacities that are much higher than those of acid and reactive dyes [5,6] probably due to the negatively charged surface of most adsorbents employed for effluent treatment, which possesses higher affinity for cationic dyes. Some studies have revealed that cationic dye sorption on to certain adsorbents followed ion-exchange mechanism [7–10]. Schramm et al. [11] proposed that crystal violet and ethyl violet adsorption on to montmorilonite clay occurred initially by ion exchange followed by some specific adsorption due to π electron interactions and hydrogen bonding with clay particle surface. Bhattacharyya and Sharma [12] adsorbing methylene blue on to Neem leaf powder observed that pH variation had only little effect on the amount of methylene blue sorbed. They proposed that methylene blue adsorption was due to a weak electrostatic interaction between the cationic dye and electron-rich sites of the surface of the Neem leaf powder.

Bhattacharyya and Sharma [12,13] measured the enthalpies of brilliant green and methylene blue dyes on to Neem leaf powder. They found that the enthalpies of adsorption of both brilliant green and methylene blue dyes on to Neem leaf powder are endothermic for all amounts adsorbed. Rytwo and Ruiz-Hitzky [14] sorbing crystal violet and methylene blue on to montmorilonite clay, found that the enthalpy of adsorption of crystal violet is exothermic for all amounts adsorbed, while the enthalpy of adsorption of methylene blue is either exothermic or endothermic, depending on the extent of loading. A comparison of the

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Table 1
The maximum sorption capacities (mg g^{-1}) of methylene blue of various sorbents

Sorbent	q_m (mg g^{-1})	Reference
Natural clay	300	[15]
Cotton waste	240	[16]
Chemviron	238	[17]
Coal	230	[16]
Hair	120	[16]
Water hyacinth	128.9	[18]
Coconut husk	99	[19]
Activated carbon (CEA 40)	370	[20]
Palm kernel fibre	223.41	This study

sorption capacities of different sorbents for methylene blue is given in Table 1.

This study is aimed at investigating the effect of varying temperature on the kinetics and equilibrium uptake of methylene blue dye from aqueous solution on to palm kernel fibre. The pseudo-first- and pseudo-second-order kinetic models and Bangham and intraparticle diffusion models were employed to analyze the kinetic data on the effect of temperature. The feasibility of the application of palm kernel fibre as adsorbent at the temperature range at which textile effluents are discharged was also investigated.

2. Experimental

2.1. Materials

Palm kernel fiber used in this study was obtained from the Nigerian Institute for Oil Palm Research (NIFOR), Benin City, Nigeria. The palm kernel fiber was allowed to dry with the residual oil, after processing for about 2 months. The raw fiber was dried in an oven at 80 °C for 6 h, grounded and screened through a set of sieves to obtain particles of size 50–60 μm. The sieved fiber was steeped in 0.02 mol L^{-1} HCl overnight. The acid solution was filtered off and the fiber washed with distilled water until the pH of the wash becomes neutral. The fiber was dried at 80 °C for 24 h and stored in an air-tight container.

The basic dye, methylene blue (BDH, 85% dye content) was used without further purification. The stock solution of 1000 mg L^{-1} was prepared by dissolving 1.127 g methylene blue in 1000 mL distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.2. Methods

2.2.1. Some characteristics of palm kernel fibre

The proximate composition of the palm kernel fibre was determined using the Association of Official Analytical Chemist (AOAC) [21]. Lipid content was determined using solvent extraction method with petroleum ether; moisture content was determined by thermal drying method at 105 °C; ash content was determined by ignition method; protein content was by the determination of the total organic nitrogen using the macro kjeldhal method and then converting to crude protein, while fibre content was determined by ashing at 500 °C for 3 h.

The IR spectra of the palm kernel fibre sample were recorded using KBr disk in conjunction with a Perkin-Elmer infrared spectrophotometer having resolution of 4 cm^{-1} and range between 4000 and 400 cm^{-1}. KBr disk were prepared by mixing a given sample with KBr crystals, the resulting mixture being ground to a fine powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr disk under vacuum conditions and used as such for IR studies.

2.2.1.1. Theory. Sorption in a methylene blue/palm kernel fibre system results in the transfer of methylene blue to the surface of the palm kernel fibre, where it increases in concentration until a dynamic equilibrium is reached between palm kernel fibre and methylene blue remaining in the liquid phase. These characters of biomaterials can be involved in chemical bonding and are responsible for their cation exchange capacity. Thus, the reaction may be expressed by the following two relationships [22–24]:

$$\mathrm{F^- + MB^+ \rightarrow MBF} \tag{1}$$

and

$$\mathrm{2HF + (MB)_2{}^{2+} \rightarrow 2MBF + 2H^+} \tag{2}$$

where F^- and HF are polar sites on the palm kernel fibre surface.

