

# Dye Sorption Mechanism: A Review Studies on Isotherm, Kinetics and Thermodynamics of Dye Sorption

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**Abstract:** The study of various isotherm, kinetics, and thermodynamics models gives an insight into the mechanisms of sorption of dyes. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface while Thermodynamics is used to evaluate parameters such as free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) change of adsorption. This research gives different isotherm, kinetics and thermodynamics models, their significance, their applicability, how to calculate their constants and how to interpret them.

**Keywords:** Mechanism, Equilibrium, Kinetics, Isotherm and Thermodynamics

## 1. Introduction

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Haghseresht and Lu, 1998). The applicability of an isotherm model is judged by comparing the closeness of its correlation

coefficients,  $R^2$  values, to 1 (Bello *et al.*, 2008). Several isotherm models have been developed to describe the behaviour of adsorption processes. Adsorption kinetics were analyzed using pseudo first order (Bello *et al.*, 2008), pseudo second order (Ho *et al.*, 2000) Elovich (Chien and Clayton, 1980) and intraparticle diffusion (Weber and Morris, 1963; Srivastava *et al.*, 1989) models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients. A high  $R^2$  value (close or equal to 1) indicates that the model successfully describes the kinetics of the adsorption. Thermodynamic parameters such as free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) change of adsorption can be evaluated from temperature parameters using Van't Hoff equation.

## 2. Adsorption Mechanics

### 2.1. Adsorption Isotherms

#### 2.1.1. Langmuir isotherm

The linear form of Langmuir isotherm model is given by the equation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_0} + \frac{1}{q_0 b} \quad (2.1)$$

Where  $C_e$  is the equilibrium concentration of adsorbate (mg/l)

$q_e$  is the amount of adsorbate absorbed per unit mass of adsorbent ( $\text{mgg}^{-1}$ ).

$q_0$  and  $b$  are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively (Bello *et al.*, 2008).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2.2)$$

Where  $C_0$  and  $C_e$  ( $\text{mg l}^{-1}$ ) are concentration of dye at initial and equilibrium respectively,

$V$  is the volume of the solution (l),  $W$  is the mass of adsorbent (g) (Bello *et al.*, 2008).

Langmuir equation is analyzed based on dimensionless equilibrium parameter, which is a constant separation factor  $r$ , to express the essential characteristics of the isotherm (Malik *et al.*, 2004; Abdelwahab *et al.*, 2005). It is a measure of the favorability of the adsorption process (Mittal *et al.*, 2007).

$r$  is calculated thus:

$$r = \frac{1}{1 + bc_0} \quad (2.3)$$

Where  $C_0$  is the initial concentration of sorbate (mg/l)

$b$  is the Langmuir constant

r values indicate the shape of the isotherm. Values of r between zero and one show that the adsorption process is favourable, if its value is one, then the adsorption is linear and if greater than one is unfavourable (Khatri and Singh, 1999; Namasivayam and Yamuna, 1999; and Sumanjit *et al.*, 2008).

### 2.1.2. Freundlich isotherm

The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (Fytianos *et al.*, 2000). The well-known logarithmic form of Freundlich isotherm model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.4)$$

$q_e$  is the amount of adsorbate absorbed per unit mass of adsorbent ( $\text{mgg}^{-1}$ ).

$K_f$  is rough indicator of the adsorption capacity related to the bond energy and  $\frac{1}{n}$  is the adsorption intensity of dye onto the adsorbent or surface heterogeneity (Prasad and Santhi, 2012). If  $\frac{1}{n}$  is less than 1, the adsorption is favourable but if it is greater than 1, the adsorption is unfavourable (Bello *et al.*, 2008).

### 2.1.3. Temkin isotherm

The Temkin isotherm assumed that because of the adsorbate – adsorbent interactions, the energy of adsorption will decrease linearly with coverage (Sekar *et al.*, 2004). The Temkin model is expressed as:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (2.5)$$

$q_e$  is the amount adsorbed at equilibrium ( $\text{mg/g}$ )

$C_e$  is the equilibrium concentration of the adsorbate

$A_T$  and  $b_T$  are Temkin constants

R is the universal gas constant ( $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ )

T is the temperature in Kelvin

### 2.1.4. Dubinin-Radushkevich (D-R) isotherm

The Dubinin- Radushkevich equation is given as (Mittal *et al.*, 2007):

$$\ln q_e = \ln X_m - K_E^2 \quad (2.6)$$

Where  $q_m$  is the maximum sorption capacity ( $\text{mg/g}$ )

K is the activity coefficient related to the mean sorption energy ( $\text{mol}^2/\text{J}^2$ )

$\varepsilon$  is Polanyi potential given by

$$\varepsilon = RT \ln(1 + q_e^{-1}) \quad (2.7)$$

Where R is gas constant and T is temperature in Kelvin. The slope and intercept of a linear plot of  $\ln q_e$  versus  $\varepsilon^2$  are K and  $\ln q_m$  respectively.

