

## Studies on the Sorption of Basic Dye by Rubber (*Hevea brasiliensis*) Seed Shell

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### Abstract

The present study investigated the ability of rubber seed shell (RSS) to abstract methylene blue (MB) from aqueous solution. The process of sorption of methylene blue from solution was analysed using 5 different isotherm models (Langmuir, Freundlich, Temkin, Harkins–Jura, and Halsey isotherm equations). The highest values of  $r^2$  were obtained when the experimental data were fitted into Freundlich and Halsey isotherm equations (0.999). The RSS/MB system was found to be affected by the sorbent dose and initial dye solution. The kinetic data showed that the sorption capacity of RSS for the dye increased with increasing initial dye concentration, while a reverse trend was observed when the effect of sorbent dosage was studied. Analysis of the data obtained from the different sorption studies revealed that the data fitted better to the pseudo-second order model than any other kinetic model, indicating that the sorption process will include chemisorptions of methylene blue dye on rubber seed shell.

**Key words:** Rubber seed shell, Methylene blue, Kinetics, Sorption, Pseudo, Order

### Introduction

Adsorption is a conventional wastewater treatment method. It reduces, to a large extent, the pollutant levels of wastewater and it is a process that is economically feasible (Choy et al., 1999). The design is simple and it is sludge free. It involves low investment in terms of both the initial and operational costs. Industrial operations that entail the use of dyes are synonymous with large consumption of water and discharge of heavily coloured wastewaters. The presence of dyes in effluent is highly visible and undesirable (Nigam et al., 2000). It is estimated that 10%-15% of dyes are lost in the dye effluent during such a dyeing process (Al-Ghouti et al., 2003). The negative impact of this coloured effluent on the environment is enormous and diverse, hence the need to stem the tide.

In Nigeria, as synonymous with developing nations, many industries involved in dyeing operations are operated at small or medium scale, or sometimes as a family business within the residential premises of the owner. These pockets of cottage industries can generate significant pollution, which often is discharged into the environment without any facilities for wastewater treatment. This is because the capital investment turnover and profit for these industries are also small (Quek et al., 1998). In Nigeria, government legislation is becoming more stringent regarding the quality of the effluent discharge into the environment, which shall definitely affect the small-scale and medium size industries where profit is small, and investment in wastewater treatment technologies and personnel cannot be afforded. Owing to these facts, the need to identify low-cost materials for colour removal is important to sustain companies involved in

the dyeing processes; otherwise, their demise is imminent.

Activated carbon has been the conventional sorbent used in the water industry but its use is limited by certain considerations. It is expensive, regeneration using solution produces a small additional effluent, and regeneration by refractory technique results in a 10%-15% loss of adsorbent and its uptake capacity (Waranusantigul et al., 2003). Consequent upon this, an alternative low-cost sorbent is required, if the advantages inherent in adsorption as a method for wastewater treatment are to be exploited. An array of sorbents of biological origin have been investigated and found to have potential for dye abstraction from aqueous systems. Some of these are peat for Basic Blue 69 and Acid Blue 25 (Ho and McKay, 1998); giant duckweed for methylene blue (Waranusantigul et al., 2003); sugar cane dust for Basic violet 10, Basic violet I, and Basic green 4 (Ho et al., 2005); rice husk for malachite green (Gou et al., 2003); carbon prepared from waste apricot for methylene blue, malachite green and crystal violet (Basar, 2006); bagasse fly ash for orange-G and methyl violet (Mall et al., 2006a); and castor seed shell for methylene blue (Oladoja et al., 2008). The majority of these biosorbents are very cheap, easy to obtain, and solid wastes; hence they can be used once and then discarded of by burning them as fuel.

The sorbent used in this study was the shell of the seed of the rubber tree (*Hevea brasiliensis*). *H. brasiliensis* belongs to the family *Spurge* or *Euphorbiaceae*. The Hevea tree produces significant quantities of milk-like sap called latex, which is an emulsion of hydrocarbons in water. It is a material of industrial significance. Rubber seed oil is extracted from the rubber seed. The rubber seed shell (RSS) is used as biofuel or manure or is discarded and allowed to rot. Recently, the use of activated carbon, prepared from rubber seed coat, for the sorption of phenol from aqueous solution was reported by Rengaraj et al. (2002).