The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of palm kernel fibre and the amount sorbed at equilibrium.

The rate expression for the sorption described is

$$\frac{\mathrm{d(F)}_t}{\mathrm{d}t} = k[(\mathrm{F})_0 - (\mathrm{F})_t]^2 \tag{3}$$

or

$$\frac{\mathrm{d(HF)}_t}{\mathrm{d}t} = k[(\mathrm{HF})_0 - (\mathrm{HF})_t]^2 \tag{4}$$

where $(\mathrm{F})_t$ and $(\mathrm{HF})_t$ are the number of active sites occupied on the palm kernel fibre at time t and $(\mathrm{F})_0$ and $(\mathrm{HF})_0$ are the number of equilibrium sites available on the palm kernel fibre. The kinetic rate equations can be rewritten as follows

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the rate constant of sorption (g mg^{-1} min^{-1}), q_e the amount of lead ions sorbed at equilibrium (mg g^{-1}) and q_t is the amount of lead ions sorbed on the surface of the palm kernel fibre at any time t (mg g^{-1}).

Separating the variables in Eq. (5):

$$\frac{\mathrm{d}q_t}{(q_e - q_t)^2} = k\,\mathrm{d}t \tag{6}$$

integrating this for the boundary conditions $t = 0$ to t and $q_t = 0$ to qt, gives

$$\frac{1}{(q_e - q_t)^2} = \frac{1}{q_e} + kt \tag{7}$$

which is the integrated rate law for a pseudo-second-order reaction and Eq. (7) can be rearranged to obtain

$$q_t = \frac{h}{1/k_2q_e^2 + t/q_e} \tag{8}$$

which has a linear form

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e t} \tag{9}$$

where h can be regarded as the initial sorption rate as q_t/t when t tends to 0, hence, $h = kq^2$.

Thus, a plot of t/q_t against t of Eq. (9) should give a linear relationship with the slope of $1/q_e$ and intercept of $1/kq_e^2$.

The analysis of the isotherm data is important to develop an equation, which accurately represents the results and could be used for design purposes. In order to investigate the sorption isotherm, two models were analyzed: the Langmuir, and the Freundlich. The Langmuir sorption isotherm [25] is perhaps the best known of all isotherms describing sorption. The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{10}$$

The constants q_m and K_a are the characteristics of the Langmuir equation and can be determined from a linearised form of Eq. (10), represented by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \tag{11}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e the amount of lead sorbed (mg g^{-1}), q_m is q_e for a complete monolayer (mg g^{-1}), and K_a is the sorption equilibrium constant (L mg^{-1}).

The Freundlich isotherm [26] is the earliest known relationship describing the sorption equation and is expressed by Eq. (12):

$$q_e = K_F C_e^{1/n} \tag{12}$$

and the equation may be linearised by taking logarithms:

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \tag{13}$$

where K_F and $1/n$ are empirical constants dependent on several environmental factors.

Adsorption is usually an exothermic process and as the temperature increases, the amount adsorbed at a given concentration decreases in accordance with Le Chatelier's principle. The thermodynamic criteria for the adsorption process were evaluated through computation of Gibbs energy (ΔG), enthalpy of adsorption (ΔH), and entropy of adsorption (ΔS) by carrying out the adsorption experiments at three different temperatures and using Eqs. (14) and (15) in agreement with [27]:

$$\Delta G = \Delta H - T\Delta S \tag{14}$$

$$\log\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{15}$$

where q_e/C_e is called the adsorption affinity and is the ratio of q_e, the amount adsorbed per unit mass at equilibrium to C_e, the equilibrium concentration of the adsorbate. The values of ΔH and ΔS were determined from the slope and the intercept of the plots of $\log(q_e/C_e)$ versus $1/T$. The ΔG values were calculated using Eq. (14).

2.2.2. *Kinetic studies*

A range of reaction temperatures (26, 36, 46, 56 and 66 °C) were used and the flasks were agitated for 60 min. All contact investigations were performed in a 1 L flask. A 0.1 g sample of palm kernel fibre was added to 150 mL volume of methylene blue solution set at pH 7.1 (optimum pH for methylene blue sorption on to palm kernel fibre was arrived at in my previous investigation [28]) and agitated at 80 rpm for all the experiments. The experiments were carried out at initial methylene blue concentration 150 mg L^{-1} for all the studies. Samples were withdrawn at suitable time interval, filtered and the filtrate analyzed for the remaining methylene blue concentration with a spectrophotometer ($\lambda_{max} = 665$ nm).