Energy of sorption, E, can be evaluated from the values of, K, the activity coefficient, thus:

$$E = (2 K)^{-1/2} \quad (2.8)$$

$q_m$  may also represent the total specific micropore volume of the sorbent or the theoretical adsorption capacity (Erdemet *al.*, 2004).

The term E is defined as the free energy change when 1 mole of dye is transferred to the surface of the solid from infinity in solution. The value of E is very useful in predicting the type of adsorption. If the value is less than 8  $\text{KJmol}^{-1}$ , then the adsorption is physical in nature due to weak vanderwaals forces and if it is between 8-16  $\text{KJmol}^{-1}$  then the adsorption is due to exchange of ions (Islam and Patel, 2007; Caperkaya and Cavas, 2008).

#### 2.1.5. Harkin-Jura isotherm

$$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log c_e \quad (2.9)$$

$q_e$  is the amount adsorbed at equilibrium (mg/g)

$C_e$  is the equilibrium concentration of the adsorbate

A and B are Harkin-Jura constants

This model takes into consideration the multilayer adsorption, which can be explained by the existence of heterogeneous pore distribution. The equation is (Basar, 2006; Oladoja *et al.*, 2008).

## 2.2. Adsorption Kinetics

### 2.2.1. Pseudo-First order equation

The pseudo-first order equation is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1 t (q_e - q_t) \quad (2.10)$$

Where  $q_t$  is the adsorption capacity at time t ( $\text{mgg}^{-1}$ ) and  $k_1$  is the rate constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ). On integration, setting the boundary conditions between  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the equation becomes:

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t \quad (2.11)$$

Where

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2.12)$$

Where  $C_o$  and  $C_t$  ( $\text{mg}^{-1}$ ) are the concentrations of dye at initial and at any time  $t$  respectively.  $V$  is the volume of the solution (l) and  $W$  is the mass of adsorbent used (g), (Bello *et al.*, 2008).

### 2.2.2. Pseudo-second order equation

The pseudo-second order adsorption kinetic rate equation is expressed (Ho *et al.*, 2000).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.13)$$

Where  $k_2$  ( $\text{gmg}^{-1}\text{min}^{-1}$ ) is the second-order-rate constant of adsorption.

On integration, setting the boundary conditions between  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the following linear form is obtained (Prasad and Santhi, 2012):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.14)$$

The term  $k_2 q_e^2 = h$

Where  $h$  is the initial sorption rate.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2.15)$$

In order to distinguish the kinetics equation based on the concentration of a solution from the adsorption capacity of solids, this second order rate equation has been termed a pseudo-second order model.

If a plot of  $\frac{t}{q_t}$  versus  $t$  is linear, then the sorption process may be described as chemisorption (Ho, 1995), and the pseudo-second order rate constant can be determined experimentally from the plot.

### 2.2.3. Elovich's equation

It is also a rate equation based on adsorption capacity of adsorbents. The linear form of the equation is:

$$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (2.16)$$

where  $\alpha$  is the initial desorption rate ( $\text{mg/gmin}$ ) and  $\beta$  is the desorption constant ( $\text{g/mg}$ ) during any experiments. Plot of  $qt$  versus  $\ln t$  gives a linear relationship with slope of  $1/\beta$  and an intercept of  $(1/\beta)$

$\ln(\alpha\beta)$ . The  $1/\beta$  value reflects the number of sites available for adsorption whereas the value of  $1/\beta \ln(\alpha\beta)$  indicates the adsorption quantity when  $\ln t$  equal to zero (Ho, 2006).

#### 2.2.4. Intra particle diffusion models

A form of intraparticle diffusion model is given by (Weber and Morris, 1963; Srivastava *et al.*, 1989; Demirbas *et al.*, 2004):

$$R = k_{id}(t)^a \quad (2.17)$$

Where R is the percentage of the amount adsorbed

t is the contact time (min)

a indicates the mechanism of sorption

$k_{id}$  is the intraparticle diffusion rate constant ( $\text{min}^{-1}$ ). It can also be taken as a rate factor i.e. percent of adsorbate removed per unit time (Demirbas *et al.*, 2004).

A linear form of equation (2.17) is:

$$\log R = \log k_{id} + a \log t \quad (2.18)$$

If the rate of a sorption process is governed by intra-particle diffusion, a plot of  $\log R$  versus  $\log t$  should be linear, and the constants  $k_{id}$  and “a” can be evaluated from the intercept and slope respectively. High values of  $k_{id}$  indicate an enhancement in the rate of adsorption while a large “a” value implies a better adsorption mechanism (Demirbas *et al.*, 2004).

