

First online: 15 August 2017

Modeling of Adsorption Isotherms for Methylene Blue Sorption onto Fly Ash Modified with Hydrochloric Acid

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Abstract-Batch adsorption experiments were conducted to investigate equilibrium, kinetic and thermodynamics of the sorption of Methylene Blue onto Fly Ash modified with various concentrations of hydrochloric acid (FAHC-4, FAHC-3, FAHC-2 and FAHC-1). Equilibrium data was best described by the Freundlich isotherm model which suggests adsorbents had heterogeneous surfaces therefore multilayer adsorption occurred in all cases. Fly Ash modified with 1M HCl exhibited the highest adsorption capacity (9.8 mg/L) and Fly Ash modified with 4M HCl had the least adsorption capacity (4.4mg/L). Kinetic data was best described by the pseudo-second-order kinetic model which means adsorption processes were controlled by chemisorption. Boyd kinetic model plots revealed that the rate determining step of each sorption process followed the film diffusion mechanism in which adsorbate ions travelled towards the external surfaces of adsorbents due to electrostatic interactions between chemically modified Fly Ash and adsorbate ions. All adsorption processes were spontaneous because Gibbs free energy of adsorption was negative in all adsorption processes.

Keywords- Adsorption; Langmuir; Freundlich; Intra-particle Diffusion; Boyd

I. INTRODUCTION

Fly ash, a product of coal combustion from coal fired power plants contains a range of toxic substances mostly heavy metals that could leach, spill or leak out of fly ash disposal sites and adversely affect human and environmental health [1]. Residual dyes from textile industries, paper and pulp industries, dye industries, tannery, craft and bleaching industries are considered to introduce a wide variety of organic pollutants into natural water resources [2]. Methylene blue is a heterocyclic aromatic compound, it is a potent cationic dye that could cause cardiovascular, central nervous system, dermatologic gastrointestinal, gastro urinary and hematologic problems [3]. Among the physico-chemical treatment processes, adsorption technology is considered to be one of the most effective and proven methods with potential application in both water and wastewater treatment [4]. It is a well-established technique for the removal of low concentrations of organic pollutants from large volumes of potable water, process effluents, wastewater and aqueous solutions [5].

In recent times, there is a growing concern for sustainable environmental quality and public health, hence this study seeks to investigate the interactions that exist between HCl modified Fly Ash and Methylene Blues which a basic dye.

II. MATERIALS AND METHODS

The fly ash used for this experiment was a class C Fly ash [6] obtained from Sasol plant in South Africa. Methylene blue powder was obtained from Kem Light Laboratories, P.V.T. Ltd, while HCl (97%) was obtained from Sigma-Aldrich, both reagents were used without further purification.

A. Preparation of Modified Fly Ash

10.0 g of unmodified fly ash was weighed into a 250 ml conical flask. 100ml of varied concentrations of hydrochloric acid (1M, 2M, 3M and 4M) was added into separate conical flasks containing 10.0 g unmodified fly ash respectively and each conical flask was covered with a stopper. The slurries were stirred on a magnetic stirrer for 24 hours [7]. The samples were filtered and the solid extracts were oven dried and crushed into fine powders and labeled accordingly [fly ash modified with 4M HCl (FAHC-4), fly ash modified with 3M HCl (FAHC-3), fly ash modified with 2M HCl (FAHC-2) and fly ash modified with 1M HCl (FAHC-1)].

B. Preparation of Adsorbate Solution

0.3 g of analytical grade Methylene blue powder was dissolved in 1000ml of distilled water (300mg/L), this served as the stock solution for serial dilutions into 25mg/L, 50mg/L and 100mg/L respectively.