The present study aimed to generate basic data on the equilibrium isotherm parameters and kinetics of RSS, with reference to methylene blue, a basic dye, at low concentration in aqueous medium. The equilibrium isotherm studies were performed using 5 different isotherm equations (i.e. Langmuir, Freundlich, Temkin, Halsey, and Harkins–Jura isotherm equations) to analyse the data obtained from the isotherm studies. The sorption process was studied by continuous variation of 2 operational parameters

(initial sorbate concentration and sorbent dosage) and the data obtained from monitoring the time-concentration profile (i.e. the kinetics) of the sorption of MB on RSS were tested with different kinetic models (pseudo-first order and pseudo-second order models).

## Theoretical Background of Studies

### Sorption isotherm studies

Analysis of the results obtained from the equilibrium isotherm studies is fundamental to evaluate the affinity of a sorbent for a particular sorbate. Equilibrium studies are described by a sorption isotherm characterised by certain constants whose values express the surface properties and affinity of the sorbent. Consequent upon this, the results obtained from these studies were tested with 5 different isotherm equations (i.e. Langmuir, Freundlich, Temkin, Halsey, and Harkins–Jura isotherm equations).

The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm. The Langmuir isotherm hints towards surface homogeneity. The linearised form of the equation can be represented thus;

$$\frac{C_e}{q_e} = \frac{1}{kq_m} + \left[ \frac{1}{q_m} \right] C_e \quad (1)$$

where  $c_e$  is the concentration of the sorbate at equilibrium (mg/l;  $q_e$  is the amount of sorbate sorbed at equilibrium per unit mass of sorbent (mg/g;  $q_m$  is the monolayer sorption capacity at equilibrium (mg/g), and;  $k$  is the Langmuir equilibrium constant (l/mg). A plot of  $c_e/q_e$  versus  $c_e$  gives a straight line, if the sorption process is described by the Langmuir isotherm equation. The values of  $q_m$  and  $k$  are obtained from the slope and intercept of the straight line plot.

The Freundlich isotherm is regarded as an empirical isotherm. It indicates the surface heterogeneity of the sorbent. The linearised form of the isotherm is expressed thus

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

where  $k_f$  and  $n$  are Freundlich coefficients, obtainable from the plots of  $\ln q_e$  versus  $\ln c_e$ .  $k_f$  and  $n$  are Freundlich adsorption constants, related to adsorption capacity and sorption intensity, respectively.

Temkin and Pyzhev (1940) studied the heat of adsorption and the adsorbent–adsorbate interaction

on surfaces. The Temkin isotherm equation is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (3)$$

The linear form of Eq. (3) is presented below:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (4)$$

where  $B_1 = \frac{RT}{b}$ ,  $T$  (K) is the absolute temperature,  $R$  is the universal gas constant (8.314 J/mol),  $K_T$  is the equilibrium binding constant (l/mg), and  $B_1$  is related to the heat of adsorption. The Temkin constants are obtained from the plot of  $q_e$  versus  $\ln C_e$ .

The Harkin–Jura adsorption isotherm can be expressed as (Harkin and Jura, 1944; Basar, 2006)

$$\frac{1}{q_e^z} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad (5)$$

The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins–Jura isotherm parameters are obtained from the plots of  $1/q_e^z$  against  $\log C_e$ .

The Halsey adsorption isotherm can be given as (Halsey, 1948; Basar, 2006)

$$\ln C_e = \left(\frac{1}{n} \ln k\right) - \frac{1}{n} \ln C_e \quad (6)$$

This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of the adsorbent (Rosen, 1978). The Halsey isotherm parameters are obtained from the plot of  $\ln q_e$  versus  $\ln C_e$ .