#### 2.2.5. Weber–Morris model

Another type of intraparticle diffusion equation was described by Weber and Morris (1963). If intraparticle diffusion has a significant presence in an adsorption process, the approach towards equilibrium is controlled by the diffusion,  $(\frac{D_t}{r^2})^{0.5}$ . The equation developed is expressed as (Marungrueng and Pavasant, 2007; Oladoja *et al.*, 2008):

$$q_t = f\left(\frac{D_t}{r_p^2}\right) = k_d t^{0.5} \quad (2.19)$$

Where  $q_t$  is the amount of adsorbate adsorbed (mg/g)

$r_p$  is the particle radius

$D_t$  is the effective diffusivity of solutes within the particle ( $\text{m}^2\text{min}^{-1}$ )

$k_d$  is intraparticle diffusion rate constant ( $\text{mgg}^{-1}\text{min}^{0.5}$ )

t is the contact time (min)

According to Weber and Morris (1963), a plot of sorption capacity at a given time,  $q_t$ , versus  $\sqrt{t}$  should be a straight line if intraparticle diffusion is involved; and if it is the only rate-determining factor, the line passes through the origin. This is from the equation:

$$q_t = K_d t^{0.5} \quad (2.20)$$

Where  $K_d$  is the intraparticle diffusion rate constant.

However, if the plot has an intercept (i.e. does not pass through the origin), it shows that intraparticle diffusion may not be the only factor limiting the rate of the sorption process (Poots, *et al.*, 1976; Ho and McKay, 2003). Poots *et al.*, (1976), however, proposed that during the early stages of sorption, some boundary layer resistance was involved. The equation was then modified as: (McKay and Poots, 1980; Abia *et al.*, 2006; Igwe and Abia, 2007)

$$q_t = K_d t^{0.5} + C \quad (2.21)$$

Where C depicts the boundary layer thickness (McKay and Poots, 1980).

$K_d$  and C can be obtained from the slope and intercept respectively.

High value of  $k_d$  indicates that particle diffusion mechanism predominates (Igwe *et al.*, 2008).

### 2.3. Thermodynamics of Adsorption

Thermodynamic parameters can be evaluated from temperature parameters using Van't Hoff equation and is given as

$$\Delta G = -RT \ln K_0 \quad (2.22)$$

Where

$$K_0 = \frac{q_e}{C_e} \quad (2.23)$$

Also,

$$\Delta G = \Delta H - T\Delta S \quad (2.24)$$

Therefore,

$$\Delta H - T\Delta S = -RT \ln K_0 \quad (2.25)$$

Linear form

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2.26)$$

Where  $K_0$  is the sorption distribution coefficient,  $\Delta G$  ( $\text{kJmol}^{-1}$ ) is the free energy of adsorption, T (Kelvin) is the absolute temperature, R is the universal gas constant,  $\Delta H$  ( $\text{kJmol}^{-1}$ ) is the heat of

adsorption,  $\Delta S$  ( $\text{kJmol}^{-1}\text{K}^{-1}$ ) is entropy change. Negative values of  $\Delta G$  indicate spontaneous nature of adsorption process, positive values of  $\Delta H$  indicate endothermic nature of the reaction while negative values of  $\Delta H$  indicate exothermic nature of the reaction and positive  $\Delta S$  indicates there is some degree of disorderliness in the system (Hengpeng and Zhijuan, 2010).

### 3. Methodology

#### 3.1. Adsorption Isotherm

The adsorption isotherm data was fitted to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkin-Jura Isotherm models. From the linear form of Langmuir isotherm model given by equation 2.1, a plot of  $\frac{C_e}{q_e}$  against  $C_e$  gives a straight line with  $\frac{1}{q_0}$  as the slope and  $\frac{1}{q_0b}$ , from which  $q_0$  and  $b$  were calculated. Using the logarithmic form of Freundlich isotherm model given by equation 2.4, a plot of  $\log q_e$  against  $\log C_e$  gives a straight line with  $\frac{1}{n}$  as the slope  $\log K_f$  as the intercept, from which  $K_f$  was calculated. Considering the Temkin model expressed in equation 2.5, a plot of  $q_e$  against  $\ln C_e$  gives a straight line with  $\frac{RT}{bT}$  as the slope and an intercept of  $\frac{RT}{bT} \ln A_T$  from where  $b_t$  and  $A_t$  were calculated from the Dubinin- Radushkevich equation given in equation 2.6, a plot of  $\ln q_e$  against  $\varepsilon^2$  gives a slope and intercept of  $K$  and  $\ln q_m$  respectively from  $q_m$  was calculated. Using the Harkin-Jura Isotherm Model given in equation 2.9, a plot of  $\frac{1}{q_e^2}$  against  $\log C_e$  gives a straight line with  $\frac{1}{A}$  as the slope and  $\frac{B}{A}$  as the intercept.

