



Kinetics of adsorption of methylene blue onto activated carbon prepared from palm kernel shell

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ABSTRACT

The kinetics of adsorption of methylene blue from aqueous solution onto activated carbon prepared from palm kernel shell has been investigated. The time dependent studies showed a rapid adsorption in the first ten minute. A batch sorption model based on the assumption of the pseudo first and second order mechanism, were applied to predict the rate constants. The adsorption process follows the pseudo-second order kinetic, having a correlation coefficient in the range between 0.98 and 1. The pseudo second order rate constant k_2 was found to generally decrease from 1.79 to 4.5×10^{-2} as the initial concentration increased from 5 to 25 ppm but increased from 4.9×10^{-2} to 2.3×10^{-1} with increased temperature, suggesting that the adsorption process is endothermic. Intra-particle diffusion was confirmed as one of the rate determining steps; as such the adsorption mechanism is controlled by particle diffusion rather than film diffusion.

INTRODUCTION

The removal of dye from wastewater, particularly, by activated carbon has been reported widely. However, a survey of literature revealed that methylene blue has been used particularly for adsorption studies, not only because of its environmental concern but also for the fact that it has been recognized as a model adsorbate for the removal of organics [1]. Methylene blue is used as model adsorbate for adsorption of organic because of its known strong adsorption to activated carbons. In spite of this, the specific mechanism by which the adsorption of methylene blue takes place on activated carbons is still ambiguous [2]. Kinetics is concerned fundamentally with the details of the process whereby a system gets from an initial state to final state and the time required for the transition, hence it gives insight about the mechanism of adsorption. According to Demirbas *et al.*, [3], the study of adsorption dynamics describes the solute uptake rate and evidently the rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of adsorption at solid-liquid interface may be controlled by several independent processes, which normally act in conjunction, and involve transport phenomena and chemical

reactions such as bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorptions) and intra-particle diffusion [4,5]. Several models have been used by a number of authors to ascertain the kinetics and mechanism of adsorption onto activated carbon surface. The availability of the kinetic model equations for the study of adsorption process in activated carbon permits a rational approach to study the mechanism of the adsorption process. It has been reported that over 25 kinetic models has been referenced in available literature, all attempting to describe quantitatively the kinetic behavior during the adsorption process [6]. Each adsorption kinetic model has its own limitation and derived according to certain initial conditions based on certain experimental and theoretical assumptions [6]. Two of the most used empirical equations worth mentioning are the pseudo first and second order. The aim of this study is to establish the mechanism of adsorption of methylene blue onto the prepared activated carbon from the kinetic study approach.

MATERIALS AND METHODS

Experimental

Laboratory grade methylene blue (MB) supplied by merck was use without further purification for the preparation of synthetic aqueous solution. The stock solution was prepared by dissolving 0.5 g in 1000 cm³ of distilled water. Serial dilutions were made to obtain the required lower concentrations in the range of 5 to 25 ppm. The initial concentration was ascertained before each experimental run. The concentration of MB in the aqueous solution was determined at λ_{\max} of 660 nm using UV-visible spectrophotometer (Helios γ). For each experiment, 25 cm³ of methylene blue solution of known initial concentration and a 0.2 g of activated carbon were taken in a 150 cm³ Erlenmeyer flasks with air tight stopper. This mixture was agitated in a temperature controlled shaker water bath, at a constant shaking speed. The flasks were agitated for a time interval of 10, 20, 30, 40, 50, 60 minutes in order to study the kinetics of the adsorption process. The initial concentration was varied from 5 to 25 ppm while the pH for the adsorbate adsorbent mixture before agitation was maintained at 7.0. Equilibrium studies was also carried out at temperature of 30, 40, 50, and 60 °C in order to study the influence of temperature on the rate of adsorption.

The percentage of methylene blue adsorbed and the amount adsorbed were calculated as [1]:

$$\% \text{ adsorbed} = 100 (C_0 - C_e) / C_0 \dots\dots\dots 1$$

Where C_0 is the initial concentration of the adsorbate (ppm) and C_e is the equilibrium concentration (ppm).

$$\text{Amount adsorbed, } q_e = V (C_0 - C_e) / m \dots\dots\dots 2$$

Where m (g) is the weight of activated carbon used for the adsorption studies and V (cm³) is the volume of the adsorbate.