C. Adsorption Studies

Equilibrium and kinetic adsorption experiments were conducted in batches at room temperature with a Stewart Reciprocating Shaker which was operated at 100 rotations per minute. The contact time was evaluated on samples of 0.2 g of fly ash modified with various concentrations of HCl [i.e. fly ash modified with 4 M HCl(FAHC-4), fly ash modified with 3 M HCl(FAHC-3), fly ash modified with 2 M HCl(FAHC-2) and fly ash modified with 1 M HCl(FAHC-1)] in 10 ml of Methylene blue dye solution, each sample was tested with 25 mg/L, 50 mg/L and 100 mg/L of Methylene blue solution for 60 minutes [8].

100 mg/L of Methylene blue solution was tested on all modified forms of fly ash for 10, 30, 60 and 90 minutes respectively. The substrates were separated from the supernatant with the use of a centrifuging machine, operated for 10 minutes at 30 revolutions per minute [9]. Equilibrium concentrations of the supernatant were analyzed with Jenway 6,300 Spectrophotometer at $\lambda_{\max} = 665$ nm after calibration.

D. Adsorption Isotherms

Methylene blue adsorption on fly ash modified with HCl was analyzed using Langmuir type II, Freundlich and Florry – Huggins Isotherms.

The Langmuir Isotherm is used to characterize the monolayer adsorption, which is represented by the following equation [10].

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abc_e} \quad (1)$$

where q_e = amount of dye adsorbed at equilibrium (mg/L), c_e = equilibrium concentration of dye (mg/L), a and b are Langmuir constants.

The Freundlich Isotherm is applicable to adsorption that occurs on heterogeneous surfaces [11]. The linear form is shown below

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \quad (2)$$

where k_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

The Florry – Huggins Isotherm considers the surface behavior of the adsorbates and adsorbents, the surface covered by the adsorbate can be calculated from the following equation [12]

$$\log \frac{\theta}{c_e} = \log k_a + n \log(1 - \theta) \quad (3)$$

where k_a = equilibrium constant of adsorption, n = number of adsorbates occupying adsorbent site, and θ = degree of surface coverage.

E. Adsorption Kinetics

To determine the adsorption rate constants, the following kinetic models were used, zero-order, first order, second-order, pseudo-second order and third-order kinetic model.

$$\text{Zero – order kinetic model.} \quad q_t = q_o + k_o t \quad (4)$$

$$\text{First – order kinetic model.} \quad \ln q_t = \ln q_o + k_1 t \quad (5)$$

$$\text{Second – order kinetic model.} \quad 1/q_t = 1/q_o + k_2 t \quad (6)$$

$$\text{pseudo – second – order kinetic model.} \quad \frac{t}{q_t} = \frac{1}{h_o} + \left(\frac{1}{q_t}\right) t \quad (7)$$

$$\text{Third – order kinetic model.} \quad \frac{1}{q_t^2} = \frac{1}{q_o^2} + k_3 t \quad (8)$$

F. Adsorption Mechanism

The adsorption mechanisms were investigated using the intra-particle diffusion model and Boyd kinetics model.

1) Intra – Particle Diffusion Model

Intra-particle diffusion model empirically noted that most common functional relationship to adsorption process where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time, t [13], according to this theory

$$qt = K_i t^{1/2} + C \quad (9)$$

where k_i is the intra-particle diffusion rate constant obtain from the intercept. According to Eq. (9), a plot of q_t versus $t^{1/2}$ should yield a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The intercept

gives an idea of the thickness of the boundary layer, i.e. the larger the intercept, the greater the boundary layer effect.

2) The Boyd Kinetics Model

To suggest the slow step involved in the adsorption process [14], the kinetics data were also subjected to Boyd kinetic model of analysis

$$B_t = -0.4977 - \ln(1 - F) \quad (10)$$

where F represents the fraction of solute adsorbed at any time, t (min), as calculated from $F = q_t/q_0$.

III. RESULTS AND DISCUSSIONS

A. Effect of Adsorbate Concentration

The effect of varying the concentration of adsorbate on percentage adsorption was studied by increasing the adsorbate dose from 25mg/L to 50mg/L and 100mg/L for all four forms of modified fly ash. The result shown on Table 1 reveals that an increase in adsorbate dose had positive effects on its uptake, which suggests that an increase in adsorbate concentration promotes the coverage of more active sites on the adsorbent.