### Kinetics of Sorption process

The time-concentration profile characteristics of the sorption of MB by RSS were tested with the Lagergren pseudo-first order; the chemisorptions pseudo-second order (Ho, 1995), and the intraparticle diffusion model (Weber and Morris, 1963).

The linearised form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \quad (7)$$

where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , respectively (mg/g).  $k_1$  is the rate constant of pseudo-first order adsorption.

If pseudo-first order kinetics is applicable, the plot of  $\log(q_e - q_t)$  versus  $t$  should give a linear relationship, from which the pseudo-first order parameters can be determined from the slope and intercept of the plot.

The pseudo-second order kinetics, represented by the linear equation presented below, was also used to test the experimental data:

$$\frac{t}{q_t} = \frac{1}{k q_e} + \frac{1}{q_e t} \quad (8)$$

where  $q_e$ ,  $q_t$ , and  $t$  have the same meaning as explained above.  $k_2$  is the overall rate constants of pseudo-second order sorption ([g/mg]/min). If pseudo-second order kinetics is applicable, the plot of  $t/q_t$  against  $t$  of Eq. (8) should give a linear relationship, from which  $q_e$ , and  $k_2$  can be determined from the slope and intercept of the plot.

The initial sorption rate can be obtained from the pseudo-second order linear plots, as  $q_t/t$  approaches zero:

$$h = k q_e^2 \quad (9)$$

where  $h$  = initial sorption rate.

Sorption of sorbate on a sorbent proceeds in several steps, involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process. The intra-particle diffusion rate constant ( $k_{id}$ ) is given by the equation

$$q_t = k_{id} t^{0.5} \quad (10)$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of  $q_t$  versus  $t^{0.5}$  yield a straight line passing through the origin and the slope gives the rate constant,  $k_{id}$ .

## Materials and Methods

### Rubber seed shell

The RSS was obtained from the Rubber Research Institute of Nigeria, Iyanomo, Nigeria. The RSS was washed with deionised water, to remove any attached dirt and soluble impurities, dried in the open air and then pulverised. The powder was sieved using a laboratory sieve and the 100  $\mu\text{m}$  fraction was separated. This fraction was washed several times with deionised water until the washings were free of

colour and turbidity. The powder was later dried in the oven at 80 °C and kept in a sealed polythene bag pending usage as an adsorbent.

### Dye solution

Methylene blue (C<sub>16</sub> H<sub>18</sub>Cl N<sub>3</sub> S), the sorbate used in the present study, is a monovalent cationic dye. It is classified in dye classification as C.I. Basic blue 9; C.I. Solvent blue 8; C.I. 52015. It has a molecular weight of 373.90. The methylene blue (MB) (BDH 85%) was used as supplied. The stock solution of 200 mg/l was prepared by dissolving an appropriate amount of MB in 1 l of deionised water. The working solutions were prepared by diluting the stock solution with distilled water to give the required concentration.

### Sorption isotherm studies

In order to determine the sorption isotherm, 0.1 g of the RSS was brought into contact with 50 ml of the working solutions of varying concentrations (5-80 mg/l). The experiment was conducted at ambient temperature and agitation speed of 100 rpm. The equilibrium concentration was determined at 60 min. The study time was based on an earlier finding that equilibrium could be achieved for this sorbent in 30 min. The residual MB in the aqueous medium was determined using a UV/visible spectrophotometer. The amount of MB sorbed per unit mass of the RSS ( $q$  in mg/g) was calculated using the mass balance procedure:

$$q_t = \frac{v(c_o - c_f)}{m} \quad (11)$$

where  $q_t$  is the amount of sorbate sorbed per gram (g) of adsorbent (mg/g),  $c_o$  is the initial concentration of MB (mg/l);  $c_f$  is the final residual MB concentration (mg/l), and  $m$  is the mass of RSS (mg).

