



METHYLENE BLUE AND IRON (II) ADSORPTION ONTO RAPHIA HOOKERI SEED: A COMPARATIVE EQUILIBRIUM ISOTHERM STUDY

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ABSTRACT

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In this study, activated carbon prepared from *Raphia hookeri* seed was employed as an adsorbent to take up methylene blue (an organic ion-in-solution) and iron (II), a metal ion-in-solution. The biosorbent was prepared using chemical activation using sodium hydroxide (NaOH) as an impregnating agent. Calibration was performed with a focus on the change in the adsorbate concentration. The equilibrium isotherms study was conducted by considering a range of sorbate concentrations, to determine the optimal conditions for the adsorption systems. The same sorbate volume (10 ml), and the same dosage (0.3g) of biosorbent were used for both adsorption processes. Linear analysis was used to compare the best-fitting isotherms. Langmuir, Freundlich, and Dubinin-Radushkevich models were tested. The highest coefficient of determination values (R^2) for both iron (II) and Methylene blue was obtained from the Langmuir isotherm as 0.9266 and 0.9572, respectively, compared to values from the other isotherms tested – indicative of Langmuir isotherm's superior fit. Estimated values of 'separation factor', K_R , for Methylene blue (0.29457), however, was lower than that of iron (II) (0.42141) – an indication that the sorbent treats methylene blue better than iron (II), though both processes are feasible.

Contribution/Originality: This study is one of very few studies which have investigated the comparative feasibility of treating water polluted by Iron (II) and Methylene blue, using biosorbent from *Raphia hookeri* seed.

1. INTRODUCTION

To optimise the design of a sorption system, where the adsorbent of consideration is feasible (or in any case), finding out the most appropriate correlation for the equilibrium adsorption study is such an important prerequisite [1, 2]. Equilibrium isotherm equations are developed and used to describe the experimental adsorption data [3]. Resultant values of various isotherm parameters obtained from their corresponding correlations provide vital information on the adsorption mechanisms, surface properties and the feasibility of the adsorption system. These isotherm equations can be used for certain purposes, such as the design of columns/systems that would perform effectively adsorption [4, 5].

An investigation of the feasibility or adsorptivity of activated carbon prepared from *Raphia palm* seed, to remove metal ions and organic pollutants from aqueous solutions, and to test the dual adsorption processes with isotherm models, is what is been studied. The experiments, to obtain relevant data, were performed over a period of

60 min. For solid-liquid systems, several isotherms are available but Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were used to analyse the adsorption equilibrium. The various forms of the isotherms are presented in Table 1.

2. MATERIALS AND METHOD

2.1. Preparation of the Biosorbent

Raphia palm (*Raphia hookeri*) seeds (which are disposed of as waste) were collected from a commercial (Raphia mesocarp) trader at Famgbe community in Yenagoa Local Government Area of Bayelsa State. They were washed and sun-dried for three days and oven-dried at 105°C for 24 hours. The oven-dried precursors, after cooling, were weighed to determine the mass before carbonization and activation. Carbonisation, each in 90 min, was done at three temperatures 400°C, 500°C and 600°C that are the optimal thermal treatment conditions for Raphia palm seed (RPS) during carbonisation, according to Akpos [6]. The carbonized precursor was treated with a 0.3 Molar solution of sodium hydroxide for 24 h; after which activation was done, for each batch, at 700°C.

2.2. Preparation of Sorbate

2.2.1. Preparation of Iron (II) Solutions

Six, 100ml volumetric, flasks were labelled with masking tapes. Five of them had inscriptions of 0.1 ppm, 0.2ppm, 0.5ppm, 1.0ppm and 2.5ppm respectively. The sixth flask was labelled 'blank'. An equivalent volume of 1.0, 2.0, 5.0, 10.0, and 25ml of the iron stock, prepared from $\text{Fe}(\text{NH}_4)_2(\text{SO}_4).6\text{H}_2\text{O}$, was pipetted into the flasks in that order; except in the blank (in which only 50 ml of distilled water was added at this stage). Then, the following reagents were serially added to all the six volumetric flasks: 1.0ml of hydroxylamine hydrochloride, 5.0 ml of 1–10 Phenanthroline and 8.0 ml of sodium acetate. The development of an orange-red colour indicates iron [7] and the intensity of the colour is in concordance with the concentration (i.e. showing serial dilution).