TABLE 1 AMOUNT (MG/G) AND PERCENTAGE OF METHYLENE BLUE ADSORBED

Initial concentration of Methylene Blue	FAHC-4		FAHC-3		FAHC-2		FAHC-1	
	mg/g	%Adsorbed	mg/g	%Adsorbed	mg/g	%Adsorbed	mg/g	%Adsorbed
25mg/L	23.2	98	23.2	92.6	23.6	94.4	23.8	95.2
50mg/L	47.2	94.4	47.4	94.8	47.4	94.8	47.4	94.2
100mg/L	95.7	95.7	95.8	95.8	96.1	96.1	96.1	96.1

B. Effect of Contact Time

The effect of contact time on the percentage of Methylene Blue adsorbed was done by carrying out batch adsorption studies, results of the experiments are shown in Table 2 below. 95.8% of 100mg/L Methylene Blue was adsorbed by FAHC-4 after 10 minutes, which means maximum adsorption was achieved within 10minutes followed by slight desorption as the percentage adsorption reduced marginally to 95.4. In like manner FAHC-3, FAHC-2 and FAHC-1 all achieved maximum adsorption within 10 minutes. This shows that equilibration time for all forms of modified Fly Ash used for this study is 10 minutes.

TABLE 2 EFFECT OF CONTACT TIME ON % ADSORPTION

Time (minutes)	FAHC-4 %adsorption	FAHC-3 %adsorption	FAHC-2 %adsorption	FAHC-1 %adsorption
10	95.8	95.6	95.8	95.4
30	95.4	95.4	95.4	95.8
60	95.4	95.4	95.4	95.8
90	95.6	95.8	95.4	95.4

C. Adsorption Isotherms

The sorption data were analyzed with following adsorption models; type II Langmuir, Freundlich and Flory-Huggins models. The parameters of the three adsorption isotherms are shown in Table 3 below.

TABLE 3 PARAMETERS OF THREE ADSORPTION ISOTHERMS FOR METHYLENE BLUE SORPTION ONTO MODIFIED FLY ASH

Isotherm model	Parameter	FAHC-4	FAHC-3	FAHC-2	FAHC-1
Langmuir	S_F	-0.46	-0.394	1.33	3.42
	R^2	0.999	0.998	0.998	0.984
Freundlich	K_F (mg/L)	4.4	4.5	7.1	9.8
	R^2	1.0	0.99	0.985	0.958
Flory-Huggins	K_a	1.6381	1.4603	2.3741	1.9719
	R^2	0.997	0.97	0.8026	0.3004

1) Langmuir Isotherm

Results obtained from the analysis of experimental data with Langmuir isotherm model shows high correlation coefficient (R^2) FAHC-4 (0.999), FAHC-3 (0.995), FAHC-2 (0.998) and FAHC-1 (0.984). However, values for the separation factor(S_F) which determines if an adsorption process is favorable or not [15] reveals that this isotherm model is not favorable because S_F

values for FAHC-4 (-0.46) and FAHC-3 (-0.394) were less than one, while S_F values for FAHC-2 (1.33) and FAHC-1 (3.42) were greater than one.

2) Freundlich Isotherm

The high correlation coefficient (R^2) values obtained for FAHC-4 (1.0), FAHC-3 (0.99), FAHC-2 (0.998), and FAHC-1 (0.958) is an indication that adsorption processes in this study can be effectively described by this model and this may be due to the heterogeneous surface of adsorbents [16]. FAHC-1 exhibited the highest adsorption capacity (9.8mg/L), FAHC-2 (7.1mg/L), FAHC-3 (4.5mg/L) and FAHC-4 (4.4mg/L).