### Kinetics of Sorption process

The kinetics of the sorption of MB on RSS were studied by carrying out a set of sorption experiments in which the effects of initial sorbate concentration and sorbent dosage were studied at constant temperature, and monitoring the amount of dye sorbed over time. The effects of initial concentration on the kinetics of the sorption process were investigated at different initial MB concentrations (10, 20, 40, 80,

and 100 mg/l), fixed sorbent dose (0.1 g), and constant agitation speed (200 rpm) in a thermostatic water bath at fixed time intervals (2, 5, 10, 15, 20, 30, and 60 min). The sorbent dose effect was investigated at varying RSS dosages (0.1, 0.2, 0.3, 0.4, and 0.5 g), and fixed sorbate concentration (100 mg/l of MB) and agitation speed (200 rpm) in a thermostatic water bath at fixed time intervals (2, 5, 10, 15, 20, 30, and 60 min). The residual MB in the aqueous medium was determined over time using a UV/visible spectrophotometer at the  $\lambda_{max}$  of the dye.

## Results and Discussion

### RSS characterisation

A proximate analysis of the RSS was carried out, using the recommended standard methods of analysis (AOAC, 1991). The results obtained from the analysis showed that the RSS contained (in % dry weight): protein 5.41%; lipid 25%; ash 8.35%; fibre 51.72%; carbohydrate 9.52%; Ca 0.75%; Mg 0.324%; Na 0.45%; K 1.25%; P 0.243%, and N 0.866%.

### Equilibrium isotherm studies

The equilibrium relationship between the concentration of the MB in the fluid phase and the MB in the RSS at a given temperature was studied. The results obtained were analysed using 5 different isotherm equations (i.e. Langmuir, Freundlich, Temkin, Halsey, and Harkins–Jura isotherm equations).

In order to understand the mechanism of MB adsorption on RSS, the experimental data were fitted to the aforementioned equilibrium isotherm equations and the different isotherm parameters, obtained from the different plots, are presented in Table 1a.

An error function is required to evaluate the fitness of each isotherm equation to the experimental data obtained from the optimisation process employed. In the present study the linear coefficient of determinations,  $r^2$ , was used. The values of the linear correlation,  $r^2$ , of each isotherm equation, when fitted to the experimental data are presented in Table 1a. The highest values of  $r^2$  were obtained when the experimental data were fitted into Freundlich and Halsey isotherm equations (0.999). The description of the sorption of MB on RSS by the Freundlich and Halsey isotherm equations is a pointer to the heterogeneity of the surface of the RSS and the multilayer adsorption nature of the MB on RSS.

**Table 1a.** Equilibrium Isotherm Parameters of sorption of MB on RSS.

Langmuir isotherm parameters			Freundlich isotherm parameters		
$q_m$ (mg/g)	K (l/mg)	$r^2$	$K_f$ (l/g)	1/n	$r^2$
82.64	1.2347	0.8029	51.75	1.2788	0.999

Temkin isotherm	Harkins–Jura isotherm	Halsey isotherm
$B_1 = 9.958$	$A = 10.62$	$n = 1.2788$
$K_T$ (l/mg) = 38.59	$B = 0.46$	$K = 155.50$
$r^2 = 0.8493$	$r^2 = 0.7191$	$r^2 = 0.999$

**Table 1b.** Comparison of the Langmuir sorption capacity ( $q_m$  in mg/g) of different sorbents for MB.

Adsorbent	$q_m$ (mg/g)	References
RSS	82.64	Present Study
Cereal chaff	20.30	Han et al., 2006
Rice husk	40.60	Vadivelan and Kumar, 2005
Mansonia sawdust	28.89	Ofomaja, 2008
Castor seed shell	158.73	Oladoja et al., 2008
Raw beech sawdust	9.78	Batzias and Sidoras, 2004

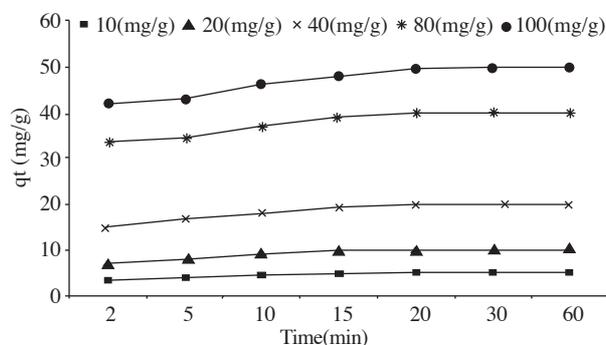
The maximum adsorption value,  $q_m$  (mg/g), obtained in the present study was compared with those of other sorbents for MB adsorption (Table 1b). The results of this comparison showed that RSS has great potential as a sorbent for MB adsorption in water systems and can compete favourably with other sorbents that have been studied by other researchers.