RESULTS AND DISCUSSION

3.1.1 Effect of contact time and initial concentration on adsorption of MB onto the activated carbon

Figure 1 showed the percent methylene blue adsorbed at different initial concentration at varying contact time. It is seen that the percent adsorbed increased with contact time.

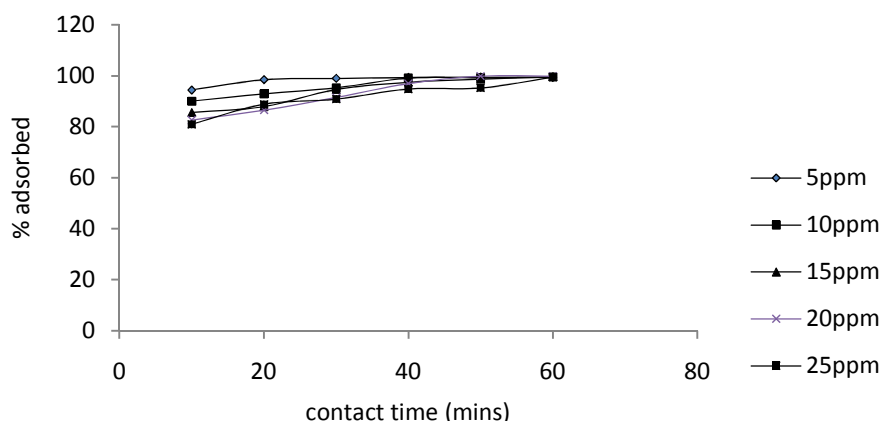


Figure 1 Effect of contact time and initial conc on adsorption of MB onto AC

The adsorption process is characterized by a rapid uptake of the adsorbate as shown by the curves. The adsorption rate however increased marginally after the first ten minutes to a near constant value with increased contact time. This trend agrees with the report of other investigators [7, 8, 9]. The percent adsorbed was maximum at 50 minutes at most initial concentration, hence 50 minutes was the optimum contact time for the adsorption of methylene blue onto the prepared carbon. The optimum concentration for the adsorption of MB onto the prepared activated carbon was found to be 20 ppm. The optimum concentration of dye refers to the concentration at which the maximum removal of dye was noticed [8]. The percentage removal, however, decreased with increase in initial concentration of the methylene blue dye. This may be attributed to lack of available active sites required for the high initial concentration of the dye [8]. The adsorption sites took up the available solute more quickly at low concentrations [10]. The percent adsorbed decreased from 94 to 80 percent after the first ten minutes of contact of the MB with the adsorbent as the initial concentration increased from 5 to 25 ppm. At the optimum contact time of 50 minutes, the percent adsorbed decreased from 99 to 95 percent while the amount adsorbed increased from 1.24 to 5.95. It is generally observed that the amount adsorbed increased with increase in contact time and initial concentrations. Similar trend has been reported in literature [9, 11].

3.1.2 Effect of temperature on adsorption kinetics of MB onto the prepared activated carbon:

The effect of temperature on the removal of methylene blue by the prepared activated carbon is presented in Figure 2.

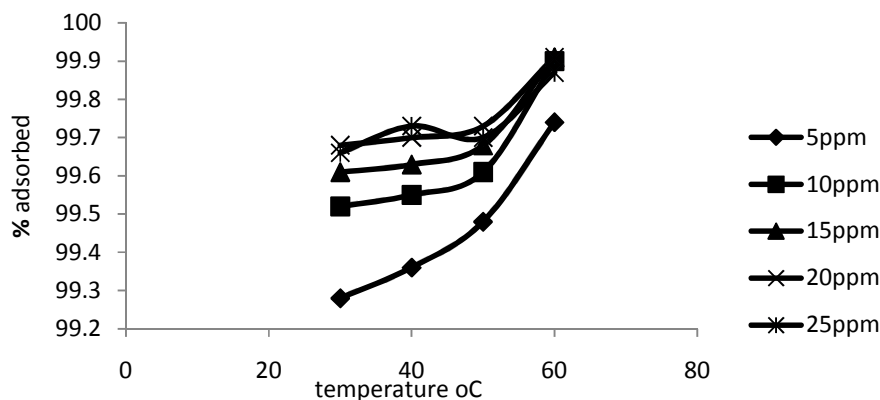


Figure 2. Effect of temperature on adsorption of MB onto activated carbon

The result generally showed that the percent adsorbed increased with increase in temperature at all initial concentrations as shown by the rising curves (Figure 2). This is characteristic of endothermic process and indicate that adsorption of MB onto the adsorbent was enhanced at higher temperature. The percentage adsorbed increased from 99.28 to 99.74 as the temperature increased from 303 to 333 K.