3) Flory–Huggins Isotherm

Low correlation coefficient (R^2) values obtained for FAHC-1 (0.3004) and FAHC-2 (0.8026) indicates noncompliance of the experimental data with this model [17]. On the other hand, high correlation coefficient values were obtained for FAHC-3 (0.97) and FAHC-4 (0.9989) and this shows that the data can be described using this model.

D. Adsorption Kinetics

Five(5) kinetic models were applied in a bid to describe the kinetic processes that took place in each of the batch experiments. Zero-order, first-order, second-order, pseudo-second-order and third-order kinetic models were used. The results of the application of these models for analysis of kinetic data are shown in Table 4.

TABLE 4 CORRELATION COEFFICIENTS FOR KINETIC MODELS OF ADSORPTION OF METHYLENE BLUE ONTO FLY ASH MODIFIED WITH HCL

Kinetic model	FAHC-4 R^2	FAHC-3 R^2	FAHC-2 R^2	FAHC-1 R^2
Zero-order	0.6553	0.1982	0.8231	0.0068
First-order	0.1045	0.1994	0.8238	0.0068
Second-order	0.004	0.3211	0.8231	0.0068
Pseudo-second-order	0.998	0.998	0.997	0.998
Third-order	0.1667	0.1932	0.8231	0.0068

The high correlation coefficient (R^2) obtained for pseudo second-order kinetic model suggests its applicability in describing the adsorption process of Methylene Blue adsorption onto FAHC-4, FAHC-3, FAHC-2 and FAHC-1. This gives a clue that the overall rate of each batch adsorption process was controlled by chemisorption which involves valency forces between adsorbates and adsorbents [18].

E. Adsorption Mechanism

Although the kinetic data were best described by the pseudo-second-order kinetic model, yet it could not identify if the adsorption mechanism was diffusion or kinetically controlled [19].

1) Intra-Particle Diffusion Model

A more appropriate quantitative approach to differentiate between kinetic and diffusion controlled adsorption mechanisms is to perform the square root of contact time analysis by Weber and Moris equation [19-21]