#### 3.2. Adsorption Kinetics

The adsorption Kinetics data was fitted to pseudo 1<sup>st</sup> order, pseudo 2<sup>nd</sup> order, Elovich and Weber-Morris Kinetic models. Using the pseudo-first order adsorption kinetic rate equation expressed in equation 2.10, a plot of  $\ln(q_e - q_t)$  against time gives a straight line with  $-k_1$  as the slope and  $\ln(q_e)$  as the intercept, from which  $q_e$  was calculated. Considering the pseudo-second order adsorption kinetic rate equation expressed in 2.14, a plot of  $\frac{t}{q_t}$  against time gives a straight line with a slope of  $\frac{1}{q_e}$  and an intercept of  $\frac{1}{k_2 q_e^2}$  from which  $q_e$  and  $k_2$  were calculated. Using the Elovich kinetic model equation given in 2.16, a plot of  $q_t$  against  $\ln t$  gives a graph with  $1/\beta$  as the slope and  $1/\beta \ln(\alpha\beta)$  as the intercept from which  $\alpha$  and  $\beta$  were calculated. While from the Weber and Morris equation is expressed in equation 2.21, a plot of  $q_t$  against  $t^{0.5}$  gives a graph with  $k_d$  as the slope and  $C$  as the intercept.

#### 3.3. Adsorption Thermodynamics

From the Thermodynamics data fitted into a plot using Van't Hoff equation given in equation 2.29, a plot of  $\ln K_0$  against  $\frac{1}{T}$  gives a graph with  $-\frac{\Delta H}{R}$  as slope and  $\frac{\Delta S}{R}$  as the intercept from which  $\Delta H$  ( $\text{kJmol}^{-1}$ ) and  $\Delta S$  ( $\text{kJmol}^{-1}\text{K}^{-1}$ ) were calculated.

## 4. Experimental Results and Discussions

### 4.1. Adsorption Isotherm

The isotherm studies of Malachite green was studied by Giwa *et al.*, 2019. The constants obtained from different five isotherm models considered are presented in Table 1. Temkin isotherm has the highest  $R^2$  values (0.967 - 0.980) for all the eight dye systems studied. This implies that, there is a linear relationship between the heat of adsorption and temperature. Furthermore, Temkin model assumes that the decrease in the heat of adsorption of all molecules in a layer with respect to increasing coverage is linear. The maximum monolayer adsorption capacity ranges between 20.00 and 26.32 mg/g. These values are higher than the values given by (Makeswari and Santhi, 2013) for adsorption of malachite green from binary systems (11.76 - 20.41). The value of  $r$  (a dimensionless constant which indicates the type of isotherm) for the systems studied ranges between 0.024 and 0.053. This means that the adsorption is favourable as values greater than one would have implied an unfavourable adsorption, and  $r$  equals to zero indicates an irreversible process (Ho 2003, Chiu and Wang 2009).

**Table 1:** Isotherm parameters for the adsorption of malachite green

ISOTHERM	LANGMUIR				FREUNDLICH			TEMKIN			HARKIN-JURA			DUBININ-RADUSHKEVICH			
ISOTHERM	$R^2$	$q_0$	B	R	$R^2$	$1/n$	$K_f$	$R^2$	$A_T$	$b_T$	$R^2$	A	B	$R^2$	$q_m$	K	E
PARAMETERS																	
DYE SYSTEM																	
MG	0.898	20.41	0.75	0.026	0.922	0.52	8.32	0.968	2.12	319.98	0.846	32.26	0.55	0.924	21.31	$4 \times 10^{-7}$	1.19
MG + MB	0.826	24.39	0.43	0.044	0.916	0.61	7.21	0.979	1.35	249.17	0.828	27.03	0.57	0.842	27.94	$7 \times 10^{-7}$	0.85
MG + CV	0.871	22.73	0.54	0.036	0.929	0.57	7.35	0.979	1.57	269.37	0.854	29.41	0.56	0.886	26.66	$6 \times 10^{-7}$	0.91
MG + RB	0.906	20.00	0.82	0.024	0.922	0.50	8.51	0.967	1.89	292.75	0.846	33.33	0.53	0.845	22.42	$4 \times 10^{-7}$	1.12
MG + MB + CV	0.859	20.83	0.50	0.038	0.893	0.54	6.87	0.968	1.33	288.36	0.809	30.30	0.67	0.875	25.15	$7 \times 10^{-7}$	0.85
MG + MB + RB	0.802	26.32	0.36	0.053	0.923	0.64	6.92	0.980	1.30	246.01	0.836	26.30	0.58	0.870	28.33	$8 \times 10^{-7}$	0.79
MG + CV + RB	0.848	23.81	0.47	0.041	0.918	0.59	7.41	0.980	1.51	267.62	0.829	28.57	0.57	0.880	26.60	$6 \times 10^{-7}$	0.91
MG + MB + CV + RB	0.880	22.22	0.41	0.047	0.941	0.57	6.49	0.975	1.22	278.97	0.882	28.57	0.024	0.902	24.63	$8 \times 10^{-7}$	0.79

The favourability of the sorption processes was also confirmed by the Freundlich constant,  $1/n$ , which is less than one (0.50 - 0.64) for all of them (Table 1). A value greater than 1 would have meant

the adsorption is unfavourable. The value of E (Energy of sorption) in Dubinin- Radushkevich isotherm is low (0.79-1.19), implying that the sorption processes may not involve an ion exchange mechanism as opposed to a higher value of E ( $> k \text{ Jmol}^{-1}$ ) which would have pointed to involvement of ion-exchange.