2.2.3. *Equilibrium studies*

A volume of 200 mL of methylene blue solution with a concentration ranging from 100 to 550 mg L^{-1} was placed in a 250 mL conical flask and set at pH 7.1. An accurately weighed amount (0.1 g) of the palm kernel fibre was to the solution. The conical flask was then shaken at a constant speed of 80 rpm in a shaking water bath with temperatures 26, 36, 46, 56 and 66 °C, respectively. After shaking the flasks for 2 h, the palm kernel fibre was separated by filtration. The filtrate was analyzed for the remaining methylene blue concentration by a spectrophotometer ($\lambda_{max} = 665$ nm).

3. Results and discussion

3.1. *Characteristics of palm kernel fibre*

The percentage proximate composition of palm kernel fibre on dry weight basis was: carbohydrate 38.15%, lipid 9.00%, fibre 19.90%, ash 6.30%, protein 14.80%, moisture 9.78%, Ca 0.63%, P 0.45% and Mg 0.29%.

IR measurement for the palm kernel fibre showed the presence of the following groups: C=O (1680.1 cm^{-1}), COOH (3300–2500, 1110.8 cm^{-1}), –OH (3426.2 cm^{-1}), C=C (1675 cm^{-1}), C–N (1030–1230 cm^{-1}), N–H (1548.8 cm^{-1}) and NH_2 (3400–3500 cm^{-1}).

3.2. *Kinetic studies*

3.2.1. *Effect of temperature*

The temperature dependence of methylene blue sorption onto palm kernel fibre was studied with a constant initial dye concentration of 150 mg L^{-1} at 80 rpm and palm kernel fibre dose 0.67 g L^{-1} at various temperature of sorption reaction. Fig. 1 shows the effect of contact time on the percentage of methylene blue dye removed from aqueous solution at different reaction temperatures. The results show that with increase in

Table 2
Kinetic parameters for methylene blue sorption by palm kernel fibre at different temperatures

T (°C)	Pseudo-first-order				Pseudo-second-order				Intraparticle diffusion			Bangham		
	q_{exp}	q_{cal}	k_1	r^2	q_{cal}	h	k_2	r^2	C	k_i	r^2	k_0	α	r^2
26	215.22	9.7701	0.0981	0.9275	217.91	289.90	0.0061	0.9999	107.500	37.081	0.9797	189.37	0.3721	0.931
36	217.71	47.2607	0.1069	0.9121	219.28	500.93	0.0104	0.9999	144.540	25.887	0.9741	264.62	0.3094	0.922
46	219.87	32.1440	0.1089	0.8990	220.85	824.61	0.0169	1.0000	170.660	17.677	0.9705	346.13	0.2663	0.920
56	221.44	22.2024	0.1110	0.8921	222.08	1286.80	0.0261	1.0000	187.890	12.157	0.9679	428.25	0.2385	0.925
66	223.10	15.1147	0.1119	0.8850	223.51	1997.50	0.0400	0.9999	200.42	8.266	0.9663	518.86	0.2406	0.955

q_{exp} is the experimentally determined equilibrium sorption capacity (mg g^{-1}), q_{cal} the calculated value of equilibrium sorption capacity (mg g^{-1}), k_1 the pseudo-first-order rate constant (min^{-1}), h the initial sorption rate of the pseudo-second-order kinetic model (mg g^{-1} min^{-1}), k_2 the pseudo-second-order rate constant (g mg^{-1} min^{-1}), C the intercept of the intraparticle diffusion curve, k_i the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$), k_0 and α are Bangham's equation constants.

reaction temperature from 299 to 399 K, the maximum percentage dye removal after 60 min of contact increased from 95.65% to 99.15%. The fact that the percentage dye removal is favored by temperature indicates that the mobility of the dye molecules increases with a rise in the temperature. It can also be said that reaction of dye molecules and surface functional groups is enhanced by increased temperature of reaction.

3.2.2. Pseudo-second-order kinetics

The effect of temperature on the pseudo-first-order sorption kinetics of methylene blue on palm kernel fibre is shown in Fig. 2. The value of rate constant estimated from the pseudo-first-order model did not follow any particular pattern with increase in reaction temperature. The values of equilibrium sorption capacity, q_e calculated were 9.77, 47.26, 32.14, 22.20 and 15.11 mg g^{-1} for 299, 309, 319, 329 and 399 K, respectively. These values were quite small and not in agreement with experimental data (see Table 2). The correlation coefficients, r^2, obtained had low values with the experimental data (between 0.8850 and 0.9275).