3.2 Kinetic studies:

3.2.1 Pseudo first order equation (Largergren model)

The Largergren model, proposed in 1898, assumes a first order adsorption kinetics and can be represented by the equation [3, 12]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots\dots\dots 3$$

Where: q_e and q_t are adsorption capacity at equilibrium and at time t , respectively (mg.g^{-1}), k_1 is the rate constant of pseudo first order adsorption (min^{-1}).

After integration and applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_e$, the integrated form becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots 4$$

The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively [3]. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter $k_1(q_e - q_t)$ does not represent the number of available sites and the parameter $\log(q_e)$ is an adjustable parameter and often found not equal to the intercept of the plot $\log(q_e - q_t)$ versus t , whereas in true first order, $\log(q_e)$ should be equal to the intercept [12].

Figure 3 and 4 depict the pseudo-first order plots at different initial concentration and temperatures respectively.

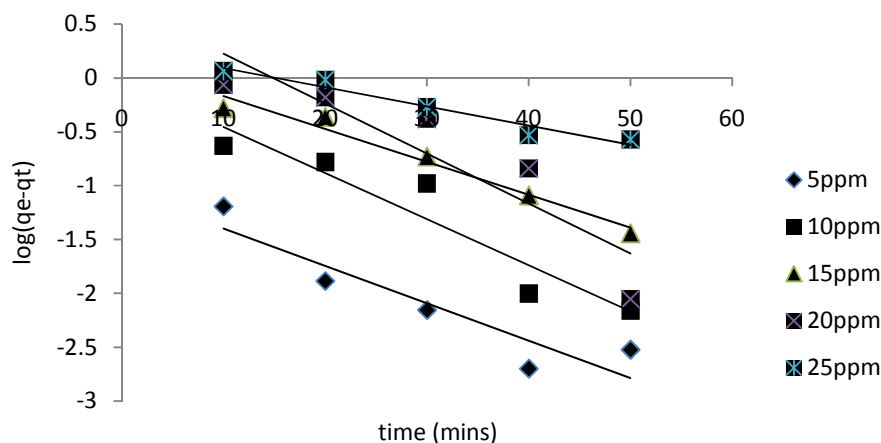


Figure 3. Pseudo First order kinetic model plot at different initial conc

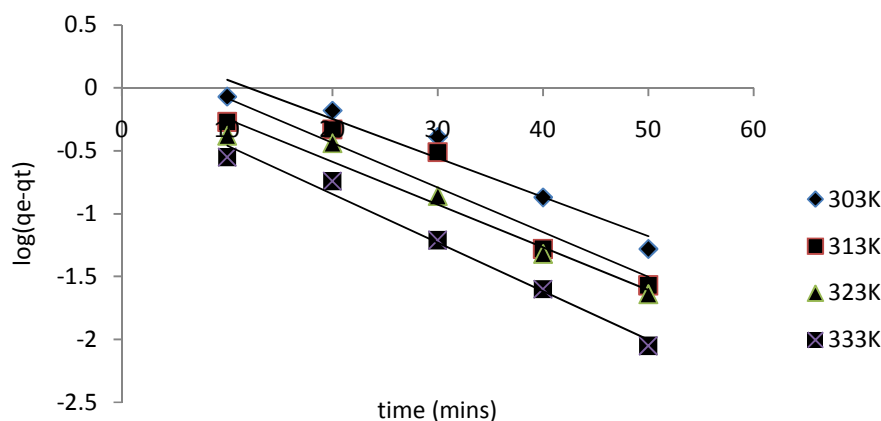


Figure 4. Pseudo First order kinetic model plot at different temperatures

The pseudo first order rate constant, k_1 ranged between 3.9×10^{-2} to 9.7×10^{-2} (Table 1). The result showed clearly that k_1 is independent of initial concentration and experimental temperature. Similar result has been presented in literature [1, 3]. However, the experimental adsorption capacity was observed to increase with increased initial concentration and temperature (Table 1).