$$q_t = K_i t^{1/2} + C \quad (11)$$

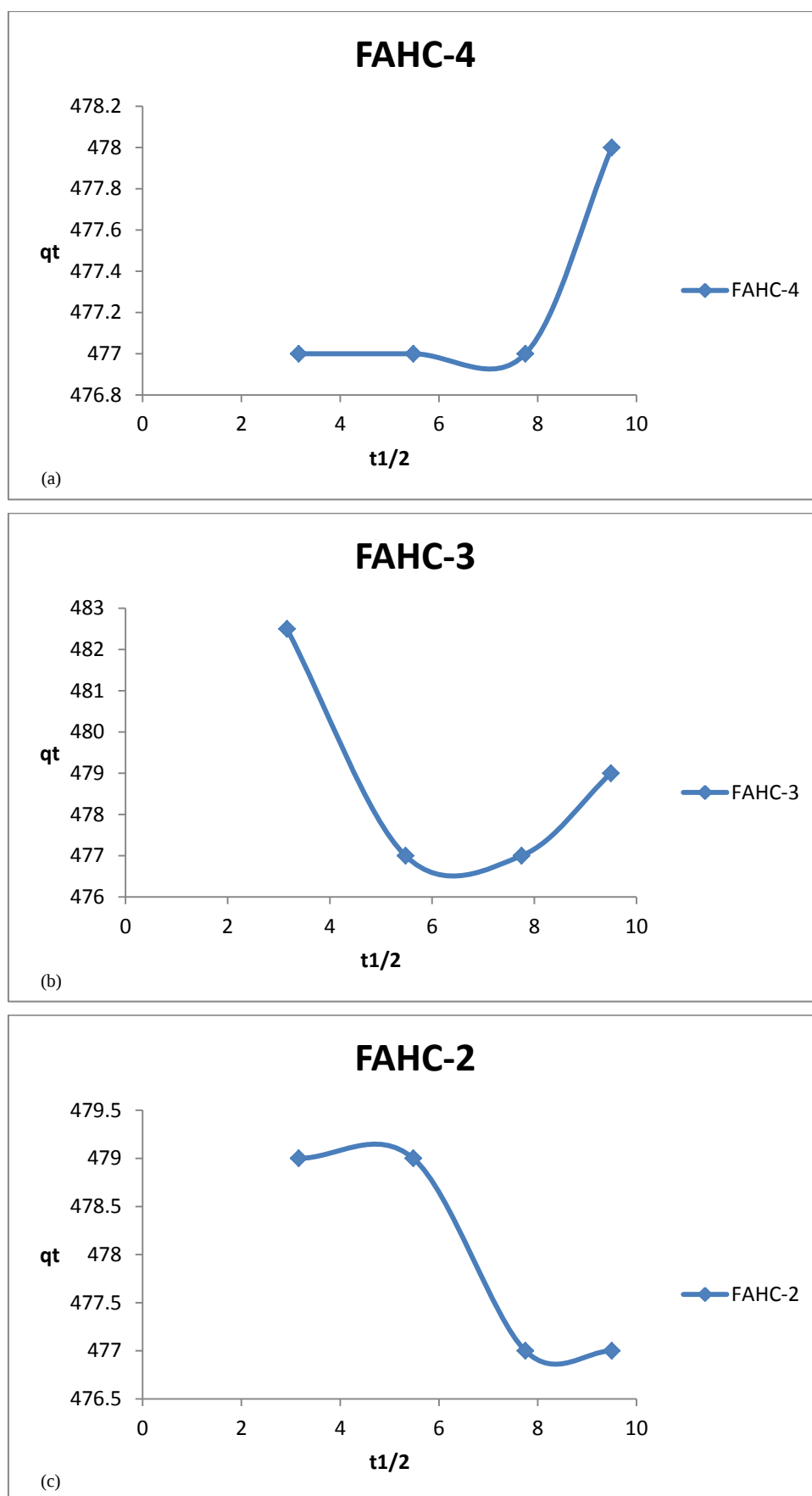
Thus the experimental data were further analyzed using the intra-particle diffusion model (Eq. (11)). The plots of $t^{1/2}$ vs q_t showed on Fig. 1 reveal that none of the plots is a straight line that passed through the origin, and this suggests that the adsorption mechanisms were not intra-particle controlled but they are rather kinetically controlled [22]. However, the plot for FAHC-1 points to the fact that the adsorption mechanism in this case followed two steps, because the first linear segment of the graph followed the boundary layer diffusion mechanism and the other segment represents the intra-particle diffusion, this shows that the adsorption mechanism was not totally controlled by intra-particle diffusion but film diffusion also played a key role [23].