#### 4.2. Adsorption Kinetics

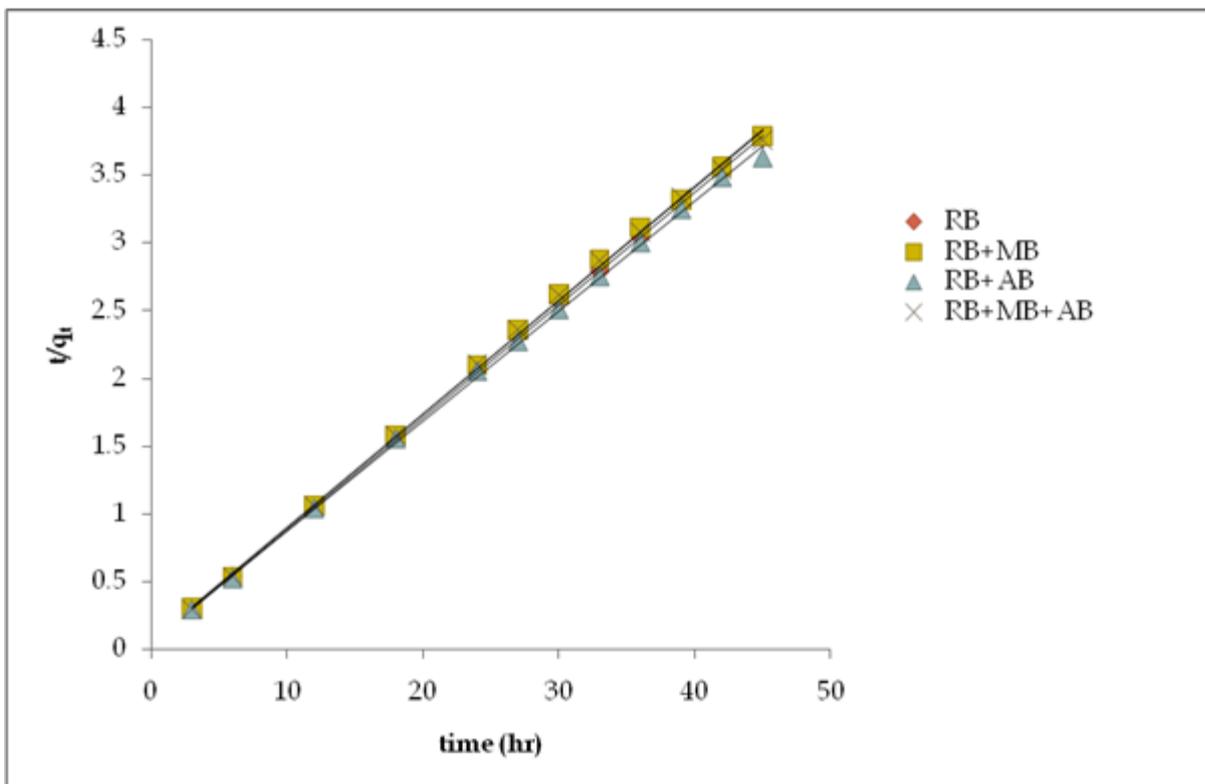
The kinetics constants and other parameters for the adsorption of methylene blue onto SDP in single, binary and ternary dye systems calculated are given in Table 2 (Giwa *et al.*, 2018). The high linear regression coefficient,  $R^2$ , values and the closeness of the equilibrium adsorption capacity,  $q_e$ , calc calculated for Pseudo-second order kinetics model to the experimentally obtained,  $q_e$ , exp, show that the biosorption of methylene blue in single, binary and ternary dye systems by the sawdust of *Parkia biglobosa*, is better described by this model. This, therefore, suggests that the biosorption process involved chemisorption.

The initial rate constant,  $h$ , is higher for the biosorption in the ternary mixture of dyes than for the single and binary systems (Table 2). The results show that the presence of Acid blue dyes may have little or no effect on the initial and even the overall rate of methylene blue uptake by the adsorbent. This suggests that there was no competition between the two dye species. In contrast, the presence of Rhodamine B in both the binary and ternary dye mixtures had significant effect on the Pseudo-second order rate constants, both the initial and overall (Table 2). The guest-guest interaction between methylene blue and Rhodamine B may be repulsive, which may have affected the guest-host relationship between methylene blue and the surface of SDP.