On analysis of the experimental data with the pseudo-second-order kinetic model, the good agreement of the sets of data is seen to be reflected in the extremely high correlation coefficient of determination obtained (Fig. 3). Table 1 shows the sorption rate constant, k_2, initial sorption rate, h, and equilibrium sorption capacity, q_e, as a function of solution temperature.

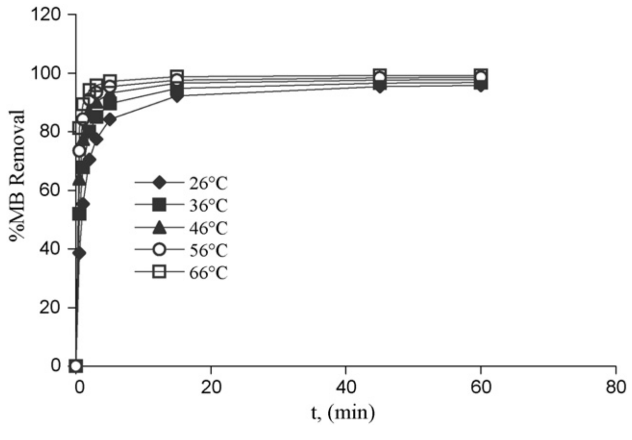

Fig. 1. Effect of initial methylene blue concentration on percentage removal. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

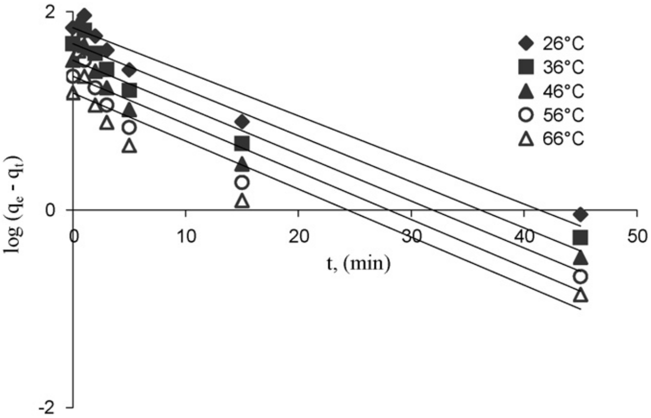

Fig. 2. Pseudo-first-order plot for methylene blue onto palm kernel fibre. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

Thus on increasing the temperature from 299 to 399 K, the sorption capacity at equilibrium, q_e, is increased from 217.91 to 223.51 mg g^{-1}. The initial sorption rate, h, increases from 289.90 to 1997.50 mg g^{-1} min^{-1}, for temperature variation from

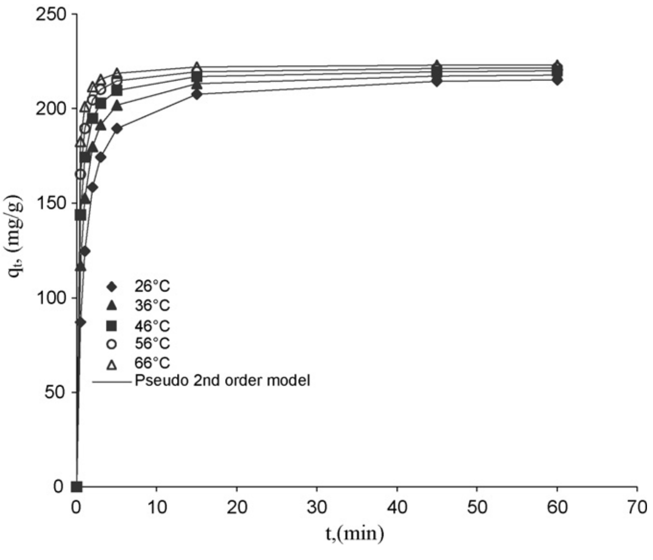

Fig. 3. Pseudo-second-order plot for methylene blue sorption onto palm kernel fibre. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

299 to 399 K. This trend suggests that a chemisorption reaction or an activated sorption between dye molecule and functional groups on palm kernel fibre surface involving valency forces through sharing or exchange of electrons between palm kernel fibre and methylene blue molecules occurs. Similar results of basic dyes and other adsorbents have also been reported in literatures, for example basic blue 69 on wood [29], methylene blue on perlite [1], basic blue 69 unto peat [30]. According to Ho et al. [31], if the dye uptake is chemically rate controlled, the pseudo-second-order constants will be independent of particle diameter and flow rate and will depend on temperature of the dye in solution. Increase in temperature will also lead to increase in the amount adsorbed at equilibrium for a chemisorption-controlled reaction. The logarithmic plots of initial sorption, h and q_e versus temperature were made and the plots where found to give straight lines whose linear regression r_2^2 are given as 0.9992 and 0.9991, indicating that dye uptake is chemically rate controlled. Mathematical expressions were therefore drawn relating the initial sorption rate, h, and equilibrium capacity, q_e and reaction temperature as follows