Table 1 The constant parameters for the pseudo First-order kinetic model

| Temp (K) | Initial Conc (ppm) | K (min ⁻¹) (10 ⁻²) | (qe) _{exp} (mgg ⁻¹) | (qe) _{cal} (mgg ⁻¹) | R ² | SSE (%) |
|----------|--------------------|--|--|--|----------------|---------|
| 303 | 5 | 6.00 | 1.24 | 0.057 | 0.71 | 5.94 |
| | 10 | 9.70 | 2.49 | 0.94 | 0.89 | |
| | 15 | 6.90 | 3.74 | 1.37 | 0.96 | |
| | 20 | 9.20 | 4.98 | 3.89 | 0.92 | |
| | 25 | 3.90 | 6.22 | 1.86 | 0.95 | |
| 313 | 20 | 8.10 | 4.98 | 1.88 | 0.89 | |
| 323 | 20 | 7.80 | 4.99 | 1.24 | 0.96 | |
| 333 | 20 | 8.80 | 5.00 | 1.18 | 0.98 | |

The experimental amount adsorbed ranged from 1.24 at initial concentration of 5 ppm to 6.22 mg/g at initial concentration of 25 ppm. It varied only slightly from 4.98 at 303 K to 5.00 at 333 K (Table 1).

The pseudo second- order equation

The pseudo second-order adsorption kinetic rate equation is expressed as [3]:

$$\frac{dq_t}{dt} = k_2(qe - q_t)^2 \dots\dots\dots 5$$

Where: k_2 is the rate constant of the pseudo second order adsorption (g.mg⁻¹.min⁻¹).

For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_e$, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \dots\dots\dots 6$$

Equation (6) can be rearranged to the linear form as below (Equation 7):

$$\left[\frac{t}{q_t} \right] = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \dots\dots\dots 7$$

If the initial adsorption rate, h (mg.g⁻¹.min⁻¹) is:

$$h = k_2 (qe) \dots\dots\dots 8$$

then equation (7) become:

$$\left[\frac{t}{q_t} \right] = \frac{1}{h} + \frac{1}{q_e} (t) \dots\dots\dots 9$$

The plot of (t/q_t) and t of equation (9) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The fit of the experimental data to pseudo second order kinetic model at different initial concentration and temperature are shown in Figure 5 and 6 respectively. The constant parameters are shown in Table 2.