2.2.2. Preparation of Methylene Blue Solutions

A stock solution of methylene blue was prepared using 1 gram of the reagent dissolved in a 1000ml volumetric flask. Serial dilutions were made into 100ml volumetric flasks. Five solutions, 0.5, 1.0, 1.5, 2.0, and 2.5ppm, respectively, were obtained for calibrating the spectrophotometer). These dilutions were also used for the adsorption process.

2.3. The Adsorption Process

To perform equilibration, 0.3 g of 300 μm biosorbent, carbonized at 600°C, was put in five test tubes for iron (II) and methylene blue experiments. For the iron (II) experiment, the concentration was varied in this order: 0.1, 0.2, 0.5, 1, 2.5 ppm, while the Methylene blue (MB) concentrations were 0.5, 1.0, 1.5, 2.0, 2.5 ppm, respectively. Each test tube contained a 10-ml solution. The tubes were stoppered, labelled and equilibrated in HY-4A Cycling Vibrator/Shaker for 1 hour at 31.5°C. Then, the tubes were centrifuged at 3500rpm for five minutes. Decantation and further filtration were done to obtain particles-free samples, for experimentation in a spectrophotometer.

3. RESULTS AND DISCUSSION

Equation 1 plays a fundamental role in the development of models for any adsorption system. Data and parameters generated, for both iron (II) and methylene blue adsorption systems, in this study, were fitted into Langmuir, Freundlich and D-R adsorption isotherms. Among other process parameters, varied concentration changes controlled the isotherm studies.

3.1. Effect of Initial Concentration

In the study of the effect of concentration, it was observed that the percentage of iron (II) adsorbed decreases with increasing initial concentration and maximum adsorption was obtained at the least concentration. However, because of the concentration driving force, from the sorbate, which favours adsorption more than possible desorption, higher concentrations recorded pretty high uptake unto the sorbent compared to the mid-range concentrations. While the plot on iron (II) sorption capacity takes the form of a parabola with two highs, the Methylene Blue counterpart is a straight line: showing a continuous increase in percentage uptake from the lowest to the highest concentration [8]. This is obviously because a higher Methylene Blue concentration means a greater driving force for mass transfer from the aqueous solution to the solid adsorbent. Figure 1 presents the data showing the effect of the initial concentration on adsorption.