$$h = 3.396 \times 10^{-36}\, T^{15.326} \tag{16}$$

and

$$q_e = 68.929 T^{0.2019} \tag{17}$$

The values of rate constant, k, were found to increase from 0.0061 to 0.0400 g mg^{-1} min^{-1}, for an increase in the solution temperature of 299–339 K. There is a linear relationship between the pseudo-rate constant and temperature with coefficient of determination of 0.9998 (Fig. 4). The sorption rate constant is usually expressed as a function of solution temperature by the relationship:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{18}$$

where k is the rate constant of sorption (g mg^{-1} min^{-1}), k_0 the temperature-independent factor (g mg^{-1} min^{-1}), E the activation energy of sorption (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T is the solution temperature (K).

Therefore, the relationship between k and T can be represented in an Arrhenius form as

$$K = 4.571 \times 10^{13} \exp\left(\frac{-39.57 \times 10^3}{8.314T}\right) \tag{19}$$

From this equation, the rate constant for sorption, k_0, is 5.04×10^4 g mg^{-1} min^{-1} and the activation energy for sorption, E, is 39.57 kJ mol^{-1}, which is outside the range of values of 8–22 kJ mol^{-1} for diffusion-controlled processes [32]. The rate controlling step in the process can be characterized in part by its activation energy. Therefore, since the sorption increased with temperature, which implies the uptake is endothermic in nature and activation energy is higher than 22 kJ mol^{-1}, then one can say that chemisorption process significant and rate controlling in the sorption of methylene blue onto palm kernel fibre. Some other basic dye sorption that have been found to be chemisorption-controlled includes: sorption of basic blue 69 onto wood with activation energy = 27.3 kJ mol^{-1} [29]; methylene blue onto modified diatomite with activation energy = 99.80 kJ mol^{-1} [33]; Telon blue onto peat with activation energy = 26.60 kJ mol^{-1} [34] and basic blue onto peat with activation energy = 22.7 kJ mol^{-1} [30].

Since the uptake of methylene blue slowed down during the later stages of the sorption reaction, Bangham's equation as suggested by Aharoni et al. [35] of the form

$$\log\log\left[\frac{C_0}{C_0 - q_t m}\right] = \log\frac{k_0 m}{2.303V} + \alpha \log t \tag{20}$$

where C_0 is the initial concentration of adsorbate in solution (mg L^{-1}), V the volume of solution (mL), m the weight of sorbent used per litre of solution (g L^{-1}), q_t the amount of sorbate retained at time t (mg g^{-1}), α (<1) and k_0 are constant. It was tested for its applicability for methylene blue adsorption. The double logarithmic plots according to Eq. (20) did not yield perfect linear curves (see Fig. 5) showing that the diffusion of sorbate into the pores of the sorbent is not the only rate controlling step [36].

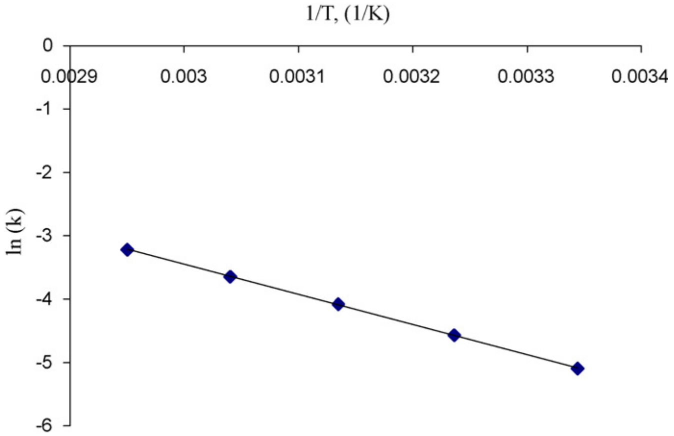

Fig. 4. Relationship between pseudo-second-order rate constant for methylene blue sorption and reaction temperature.