**Table 2.** Kinetic Parameters for Adsorption of Methylene Blue onto PSD Kinetic model First-order kinetics Second-order Kinetics. (Source: Giwa *et al.*, 2018)

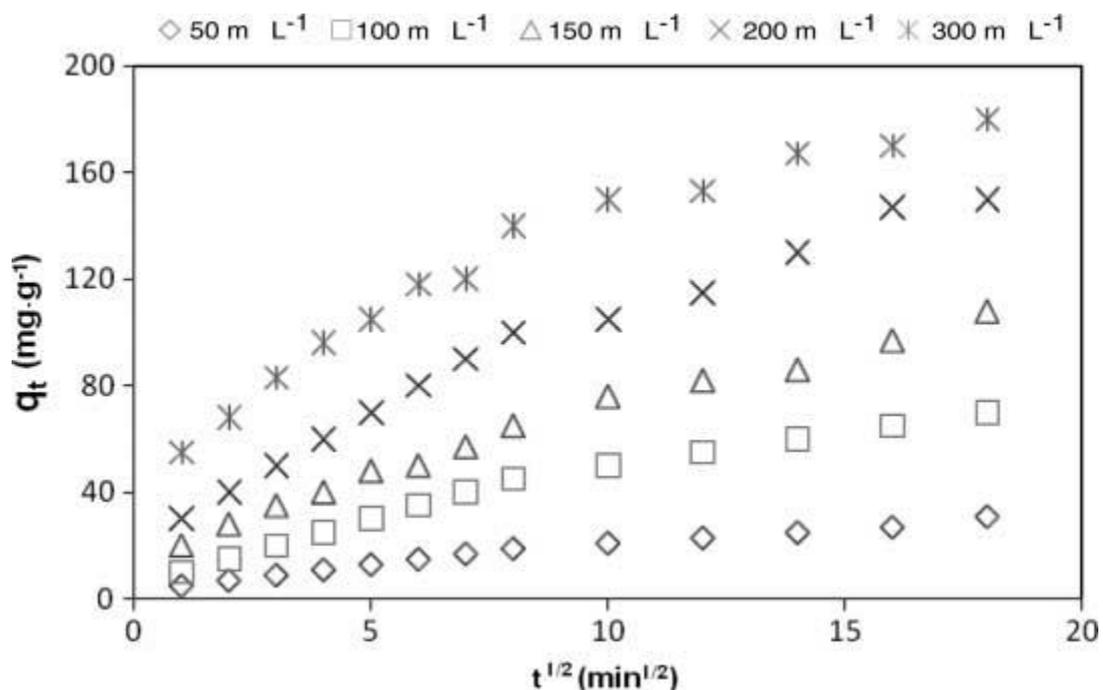
Dye System	$q_e(\text{exp})$	R2	$q_e(\text{calc})$	K1	$\chi^2$	R2	$q_e(\text{calc})$	K2	h	$\chi^2$
MB	24.90	0.951	0.863	0.025	0.93	1.00	25.00	0.10	62.50	$1.6 \times 10^{-5}$
MB+RB	24.92	0.845	0.758	0.029	0.94	1.00	25.00	0.12	76.92	$1.0 \times 10^{-7}$
MB+AB	25.00	0.067	0.372	0.003	0.97	1.00	25.00	0.10	62.50	$3.2 \times 10^{-5}$
MB+RB+AB	24.86	0.914	0.567	0.027	0.96	1.00	25.00	0.16	100.00	$3.2 \times 10^{-5}$

The plots Pseudo second order kinetics for the removal of Rhodamine B from single, binary and ternary dye systems in aqueous solution (Giwa *et al.*, 2015) was given in Fig. 1. The adsorption processes follow pseudo-2nd – order kinetic model which suggest a chemisorption process.



**Fig. 1:** Pseudo-second order kinetics plot for the adsorption of rhodamine B in single, binary and ternary system

In the Intraparticle diffusion studies for the adsorption of CR dye onto AA at different dye concentrations by Bello *et al.*, 2013, the value of  $C$  gives an idea of the thickness of boundary layer, the larger the intercept, the greater the boundary layer effect. From the plots of  $qt$  against  $t^{1/2}$  at various initial CR dye concentrations, multi-linear profiles were observed (Figure 2) indicating that intraparticle diffusion plays a significant role, but it's not the only rate-controlling step. The first and sharper portion is attributed to the boundary layer diffusion of CR dye molecules, whereas the second portion corresponds to the gradual adsorption stage, where intra-particle diffusion was the rate-limiting step. The slope of the second linear portion of the plot was defined as the intraparticle diffusion parameter  $ki2$ . The observed values of  $ki2$  are lower than  $ki1$ , indicating that intra-particle diffusion mainly controls the adsorption rate. However, external mass transfer resistance cannot be neglected, although this is only significant during the initial period.