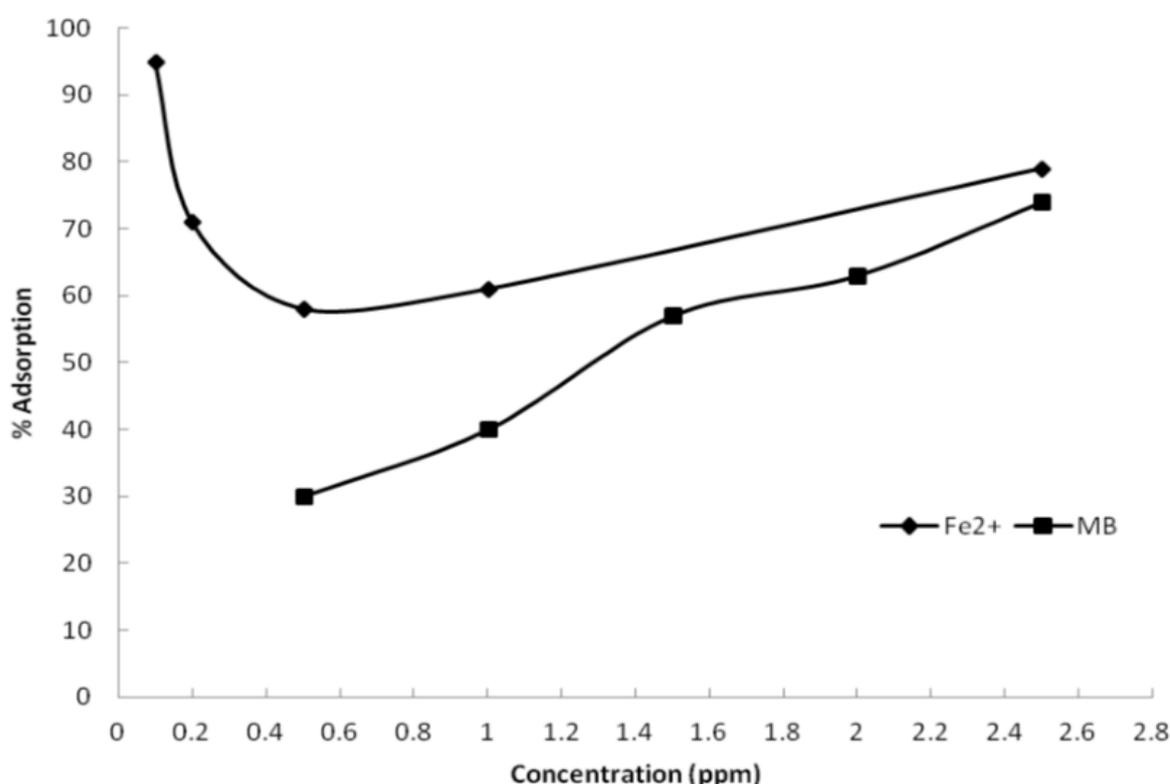


Figure-1. Effect of initial concentration of Fe²⁺ and MB. Dosage = 0.3g; particle size = 300 μ m, carbonised at 600 $^{\circ}$; contact time = 1 hour.

3.2. Adsorption Isotherm Studies

To generate data for equilibrium studies Equation 1 presents the choice of the parameter to vary and which to keep constant in determining equilibrium concentrations that would be used in developing models representing each isotherm. This implies that anyone between adsorbate concentration, adsorbent dosage or sorbate volume can be varied at a time while the remaining two of the trio (and other parameters considered in the experiment) are kept constant. Ho, in his studies, made similar assertions in trying to explain how to obtain data for isotherm studies [9].

$$q_e = \frac{(C_i - C_e)V}{w} \text{ (mg/g)} \quad (1)$$

Where q_e = adsorption capacity; C_i = Initial concentration of adsorbate; C_e = Final or equilibrium concentration of the adsorbate; V = volume of adsorbate used; w = quantity of adsorbent used.

Table-1. Non-linear and linear forms of adsorption isotherms.

Isotherm		Linear Form	Plot	Reference(s)
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$	$\log(q_e)$ vs $\log(C_e)$	
Langmuir- 1	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs C_e	[2, 10]
Langmuir - 2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$	
Langmuir - 3		$q_e = q_m - \left(\frac{1}{K_a}\right) \frac{q_e}{C_e}$	q_e vs $\frac{q_e}{C_e}$	
Langmuir - 4		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs q_e	
D-R		$\ln q_e = \ln q_m - \beta \varepsilon^2$	$\ln q_e$ vs ε^2	[11]

3.3. Langmuir Isotherm Analysis

The simple assumption of the Langmuir isotherm is that adsorption occurs at specific homogeneous sites within the adsorbent [12]; expressing a monolayer behaviour, which implies that once an adsorbate molecule enters a certain pore space inside the adsorbent no other molecule goes into the same space. The Langmuir equation and its linear forms are expressed in Table 1. Where: q_e = amount of metal iron adsorbed ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium; q_m = maximum amount of metal iron adsorbed ($\text{mg}\cdot\text{g}^{-1}$); C_e = Final concentration of metal iron in solution ($\text{mg}\cdot\text{L}^{-1}$); K_a = Langmuir or equilibrium constant for adsorption ($\text{L}\cdot\text{mg}^{-1}$). K_a , and q_e are obtained from the intercept and slope when any linear form of the isotherm is plotted. The essential isotherm parameters of the Langmuir adsorption isotherm can be used to obtain a dimensionless quantity (called separation factor), which is used to predict the affinity between the sorbate and sorbent [13, 14]. As presented in Equation 2, the *separation factor* also called *equilibrium parameter*, K_R , is expressed as one divided by the encapsulation of one plus the product of the Langmuir (or equilibrium) constant, K_a and the initial concentration, C_0 , shown below:

$$K_R = \frac{1}{1+K_a C_0} \quad (2)$$

In this study, a test on the four forms of Langmuir was done using the experimental data. It was observed that both adsorption systems fitted better into the linear form of *Langmuir 2* compared to the other three forms. Hence, it was used as the choice linear form for the Langmuir isotherm studies with the plots shown in Figure 2. An estimation of the K_R values (in Table 2) justifies the conclusion that iron II (Fe^{2+}) and MB adsorption on modified raphia palm seed activated carbon (RPSAC) is favourable; since $0 < K_R < 1$ is true for both sorbate [15]. However, the smaller value for MB compared to that of Fe^{2+} indicates that the sorption of MB is more favourable [16]. Nonetheless, the adsorbent is observed as appropriate in treating both classes of pollutants in water: this conclusion is because, though the average coefficient of determination for the Fe^{2+} experiments is lower than that of MB, its nearness to unity is a sufficient indication that enough iron-deposit is removed from the water body and has reduced iron-in-water to a permissible range.

3.4. Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is originally an empirical model but was later interpreted as biosorption onto heterogeneous surfaces (that is, surfaces supporting sites of varied affinities). And it is now widely used for data obtained from experiments [17]. The Freundlich isotherm is applied to estimate the adsorption intensity of the adsorbent towards the adsorbate [18]. From the Freundlich equation in Table 1 above K_F and $1/n$ are

Freundlich constants representing adsorption capacity and adsorption intensity, respectively [19]. The Freundlich isotherm is commonly considered an empirical proposition, relating q and c using the power of the inverse of n and K_F as the equilibrium constant. Despite being empirical, the Freundlich model often provides a brilliant explanation for isotherms experimentally obtained from liquid-phase adsorption studies [20].

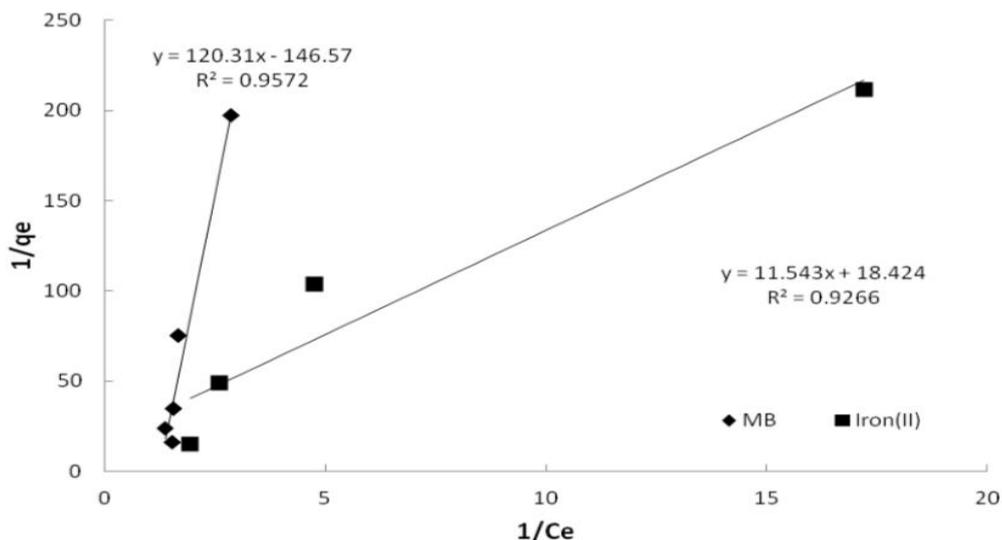


Figure-2. Langmuir adsorption isotherms for the adsorption of Fe^{2+} and Methylene Blue onto RPSAC at $31.5^{\circ}C$; adsorbent size = $300\ \mu m$; carbonisation temperature = $600^{\circ}C$.