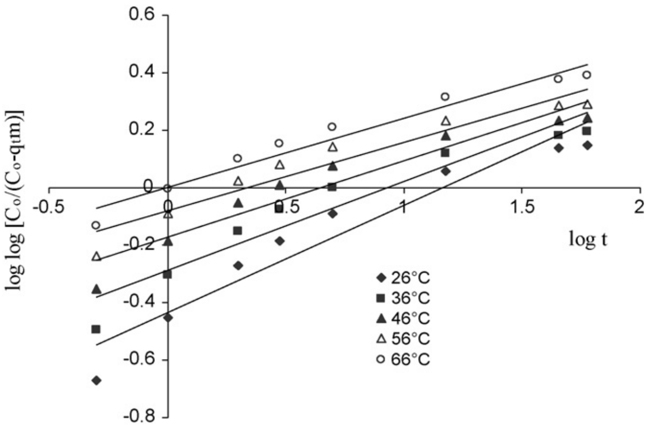

Fig. 5. Bangham plot for the sorption of methylene blue on palm kernel fibre. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

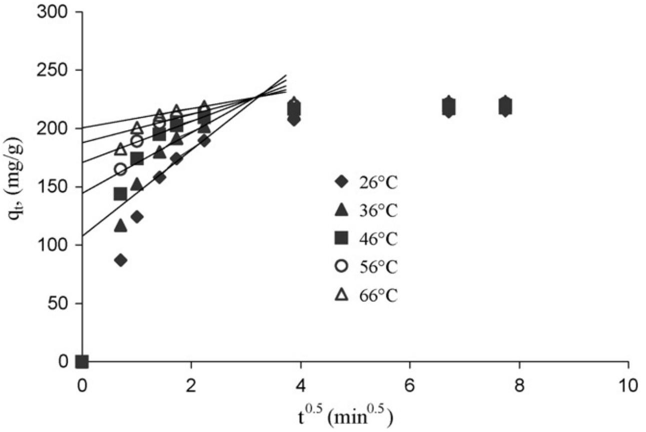

Fig. 6. Effect of initial dye concentration on intraparticle diffusion kinetics of methylene blue on palm kernel fibre. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

To investigate the effect of temperature on the contribution of intraparticle diffusion to the overall sorption process, the kinetic data at different temperatures was plotted according to the intraparticle diffusion equation proposed by Weber and Morris [37]. Fig. 6 shows the plot of the amount adsorbed per unit weight at any time, t, versus the square of time. All the plots had the same general features, an initial curve portion, a linear portion and a plateau. The values of intraparticle diffusion rate constant, k_i, estimated are 37.081, 25.887, 17.677, 12.157 and 8.266 mg g^{-1} min$^{-0.5}$ for 299, 309, 319, 329 and 339 K, respectively. The values of r^2 from the linear portion in Fig. 5 are found to be 0.9797, 0.9741, 0.9705, 0.9679 and 0.9663 for 299, 309, 319, 329 and 339 K, respectively. As shown Fig. 5, the linear plots of q_t versus $t^{0.5}$ do not pas through the origin signifying that intraparticle diffusion is not solely rate controlling. The logarithmic plot of intraparticle diffusion rate constants was found to be linearly related with the logarithmic values for reaction temperature with a correlation coefficient r^2, 0.9991. A mathematical expression was then drawn between log k_i and log T as shown

$$k_i = 1.690 \times 10^{31} T^{-11.977} \tag{21}$$

This shows that intraparticle diffusion is also important in the rate controlling process.

Moreover, the intercept C of the linear portion of the curve gives an idea about boundary layer thickness, the larger the value of the intercept the greater the boundary effect [38]. The values of intercept obtained from the plot were increasing with increasing temperature, indicating that more of the solute is being sorbed at the boundary layer.

3.3. Equilibrium studies

In order to assess the different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been plotted with experimental data for sorption of methylene on palm kernel fibre at 26 °C (Fig. 7). The coefficient of determination, r^2, was employed to ascertain the fit of both isotherms with experimental data. From Table 3, the coefficient of determination, r^2, values were higher for Langmuir than for Freundlich isotherm. This indicates that the Langmuir isotherm is clearly the better fitting isotherm to the experimental data at all reaction temperatures. Ho and Ofomaja [39] also observed that Langmuir isotherm was best fitting out of three isotherms tested for the sorption of lead ions on palm kernel fibre.