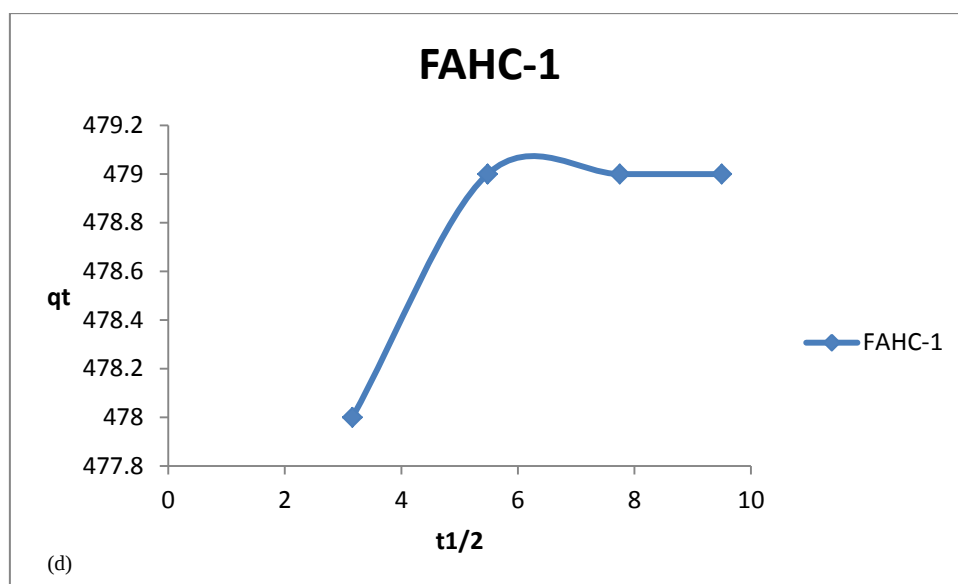
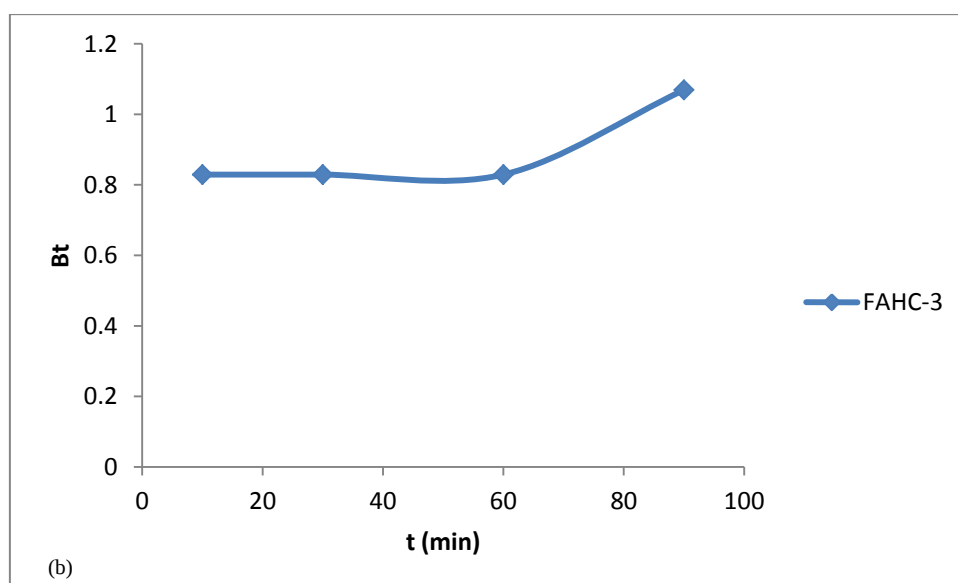
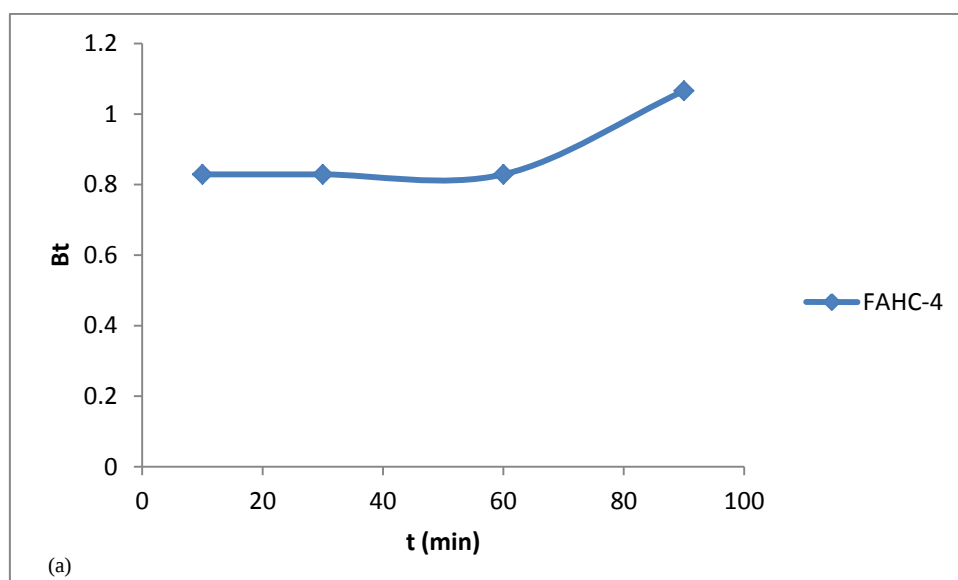
2) Boyd Kinetic Model