**Figure 2.** Intraparticle diffusion plots for the adsorption of CR dye onto AA at different dye concentrations (Conditions: 0.2 g adsorbent dosage, 120 rpm, temperature 303 K). (Source: Bello *et al.*, 2013)

#### 4.3. Adsorption Thermodynamics

The thermodynamics study for the adsorption of methylene blue onto SDP in single, binary and ternary dye systems was given by Giwa *et al.*, 2018.  $K_0$  is the sorption distribution coefficient,  $\Delta G$  (kJmol<sup>-1</sup>) is the free energy of adsorption,  $T$  (Kelvin) is the absolute temperature,  $R$  is the universal gas constant,  $\Delta H$  (kJmol<sup>-1</sup>) is the heat of adsorption,  $\Delta S$  (Jmol<sup>-1</sup>K<sup>-1</sup>) is the change in entropy associated with the adsorption. Values for  $\Delta H$  and  $\Delta S$  calculated from the slope and intercept of the plots (Fig. 3), and  $\Delta G$  obtained from equation (11) above for the adsorption of methylene blue from the various adsorbate systems are presented as Table 3.

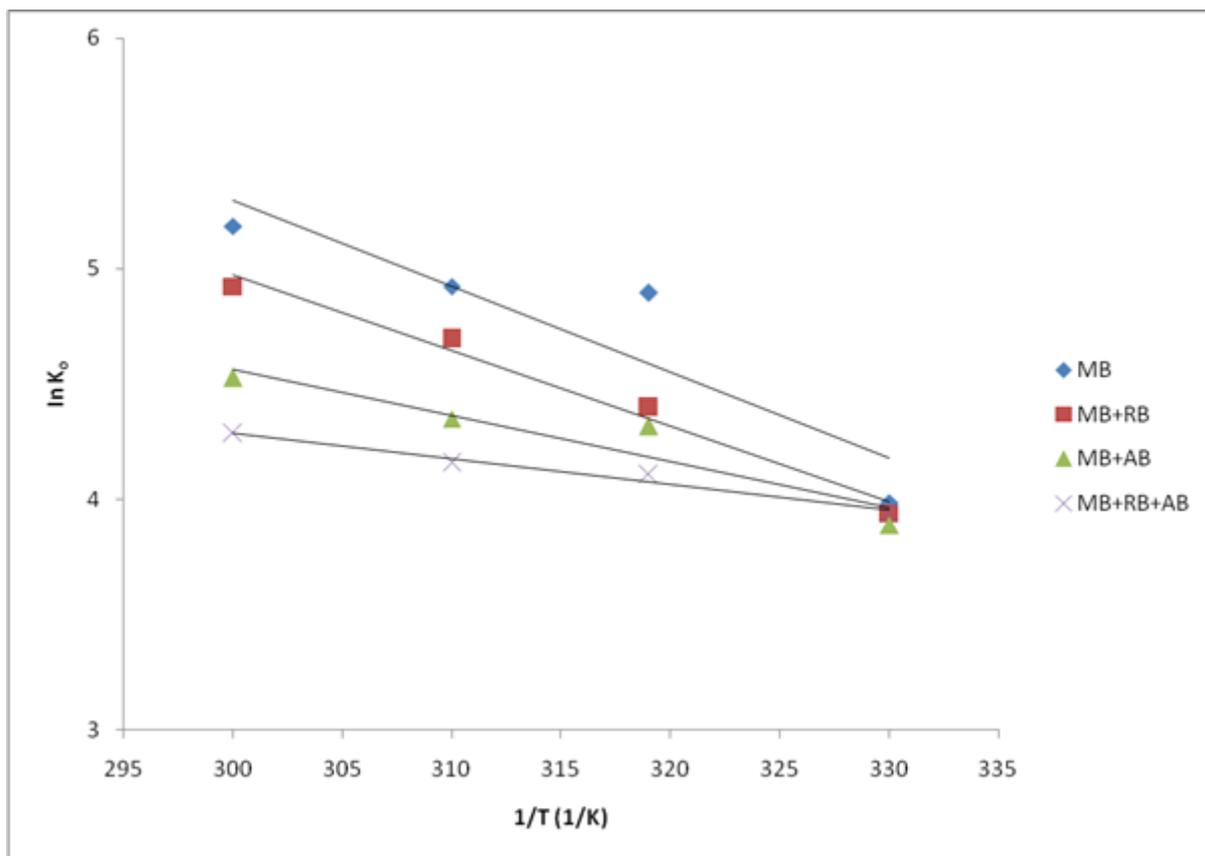
**Table 3:** Thermodynamic Parameters for Adsorption of Methylene Blue onto PSD (Source: Giwa *et al.*, 2018)

Temp	Single system			Binary system (MB+RB)			Binary system (MB+AB)			Ternary system (MB+AB+RB)		
	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)	$\Delta G$	$\Delta H$ (KJ)	$\Delta S$ (J/Kmol)
303				-9928.88			-9795.64			-9928.88		
313	-10040.7	30745.17	136.2665	-11450	27319.8	123.2966	-11236.9	16461.72	87.297	-10684.9	9153.714	63.10326
323	-13224.8			-12607.8			-11681.8			-11167		
333	-14355			-13634.2			-12533.3			-11869.2		