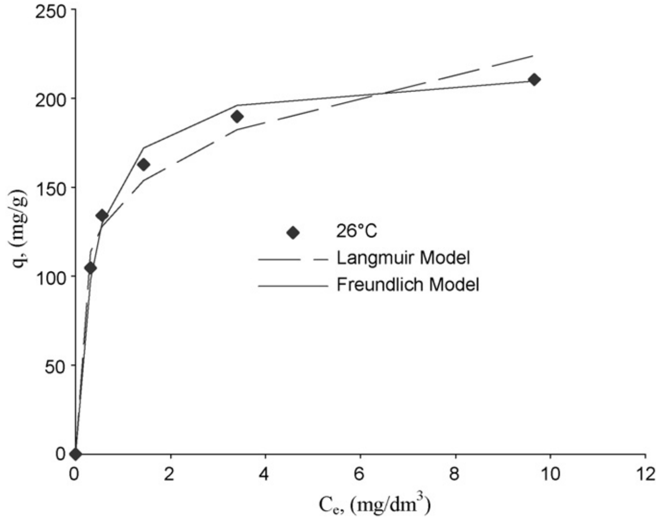

Fig. 7. Isotherms for sorption of methylene blue using palm kernel fibre. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

The effect of temperature on the sorption isotherm is shown in Fig. 8. The results indicate that the capacity of palm kernel fibre for sorption of methylene blue increases with temperature. Several authors have also reported increase in methylene blue sorption with increase in temperature for other sorbents [1,12,40].

When the system is in a state of equilibrium, the distribution of methylene blue between the palm kernel fibre and the methylene blue in solution is of fundamental importance in determining the maximum capacity of palm kernel fibre for methylene blue from the isotherm. The Langmuir isotherm is applicable to homogeneous sorption where each methylene blue/palm kernel fibre sorption process has equal sorption activation energy. The Langmuir constants K_a and q_m at various temperatures have been determined and shown in Table 4. The equilibrium capacity, q_m, was found to increase from 217.96 to 223.41 mg g^{-1} for an increase in temperature from 299 to 339 K. It is therefore clear that the sorption of methylene blue on palm kernel fibre is an endothermic process. However, the sorption

Table 3
A comparison of coefficient of determination for two isotherms

T (°C)	Langmuir (r^2)	Freundlich (r^2)
26	0.9997	0.9416
36	0.9992	0.9751
46	0.9997	0.9361
56	0.9998	0.9398
66	0.9997	0.9396

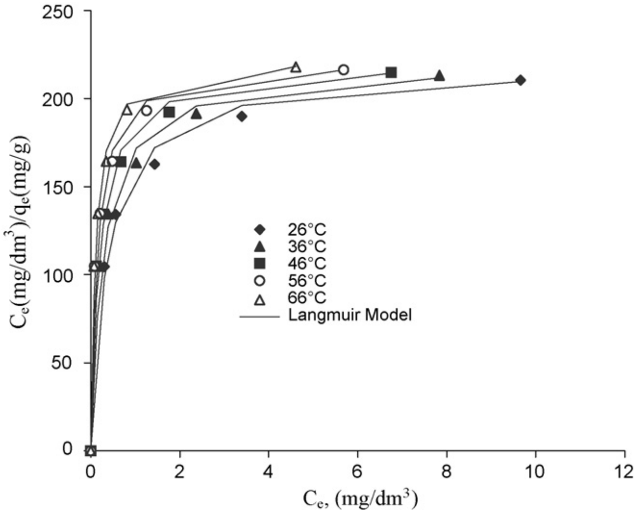

Fig. 8. Langmuir isotherms for the sorption of methylene blue on palm kernel fibre at various temperatures. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

constant, K_a, increases from 2.6292 to 9.1162 L mg^{-1} as temperature is varied from 299 to 339 K. Mathematical relationships between the sorptive capacities, q_m, sorption constants, K_a, and reaction temperatures were derived by regression of the linear plots of the values of q_m and K_a against T. The relationships derived have high coefficients of determination (>0.991) and are shown in Eqs. (22) and (23):

$$q_m = 70.70T^{0.1975} \tag{22}$$

and

$$K_a = 9.036 \times 10^{-26}T^{10.279} \tag{23}$$

Table 4
Langmuir isotherm constants for methylene blue sorbed on palm kernel fibre

T (°C)	Langmuir, q_m (mg g^{-1})	K_a (dm^3 mg^{-1})
26	217.96	2.6292
36	219.30	3.5368
46	220.85	4.9977
56	222.12	6.7396
66	223.51	9.1122

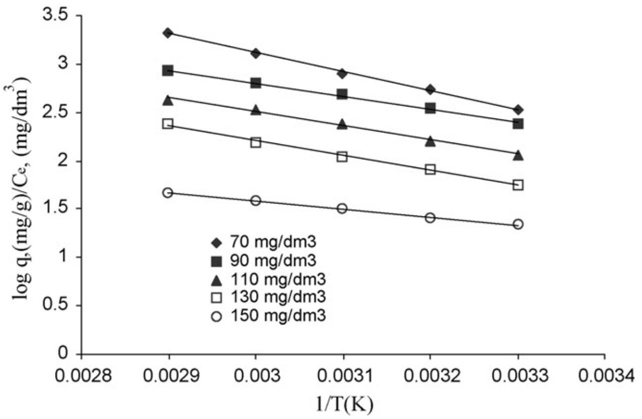

Fig. 9. Plots of log(q/C_e) for adsorption of methylene blue on palm kernel fibre vs. 1/T for different concentrations. Experimental conditions: initial dye concentration = 150 mg L^{-1}; dose: 0.67 g L^{-1}; agitation: 80 rpm; pH 7.1.