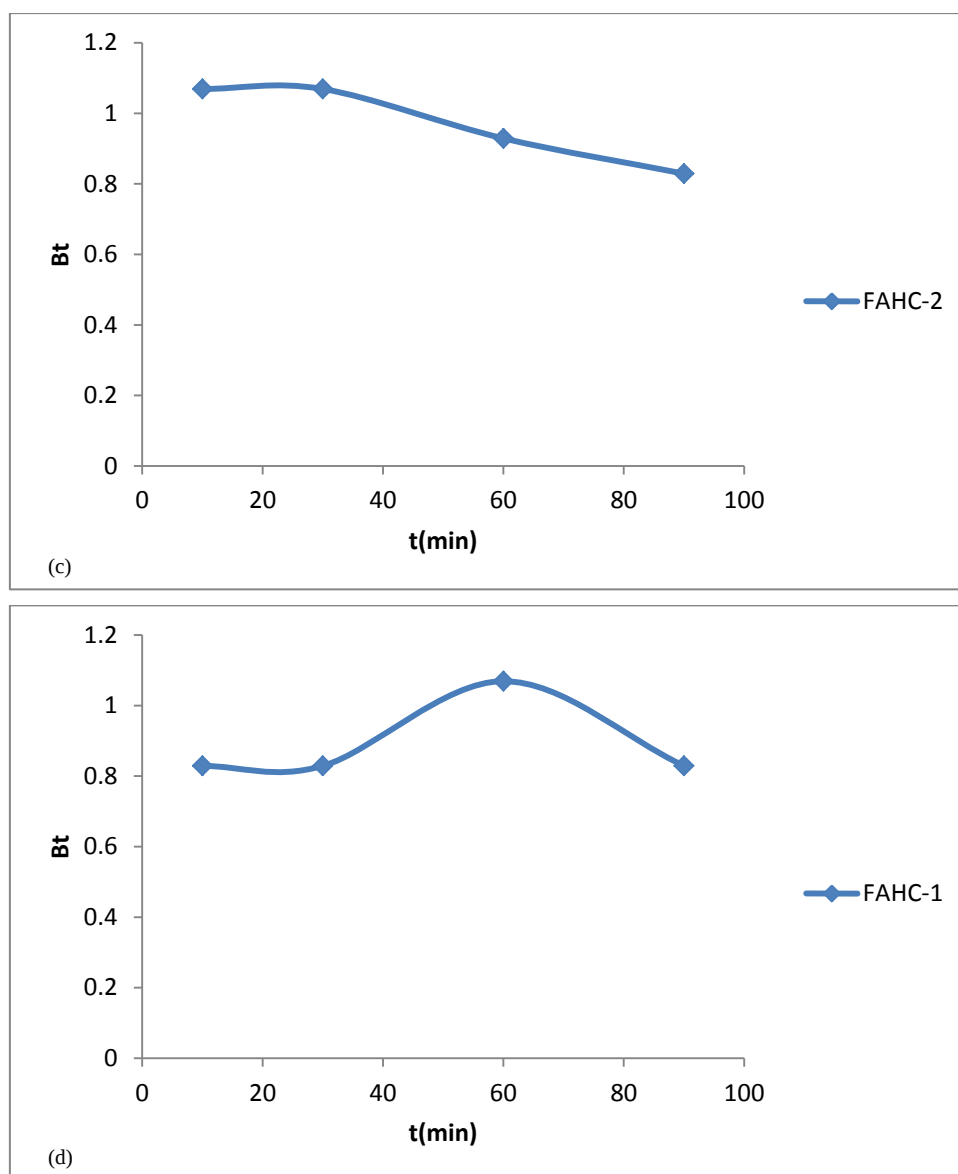
In a bid to determine the actual rate-determining step involved in the adsorption processes, the kinetic data were also analyzed using the Boyd kinetic model according to the following equation [24].