MB- Methylene blue; RB- Rhodamine B; AB- Acid blue 161

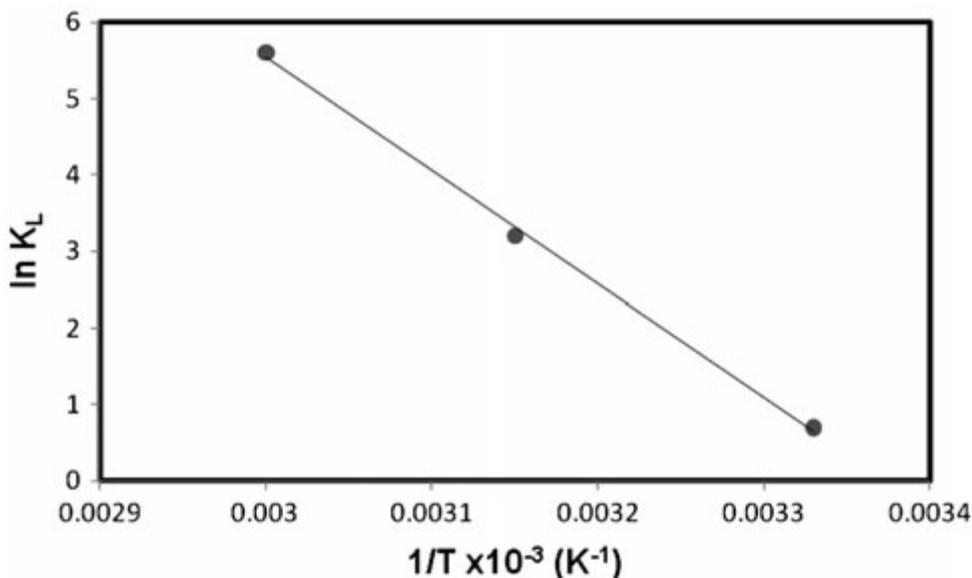
It can be seen from the negative values of the Gibb's free energy given in Table 3, that the adsorption of Methylene blue in all the systems (single, binary and ternary) being studied in this work are spontaneous and thermodynamically feasible as they were accompanied with reduced energy of the systems. The spontaneity of the process increased with increasing temperature in the single adsorbate system and the various mixtures. This is a pointer to an endothermic change. However, at the same temperature, the adsorption of the dye was generally more feasible in the single system than for the mixtures as it has more negative  $\Delta G$ . The adsorption in the ternary mixture is generally less spontaneous than in the binary mixtures (Table 3). These observations indicate that the feasibility and spontaneity of the bio-sorption decreases with International the level of complexity and competitiveness of the system.

The enthalpy change,  $\Delta H$ , has positive values for all the systems investigated. This further confirms that the process is endothermic. As for change in entropy,  $\Delta S$ ; it is positive for all the processes studied. The value, however, decreases with increasing complexity of the composition of the systems. That is,  $\Delta S$  is of the trend Single system > Binary systems > Ternary system. This suggests that, though the adsorption process in all the adsorbate systems is feasible, the degree of disorderliness at the solution-adsorbent interphase decreases with the total number of all the dye molecules in the systems. Similar reports were given by Inbaraj and Sulochana (2006); Ahamad *et al.*, (2011) and Giwa *et al.*, 2015a.



**Figure 3.** A plot of  $\ln K_o$  against  $1/T$  for the adsorption of methylene blue in single, binary and ternary mixture on PSD (Source: Giwaet *et al.*, 2018)

In the thermodynamics study for adsorption of MG dye onto PPAC by Bello *et al.*, 2014, a plot of  $\ln K_L$  against  $1/T$  gave linear plots (Figure 4) from which  $\Delta H^\circ$  and  $\Delta S^\circ$  values were obtained from the slopes and intercepts, respectively. The negative values of  $\Delta G^\circ$  indicate that the adsorption of MG dye onto PPAC is spontaneous and thermodynamically favored. Moreover, when the temperature increases from 303 to 333 K,  $\Delta G^\circ$  changes from  $-21.55$  to  $-24.22$  kJ/mol, suggesting that adsorption is more spontaneous at higher temperature. The positive value of  $\Delta H^\circ$  (9.162 kJ/mol) indicates that the process is endothermic in nature, which is supported by the increase in the adsorption capacity of PPAC for MG dye with increasing temperature. Moreover, the positive value of  $\Delta S^\circ$  0.146 kJ/mol/K suggests that there was increased randomness at the solid–liquid interface during the adsorption of MG dye onto PPAC.



**Figure 4.** Van't Hoff plot for adsorption of MG dye onto PPAC (Source: Bello *et al.*, 2014)

## 5. Conclusion

Through the various isotherm, kinetics and thermodynamics studies considered in this research, the suitability of the models, the significance of their constants and applicability of the models to design are been provided.

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