3.4. Thermodynamics of adsorption

The thermodynamic parameters for the sorption process shown in Table 5 were computed from the log(q_e/C_e) versus 1/T plots in Fig. 9. For a sorbent dose of 0.67 g L^{-1} of methylene blue solution with agitation time of 2 h. The plots had high values of correlation coefficients, r^2, ranging from 0.9915 to 0.9989. The enthalpy change for the sorption process using methylene blue solutions of concentrations ranging from 70 to 150 mg L^{-1} and temperature ranging 299–339 K, varied between 16.082 and 37.612 kJ mol^{-1} with a mean value of 27.439 kJ mol^{-1}. The positive value for enthalpy change indicates that the sorption is endothermic in nature. This is also observed from the in sorption capacity with temperature. The relatively high values of enthalpy change are compatible with the formation of strong chemical bonds between dye molecules and functional groups on the palm kernel fibre surface (carbonyl, alcoholic, carboxylic and amine groups). Similar endothermic sorption of methylene blue on Neem leaf powder [12], Gauyava leaves [41], kaolinite [42] have been reported in literatures.

The adsorption process results in an increase in enthalpy of the system from 78.618 to 172.564 kJ mol^{-1} with mean value of 129.105 kJ mol^{-1} when temperature was varied from 299 to 339 K. This indicates that the adsorbed methylene blue molecules on the palm kernel fibre surface are organized in a more random fashion compared to the solution in the aqueous phase. The positive values of entropy change confirms a high

Table 5
Thermodynamic parameters for adsorption of methylene blue on palm kernel fibre

MB (mg dm^{-3})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1}) at temperature				
			299 K	309 K	319 K	329 K	339 K
70	37.612	172.564	13.985	15.710	17.436	19.162	20.887
90	26.072	131.875	13.359	14.677	15.996	17.315	18.634
110	27.909	131.680	11.463	12.780	14.907	15.414	16.731
130	29.519	130.787	9.586	10.894	12.202	13.510	14.818
150	16.082	78.618	7.425	8.211	8.997	9.783	10.570
Mean	27.439	129.105	11.164	12.454	8.207	9.153	10.093

preference of methylene blue molecules for the palm kernel fibre surface and suggests the possibility of some structural changes or readjustments in the methylene blue–palm kernel fibre complex [42].

Although the sorption of methylene blue from aqueous solution onto palm kernel fibre is endothermic in nature, the sorption is still spontaneous as shown by the negative value of Gibbs free energy of the system that decreases. The ΔG values varied from -6.315 to $-10.095\,\mathrm{kJ\,mol^{-1}}$ for temperature increases from 299 to 339 K. The ΔG values increased most with increasing temperature (e.g. from -13.985 to $-20.887\,\mathrm{kJ\,mol^{-1}}$ in the temperature range of 299–339 K for methylene blue concentration of $70\,\mathrm{mg\,L^{-1}}$), which indicates that the adsorption of methylene blue on palm kernel fibre becomes more favorable at higher temperatures. On the other hand, increasing loading of methylene blue produced a reduction in the ΔG values at a particular temperature (e.g. ΔG values from -13.985 to $-7.425\,\mathrm{kJ\,mol^{-1}}$ at concentrations ranging from 70 to $150\,\mathrm{mg\,L^{-1}}$ at 299 K) indicating that sorption becomes less favorable with increasing dye loading.

4. Conclusion

Palm kernel fibre is a waste product of palm oil production. This study has revealed that palm kernel fibre is an effective sorbent for methylene blue sorption from solution at the temperature range used in this study. Temperature increase between 299 and 339 K produced an increase in equilibrium sorption form 217.95 to $223.41\,\mathrm{mg\,g^{-1}}$. The pseudo-second-order model best described the sorption and was applied in the determination of rate constants of sorption. The isotherm data obtained at varying temperatures (299–339 K) were described by the Langmuir equation. Increase in reaction temperature also increased the monolayer capacity palm kernel fibre from 217.95 to $223.41\,\mathrm{mg\,g^{-1}}$. The equilibrium sorption capacities obtained by the pseudo-second-order were quite close to Langmuir capacity values.

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