$$B_t = -0.4978 - \ln(1 - q_t/q_o) \quad (12)$$

The plots of B_t against time (minutes) shown in Fig. 2 are not straight lines, and these lines do not pass through the origin therefore the adsorption mechanism is mainly governed by film diffusion.



Fig. 1 Plots of $t^{1/2}$ vs q_t (intra-particle diffusion model)

Fig. 2 Plots of B_t against time (minutes)

F. Gibbs Free Energy Of Adsorption (ΔG_{ads}^0)

The value of apparent Gibbs free energy of sorption (ΔG_{ads}^0) is a fundamental criterion of spontaneity [7]. Therefore, adsorption occurs spontaneously at a given temperature if the apparent Gibbs free energy of adsorption is negative. The Gibbs free energy of Methylene Blue adsorption onto FAHC-4, FAHC-3, FAHC-2 and FAHC-1 were calculated at room temperature (303 K) using the following equation

$$(\Delta G_{ads}^0) = -RT \ln(K_a) \quad (13)$$

Where, R = Universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T = Temperature (303K), K_a = Equilibrium constant of adsorption obtained from Flory-Huggins plot.

The values obtained are shown in Table 5, the figures in the table reveal that the adsorption of Methylene Blue onto FAHC-4, FAHC-3, FAHC-2 and FAHC-1 were all spontaneous.

TABLE 5 GIBBS FREE ENERGY OF SORPTION OF METHYLENE BLUE ONTO FLY ASH MODIFIED BY FAHC-4, FAHC-3, FAHC-2 AND FAHC-1

Modified fly ash sample	K_a	$(\Delta G_{ads}^0) \text{ Jmol}^{-1}$
FAHC-4	1.6281	-1227.9
FAHC-3	1.4603	-953.89
FAHC-2	2.3741	-2178.1
FAHC-1	1.9719	-1710.5

IV. CONCLUSION

This study investigated the equilibrium, kinetic and thermodynamics of the sorption of Methylene Blue onto Fly Ash modified with various concentrations of hydrochloric acid (FAHC-4, FAHC-3, FAHC-2 and FAHC-1). Equilibrium data were best described by the Freundlich isotherm model which suggests the adsorbents used for this study had heterogeneous surfaces thus multilayer adsorptions occurred in all cases [25]. Fly Ash modified with 1M HCl exhibited the highest adsorption capacity (9.8 mg/L) and Fly Ash modified with 4M HCl had the least adsorption capacity (4.4mg/L).

Kinetic data were best described by the pseudo-second-order kinetic model which means the overall rate for each of the adsorption processes was controlled by chemisorption [26]. Adsorption data were further tested with intra-particle diffusion and Boyd kinetic models to determine if sorption processes were diffusion or kinetically controlled. Results from the q_t vs $t^{1/2}$ plots showed that adsorption processes were not diffusion controlled, but the Boyd kinetic model plots revealed that the rate determining step of each sorption process followed the film diffusion mechanism, in which adsorbate ions travelled towards the external surface of adsorbents due to electrostatic interactions between chemically modified Fly Ash and adsorbate ions. The fact that film diffusion played a major role in all the sorption processes suggests that sorption happened mainly by covalent bonding. The Gibbs free energy of adsorption values for all adsorbents used for in this study was negative, therefore adsorption was spontaneous in all cases.

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