### Kinetics of the sorption process

*Initial sorbate concentration* The initial methylene blue concentration was studied to observe if the initial concentration of sorbate would have an influence on the sorption process. In the range of MB concentration studied, the uptake of the MB was rapid in the first 2 min. The rapid uptake then gave way to a much slower adsorption, which became constant at 30 min (Figure 1). This initial rapid uptake can be attributed to the concentration gradient created at the start of the adsorption process between solute concentration in solution and that at the RSS surface. As the dye loading increases this gradient reduces and gives way to slower uptake.

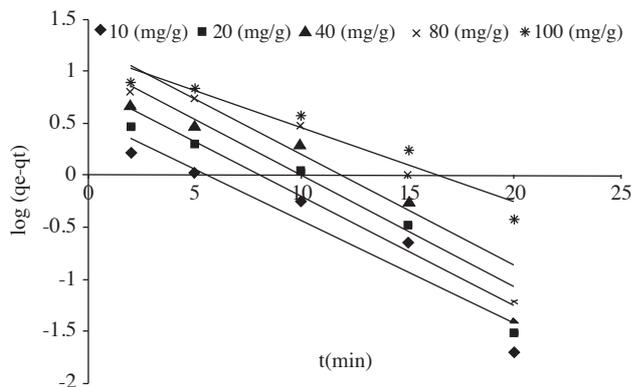
The kinetic studies of a sorption process are paramount because the data obtained from such studies are necessary to understand the variables that influence the sorption of solutes. The results can also be used to determine the equilibrium time and the rate of adsorption can be used to develop predictive models for column experiments. Owing to these facts, Lagergren pseudo-first order; the chemisorp-

tions pseudo-second order (Ho and McKay, 1999, 2000, 2002), and the intraparticle diffusion model (Weber and Morris, 1963) were employed to study the concentration-time profile features of the sorption processes.



**Figure 1.** Time variation of MB sorption on RSS at different initial MB concentrations.

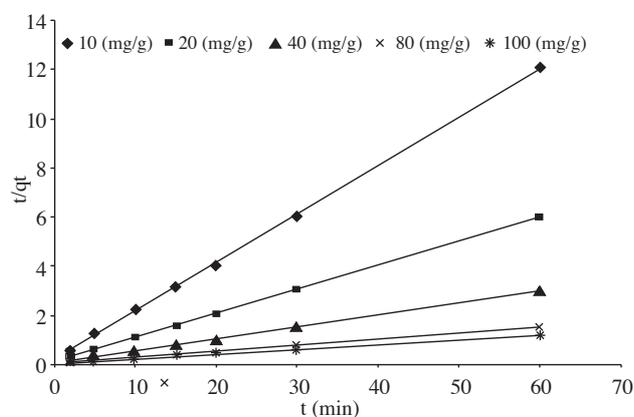
The results presented in Figure 2 were obtained when the data obtained from the sorption experiment were analysed with the Lagergren pseudo-first order kinetic model. The values of  $\log(q_e - q_t)$  were plotted against time. The linearity of the plots was not very high ( $R^2 = 0.8641-0.9302$ ). The first order rate constant ranged between  $7.1 \times 10^{-2}$  and  $10.76 \times 10^{-2}$ . Owing to the low linearity of the plots obtained from this study the chemisorptions pseudo-second order kinetic model was also used to test the data obtained from the same studies.