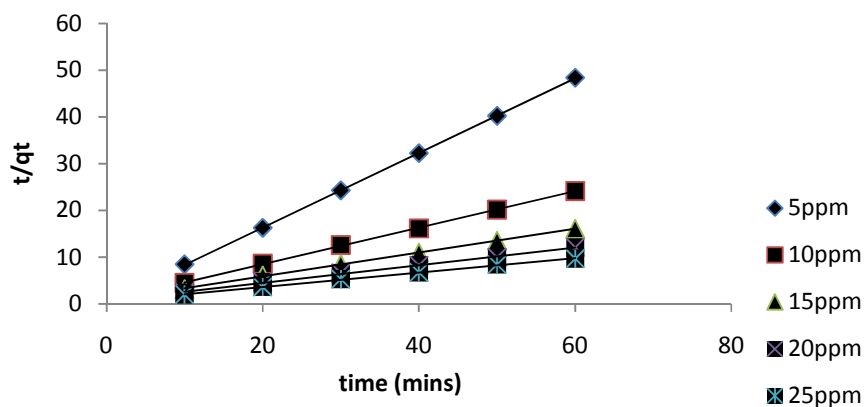


Figure 5 Pseudo Second order kinetic plot at different initial conc

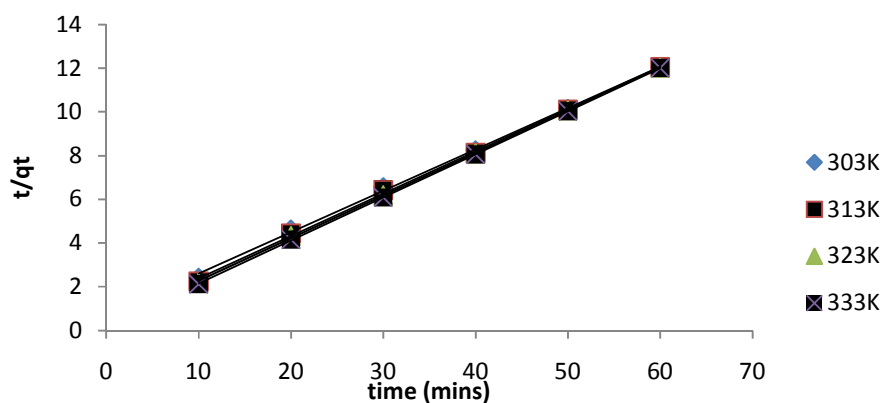


Figure 6. Pseudo Second order kinetic model plot at different temperatures

Table 2 The constant parameters for the pseudo second-order kinetic mode

| Temp (K) | Initial Conc (ppm) | K ₂ | (qe) _{exp} (mgg ⁻¹) | (qe) _{cal} (mgg ⁻¹) | h (mg/g mins) | R ² | SSE (%) |
|----------|--------------------|------------------------|--|--|---------------|----------------|---------|
| 303 | 5 | 1.79 | 1.24 | 1.26 | 2.82 | 1 | 0.045 |
| | 10 | 2.2 x 10 ⁻¹ | 2.49 | 2.56 | 1.45 | 0.99 | |
| | 15 | 8.8 x 10 ⁻² | 3.74 | 3.92 | 1.35 | 0.99 | |
| | 20 | 4.9 x 10 ⁻² | 4.98 | 5.32 | 1.39 | 0.99 | |
| | 25 | 4.5 x 10 ⁻² | 6.22 | 6.49 | 1.91 | 0.99 | |
| 313 | 20 | 8.1 x 10 ⁻¹ | 4.98 | 5.18 | 2.17 | 0.89 | |
| 323 | 20 | 1.2 x 10 ⁻¹ | 4.99 | 5.13 | 3.15 | 0.96 | |
| 333 | 20 | 2.3 x 10 ⁻¹ | 5.00 | 5.08 | 5.81 | 0.96 | |

The value of the pseudo second order rate constant k_2 was found to generally decrease from 1.79 to 4.5×10^{-2} as the initial concentration increased from 5 to 25 ppm. Increasing MB concentration in solution seems to reduce the diffusion of MB in the boundary layer and to enhance the diffusion in the solid. The value of k_2 , on the other hand, increased from 4.9×10^{-2} to 2.3×10^{-1} as the temperature increases, confirming that the adsorption process is endothermic in nature. The increase in value of k_2 with temperature is due to increased mobility of the MB solute and an enhanced diffusion at higher temperature. This agrees with the value of the initial sorption rate indicated by the value of 'h'. The value of h increased from 1.39 to 5.81 as the temperature increased from 303 to 333 K, as shown in Table 2. It can also be seen from the Table 2 that the equilibrium sorption capacity $q_{e(cal)}$ increased from 1.24 to 6.22 and from 4.98 to 5.00 as the initial concentration and temperature varied from 5-25 ppm and 303 to 333 respectively.

Test of kinetic models:

The sum of error squares (SSE,%) is one method which has been used in literature to test the validity of each model that has been used. The sum of error squares is given as [1]:

$$SSE(\%) = \sqrt{\sum \frac{[(qe)_{exp} - qe(cal)]^2}{N}} \dots \dots \dots 10$$

Where N is the number of data points.

The values of SSE (%) for the pseudo first and pseudo second kinetic models are given in Table 1 and 2 respectively. It can be seen that the SSE (%) value is lower for the second order kinetic model (0.045) than that for the pseudo order first model (5.94). This confirms a better applicability of the pseudo second order model.

The correlation coefficient for the pseudo first order ranged between 0.73 and 0.98 whereas the value for the second order ranged between 0.98 and 1. The higher the correlation coefficient and the lower the SSE (%) value, the better the goodness of fit to the model. The correlation coefficient indicates that the experimental data best fitted into the pseudo second order and suggest that the process of adsorption follows pseudo second order kinetics.

Tables 1 and 2 also showed the $(q_e)_{\text{exp}}$ and the $(q_e)_{\text{cal}}$ for the two models. It can be observed that the $(q_e)_{\text{exp}}$ differs significantly from $(q_e)_{\text{cal}}$ for the first order model, whereas the values are much more closer for the pseudo second order model. This again, indicates that the experimental data follows the pseudo second order model. Similar report has been presented in literature for adsorption of MB onto bamboo based activated carbon [1, 13].

The intra-particle diffusion model

The possibility of intra-particle diffusion of MB onto the prepared activated carbon was investigated using the intra-particle diffusion model [8].

$$qt = K_p t^{1/2} + C \dots\dots\dots 11$$

Where: qt is the amount of dye adsorbed (mg g^{-1}) at time t ; C is the boundary layer thickness and K_p is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). The plots of the amount adsorbed, qt versus $t^{1/2}$ at different initial concentration and temperatures are shown in Figure 7 and 8 respectively. The intra-particle diffusion constants at different initial concentration and different temperatures are shown in Table 3.