A straight line from a plot of the Freundlich isotherm, as shown in Figure 3, explains the degree of linearity and further tells the type of adsorption. If $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process [21, 22]. In this study, the n values for iron (II) and methylene blue are 0.942 and 0.330 respectively. This result indicates that the adsorption of each adsorbate onto RPSAC is a chemisorption process.

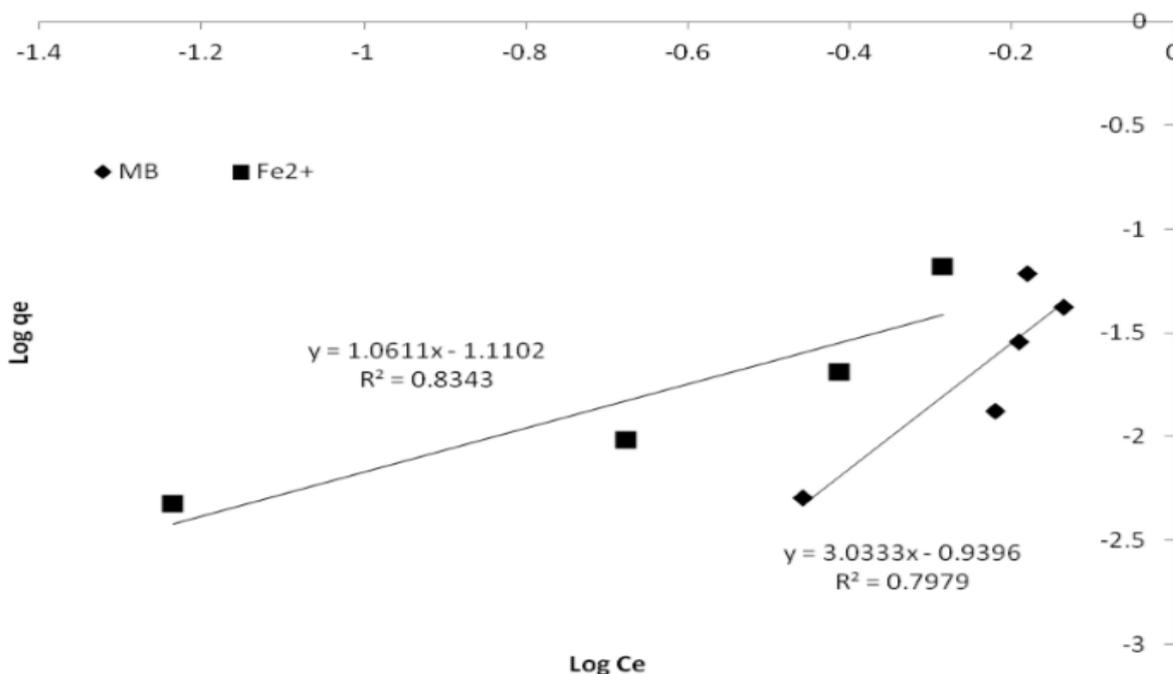


Figure-3. Freundlich adsorption isotherms for the adsorption of Fe^{2+} and Methylene Blue onto RPSAC.

3.5. Dubinin-Radushkevich Isotherm

This isotherm model is commonly used to estimate the characteristic porosity of the biomass/adsorbent and the apparent or mean free energy of the adsorption process [23, 24]. The terms expressed in Table 1 for the D-R isotherm are defined as follows:

q_m = theoretical saturation capacity. The higher the values of q_m , the higher the adsorption capacity.

q_e = equilibrium solid phase concentration.

ε = Polanyi potential is expressed mathematically, in Equation 3:

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (3)$$

Where:

T = Absolute temperature (K).