**Figure 2.** Pseudo-first order plot of sorption of MB on RSS at varying initial MB concentrations.

The pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. In contrast to the other kinetic models, it predicts the behaviour over the whole range of studies supporting a pseudo-second order equation and is in agreement with chemisorptions being the rate controlling step (Ho and McKay, 1998). The plot of  $t/q_t$  against  $t$  (Figure 3) yields very good straight lines (Table 2). An inverse relationship was observed in the values of the overall pseudo-second order reaction rate ( $k_2$ ) and initial MB concentration, while a direct relationship was noted between the initial reaction rate ( $h$ ) and initial MB concentration. The initial sorption rate constant ( $h$ ) was greatly affected by the increase in the initial concentration of MB (Table 3). This was consistent with the observations reported by Low et al. (1993, 1995) for the biosorption of basic dyes by water hyacinth roots and *H. verticillata*; and Waranusantigul et al.;2003) for basic dye biosorption by giant duckweed (*Spirodella polyrrhiza*). It was

noted that variation in the initial concentration of MB did not affect the time in which equilibrium was attained. The rapid uptake of dye indicates that the sorption process could be ion exchange in nature, where the cationic dye molecules bind with the various negatively charged organic functional groups present on the surface of the aquatic plants (Low et al.;, 1993, 1995). Based on the results obtained from the analysis of the sorption data with pseudo-second order kinetic model it can be suggested that the pseudo-second order kinetic model described the sorption of MB on RSS better.



**Figure 3.** Pseudo-second order plot of sorption of MB on RSS at varying initial MB concentrations.

Consequent upon the established relationship between the pseudo-second order overall rate parameters,  $k$ , and initial MB concentration ( $C_o$ ), an empirical correlation was made between this parameter and the initial MB concentration. A straight line plot with a correlation coefficient of 0.9862 was obtained and an empirical relationship between  $k$  and  $C_o$  can be expressed thus:

**Table 2.** Kinetic parameters for the sorption of MB by RSS at different initial MB concentrations (mg/l).

Pseudo-first order parameters				Pseudo-second order parameters			
Initial Conc. (mg/l)	$q_{e1}$	$k_1$	$R^2$	$q_{e2}$	$k_2$	$h$	$R^2$
10	3.60	0.0993	0.9128	5.10	0.176	4.578	0.9996
20	7.15	0.1052	0.9148	10.18	0.097	10.052	0.9996
40	12.00	0.1076	0.8893	20.28	0.063	25.911	0.9998
80	19.01	0.1068	0.8641	40.49	0.040	65.578	0.9998
100	14.75	0.071	0.9302	50.76	0.027	69.568	0.9999

N.B:  $k_1 = \text{min}^{-1}$ ;  $q_{e1} = \text{mg/g}$ ;  $k_2 = \text{g mg}^{-1} \text{min}^{-1}$ ;  $h = \text{g mg}^{-1} \text{min}^{-1}$

$$K = 0.0045C^{-0.7615}$$

The negative slope obtained in this relationship could be ascribed to the inverse relationship in the values of the pseudo-second order rate constant and the initial MB concentration. In the sorption of dye (AB25) onto chitin, McKay et al. (1992) reported that, if the slope of the plot of the above relationship centred on the 0.5 value; it confirms that intraparticle diffusion was a prominent factor in the sorption process. The value of  $n$  (-0.7615) obtained in the present study is different from 0.5, based on intraparticle diffusion. This indicates that pseudo-second order chemisorption is important in the sorption of MB onto RSS.

### Sorbent dosage

The effects of sorbent dosage on the sorption process are presented in Figure 4. The extent of sorption, calculated as a percentage of MB sorbed by the RSS, increased as the dosage of the RSS was increased. This is expected because an increase in RSS dosage will lead to an increase in the quantity of sorption sites available for sorbent-sorbate interaction (Kumar et al., 2005). A reverse trend was observed in the loading capacity ( $q_t$ ) as the RSS dosage was increased. The loading capacity decreased as the sorbent dosage was increased. This can be explained by the fact that a fixed mass of sorbent can only sorb a certain amount of dye. Therefore, the higher the sorbent dose, the larger the amount of dye that the fixed dose can sorb. The decrease in the amount sorbed per unit mass with increasing sorbent dosage is due to the split in the flux or the concentration gradient between solute concentration in solution and the solute in the surface of the adsorbent (Vadivelan and Kumar, 2005).