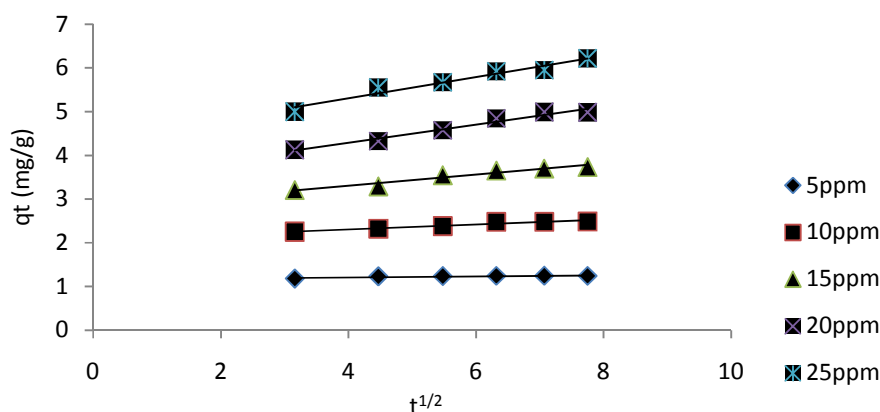


Figure 7. The intra particle diffusion plots for the adsorption of MB by sample C1 at different initial concentrations

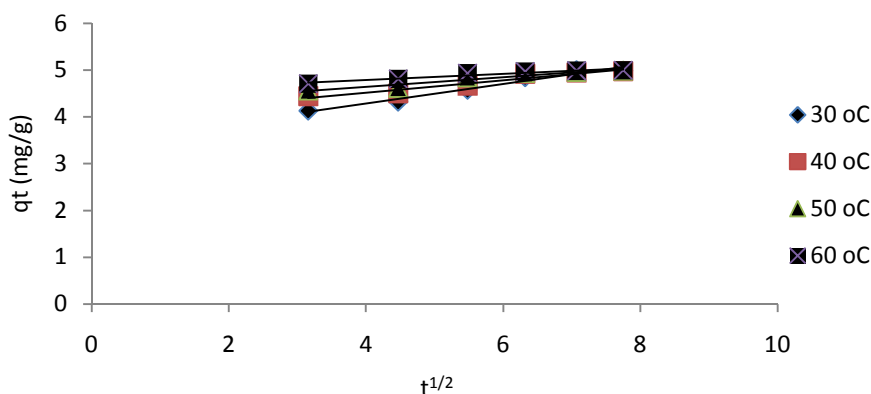


Figure 8. intra particle diffusion plots for the adsorption of MB at different temperatures

Table 3 The intra-particle diffusion constants at different initial concentration and different temperatures

| Temp (K) | Initial Conc (ppm) | Kp (min ^{-1/2}) mgg ⁻¹ | C | R ² |
|----------|--------------------|---|------|----------------|
| 303 | 5 | 0.012 | 1.16 | 0.69 |
| | 10 | 0.056 | 2.08 | 0.94 |
| | 15 | 0.13 | 2.08 | 0.96 |
| | 20 | 0.21 | 3.45 | 0.96 |
| | 25 | 0.24 | 4.34 | 0.95 |
| 313 | 20 | 0.13 | 3.98 | 0.92 |
| 323 | 20 | 0.10 | 4.23 | 0.92 |
| 333 | 20 | 0.004 | 4.53 | 0.92 |

The high correlation coefficient indicates the presence of intra-particle diffusion as the rate determining step. The correlation coefficient ranged from 0.69 to 0.96 as the initial concentration varied from 5 to 25 ppm, but varied from 0.92 to 0.96 as the temperature of adsorption varied from 303 to 333 K.

CONCLUSION

The adsorption of methylene blue onto palm kernel shell based-activated was investigated in this research work. The adsorption process followed a pseudo-second order kinetic model. The result showed that intra-particle diffusion is one of the rate determining steps, as such the adsorption mechanism is controlled by particle diffusion rather than film diffusion. It is also observed that the rate of adsorption increased with increase in experimental temperature. This suggested that more MB were adsorbed at higher temperature and implied that the adsorption process was endothermic in nature.

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