R = Universal gas constant.

β = a constant related to the adsorption energy as presented in Equation 4:

$$E = (2\beta)^{-1/2} \quad (4)$$

Where E = Sorption mean free energy.

Linear plots of the D-R isotherm for sorption of both iron (II) and methylene blue

Onto raphia hookeri seed is presented in Figure 4 below.

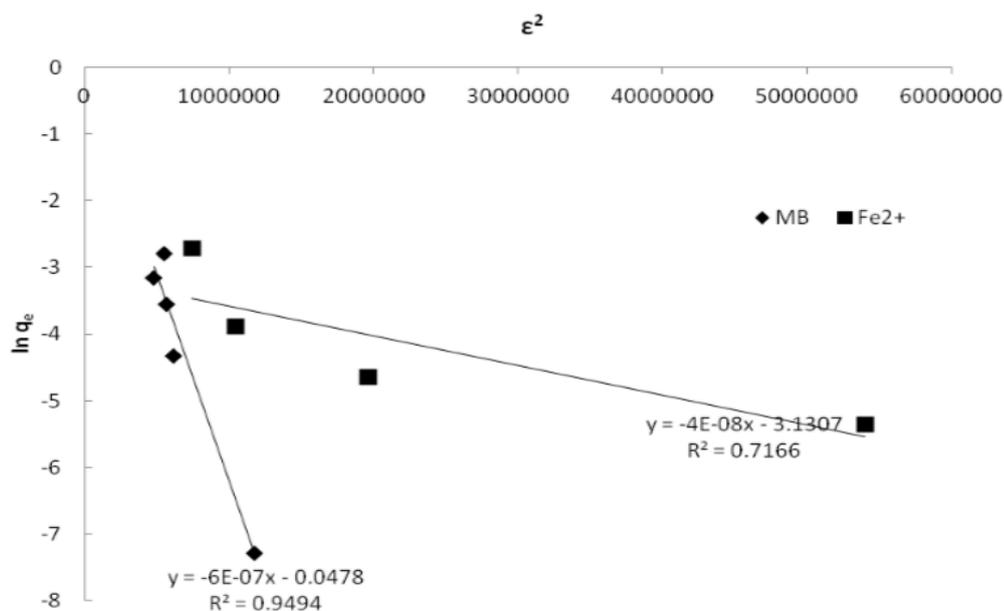


Figure-4. Dubinin-Radushkevich adsorption isotherms for the adsorption of Fe^{2+} and Methylene blue onto RPSAC at 31.5°C; adsorbent size = 300 μm ; carbonisation temperature = 600°C.

Table-2. Isotherm parameters obtained using the linear method.

Isotherm	Parameters	Unit	Fe^{2+}	MB
Langmuir	q_m	mg/g	0.0543	0.00687
	K_a	gm^3/mg	1.59652	1.215079
	K_R		0.42141	0.29457
	R^2		0.9266	0.9583
Freundlich	$1/n$		1.0611	3.0333
	K_F	$(mg/g)(dm^3/mg)^{1/n}$	0.07759	0.114921
	R^2		0.8343	0.7979
D-R	β	Mol^2/J^{2S}	-4.0E-08	-6.00E-07
	q_m	mg/g	0.04369	0.953324
	R^2		0.7166	0.9494

4. CONCLUSION

The result indicates the suitability of raphia palm seed activated carbon for the removal of both pollutant types. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were used to represent the experimental data. Based on the high values of the coefficient of correlation ($R^2 = 0.9266$ and 0.9572 for iron and MB respectively) obtained from the linear plots, Langmuir isotherm was found to give the best fit for both adsorption systems. Moreover, separation factors, for both sorbate, obtained from the Langmuir isotherm parameters showed favourability of the twain adsorption processes; with K_R values less than 1. However, the K_R value for MB (0.29457) was lower than that of Fe^{2+} (0.42141), which is a suggestion that the biosorbent treats methylene blue better than iron (II).

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Competing Interests: The authors declare that they have no competing interests.

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