The results obtained when the sorption data obtained from this study were tested with both pseudo-first and second-order kinetic models are presented in Figures 5 and 6 and Table 3. A comparative analysis of the linearity of the plots obtained from the test of the 2 kinetic models with the sorption data showed that the pseudo-second order kinetic model had better linearity ( $R^2 = 0.9931-1.0000$ ) and could be said to describe the mechanism of sorption of MB by RSS at varying sorbent dosages.

### Intraparticle diffusion

Despite the results obtained, from the empirical correlation of the overall pseudo-second order parameters,  $k_2$ , and the initial MB concentration, that showed that intraparticle diffusion could not have played any significant role in the sorption of MB on RSS in the present studies, an attempt was made to further establish the possibility of MB being transported within the pores of RSS particles. The amount of dye sorbed per unit mass of sorbent ( $q_t$ ) was plotted against the square root of time. If intraparticle diffusion has a significant presence in the sorption process, the approach towards equilibrium is governed by the diffusion  $(D_t/r^2)^{0.5}$ , where  $r$  is the radius of the particle and  $D$  is the diffusivity within the particle (Weber et al., 1963). According to the intraparticle diffusion model, a linear plot indicates a rate controlled by intraparticle diffusion. This is due to the fact that fractional uptake will vary with the function  $(D_t/r^2)^{0.5}$ .

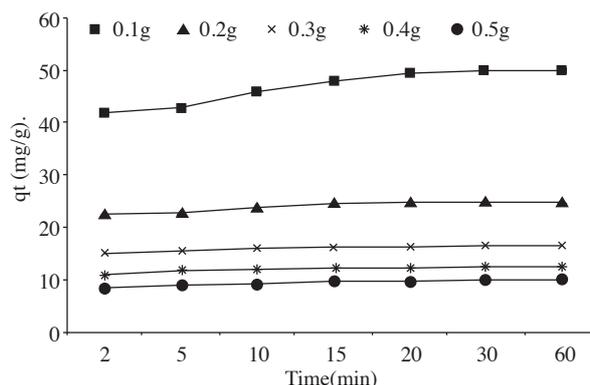


Figure 4. Time variation of MB sorption on RSS at different sorbate dosages.

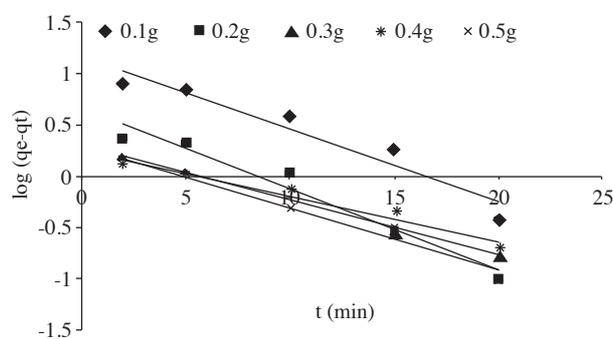
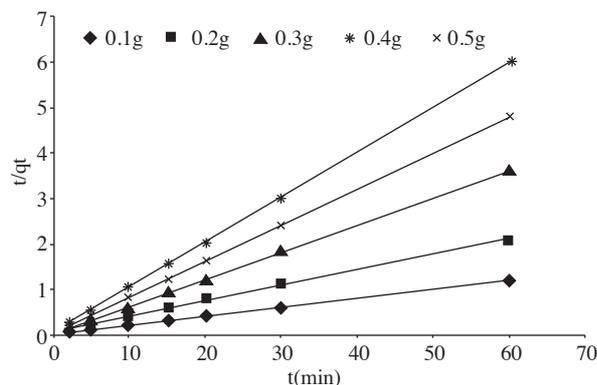


Figure 5. Pseudo-first order plot of sorption of MB on RSS at varying sorbent dosages.

**Table 3.** Kinetic parameters for the sorption of MB at different RSS dosages (g).

Pseudo-first order parameters				Pseudo-second order parameters			
Initial Conc. (mg/l)	$q_{e1}$	$k_1$	$R^2$	$q_{e2}$	$k_2$	$h$	$R^2$
0.1	14.75	0.071	0.9302	50.76	0.027	69.568	0.9999
0.2	4.58	0.079	0.9671	29.24	0.015	12.825	0.9931
0.3	2.02	0.054	0.9896	16.78	0.180	50.682	1.0000
0.4	1.93	0.060	0.9689	12.58	0.209	33.076	1.0000
0.5	1.78	0.045	0.9776	10.11	0.159	16.252	0.9999

N.B:  $k_1 = \text{min}^{-1}$ ;  $q_{e1} = \text{mg/g}$ ;  $k_2 = \text{g mg}^{-1} \text{min}^{-1}$ ;  $h = \text{g mg}^{-1} \text{min}^{-1}$



**Figure 6.** Pseudo-second order plot of sorption of MB on RSS at varying sorbent dosages.

In contrast, the plot obtained from this study shows multi-linearity with 2 or more steps. A similitude of this trend has been reported by Wu et al. (2000); Bhattacharyya and Sharma (2004), and Lazaridis and Asouhidou (2003). The first part of the multi-linear plot is attributed to boundary layer diffusion, the second to the intraparticle diffusion, and the third to the chemical reaction. The multi-linearity curve indicates that intraparticle diffusion is not a fully operative mechanism in the sorption of MB by the RSS.

The linear portion of the plot attributed to the intraparticle diffusion was linearised at different initial concentrations. The range of the linear regression coefficients obtained was 0.9858-0.9942. It is possible that some of the MB<sup>+</sup> ions diffuse into the pores before chemisorptions took effect. The intraparticle diffusion rate constants,  $k_{id}$ , have values from 2.911 to 0.407 (Table 4). The rate constant increased with an increase in MB concentration. This observation agreed with the studies by Namasivayam and Ranganathan (1995), Low et al. (1995), Nasar (1999), and Waranusantigul et al. (2003).

Despite the high linearity of the plots it is of note that none of the plots have zero intercepts, as proposed by Weber et al. (1963). The intercept varied from 2.917 to 36.551. This could also be a pointer to the possibility that intraparticle diffusion may not be a prominent rate controlling step.

The intraparticle diffusion model was also used to test the data obtained when the RSS dosage was optimised. The results obtained are presented in Table 4. The linearity of the plots was as high as when the intraparticle diffusion model was tested with varying MB concentrations but the intercepts of the plots were farther from point zero (8.065-36.551). The intraparticle rate parameters decreased with increases in RSS dosage.

**Table 4.** Intra-particle diffusion model parameters for the sorption of MB by RSS at varying initial MB concentration and RSS dosages.

Initial conc. (mg/l)	$R^2$	Intercept	$k_{id}(\text{mg/gmin})^{0.5}$	Sorbent dosage (g)	$R^2$	Intercept	$k_{id}(\text{mg/gmin})^{0.5}$
10	0.9906	2.917	0.467	0.1	0.9942	36.551	2.911
20	0.9858	5.999	0.906	0.2	0.9661	20.952	0.917
40	0.9862	13.756	1.401	0.3	0.9713	14.633	0.433
80	0.9892	28.667	2.568	0.4	0.9992	10.945	0.322
100	0.9942	36.551	2.911	0.5	0.9977	8.065	0.388

## Conclusion

The ability of RSS to abstract MB from aqueous solution was studied using equilibrium isotherm analysis. Langmuir, Freundlich, Temkin, Harkins–Jura, and Halsey isotherm equations were used to describe the sorption process. Freundlich and Halsey isotherm equations had the best correlations

amongst all the isotherm equations used. This shows the heterogeneity of the surface of the RSS and the multilayer adsorption nature of the MB on RSS. Both the initial sorbate solution and sorbent dose were found to affect the sorption process and the sorption process was found to follow the pseudo-second order mechanism more than any other kinetic model.

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