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Effect of temperatures and pH on methyl violet biosorption by *Mansonia* wood sawdust

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Abstract

In this study, the effect of temperature on the equilibrium biosorption of methyl violet dye from aqueous solution using *Mansonia* wood sawdust was studied. The equilibrium biosorption data were analyzed using three widely applied isotherm models; Langmuir, Freundlich and Redlich–Peterson isotherm. The fit of three linear Langmuir isotherm forms, the Freundlich isotherm, and the Redlich–Peterson isotherm were determined using linear and the non-linear methods. Langmuir isotherm parameters obtained from the three Langmuir linear equations by using linear method were dissimilar, except, when the non-linear method was used. Best fits were yielded with Langmuir and Redlich–Peterson isotherms. The methyl violet biosorption was strongly dependent solution pH and percentage dye removal became significant above pH 7, which was slightly higher than the pH_{PZC} of the sawdust material. In addition, various thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° were calculated. Results suggested that the biosorption was a spontaneous and endothermic process.

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Keywords: Adsorption; Methyl violet; Langmuir isotherm forms; Temperature; *Mansonia* wood sawdust

1. Introduction

Dyes are used extensively in the paper, textile, leather, dye house, pharmaceutical, food, cosmetics, and printing industries (Aksu, 2005). These dyes are primarily of synthetic origin and have complex aromatic structures, which makes them biochemically stable (Aksu and Tezer, 2005). Stability of dyes to light, oxidizing agents and heat are important for their application in most industries. Therefore most dye bearing wastewaters have high COD to BOD ratio and offer considerable resistance to biodegradation (Wong and Yu, 1999). As a result, the removal of dye color from waste effluents has become environmentally important (Sanghi and Bhattacharya, 2002; Malik 2003). Dying industry effluents constitutes one of the most prob-

lematic wastewaters for treatment not only for their high chemical and biological oxygen demands, suspended solids and content in toxic compounds but also for color, which being visible to human eye is often the first contaminant to be recognized (Otero et al., 2003). Colour removal from industrial wastewaters by adsorption techniques has become prominent in the past few years. The chemical and biological stability of dyes to conventional wastewater treatment methods and the growing need for better treatment have made adsorption a very favourable treatment process. The need to achieve high quality treatment at low cost and with high efficiency has led researchers to search for new sources inexpensive, readily available adsorbent materials.

Mansonia is classified as hard wood and is generally grayish brown in color (Rosevear, 1954). *Mansonia* wood is used in many applications due to its high bending strength, low stiffness, and medium resistance to shock and high crushing strength. *Mansonia* is used by the automobile industry for

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interior applications such as fascias, dashboards and window trims. It is also used extensively in the furniture industry.

In this study, the temperature effect on the equilibrium biosorption of methyl violet on to *Mansonia* wood sawdust was examined and the resulting isotherm compared using the linear least-square method and a trial and error non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel of three widely used isotherms, including Langmuir (three different linear forms), Freundlich, and Redlich–Peterson was also examined (Ho, 2006). Thermodynamic parameters were also calculated.

2. Experimental procedure

2.1. Materials

Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with distilled water to remove surface impurities, and this was followed by drying at 100 °C for 24 h. The sawdust was ground and sieved. Sawdust particles used were retained between the sieves: 400–150 µm. The sieved sawdust was then stored in an airtight container.

The basic dye, methyl violet, was used without further purification. A stock solution of 1000 mg/dm³ was prepared by dissolving a weighed amount of methyl violet in 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.2. Methods

The proximate composition of the *Mansonia* sawdust was determined using methods of the Association of Official Analytical Chemists (AOAC) (1990). The infrared (IR) spectra of the *Mansonia* sawdust samples were recorded using KBr disk in conjunction with a Perkin–Elmer infrared spectrophotometer. KBr disks were prepared by mixing a given sample with KBr crystals, the resulting mixture being ground to a fine powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies.

2.3. Point of zero charge

The pH at point zero charge (pH_{PZC}) of the *Mansonia* wood sawdust was determined by the solid addition method (Mall et al., 2006). To a series of 100 ml conical flasks, 45 ml of KNO₃ solution of known concentration was transferred. The pH_i values of the solution were roughly adjusted from pH 2 to 12 by adding either 0.1 N HCl or NaOH. The total volume of the solution in each flask was made up to 50 ml by adding the KNO₃ solution of the same strength. The pH_i of the solution was accurately noted, and 0.1 g of *Mansonia* wood sawdust was added to the flask, which was

securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquids were noted. The difference between the initial and final pH values ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i$) was plotted against the pH_i. The point of intersection of the resulting curve at which $\Delta\text{pH} = 0$ gave the pH_{PZC}.

2.4. Effect of temperature on biosorption

A volume of 100 ml of Methyl Violet solution with a concentration ranging from 30 to 120 mg/dm³ was placed in to five 250 ml conical flasks and set at pH 10. A weighed amount (0.4 g) of the *Mansonia* wood sawdust ($d_p = 275 \mu\text{m}$) was added to the solution. The conical flask were then shaken at a constant speed of 200 rpm in a shaking water bath with temperatures 299, 309, 319 and 329 K, respectively. After shaking the flasks for 2.5 h, the *Mansonia* wood sawdust was separated by filtration. The filtrate was analyzed for the remaining methyl violet concentration by a spectrophotometer ($\lambda_{\text{max}} = 580 \text{ nm}$).

2.5. Desorption study

Sawdust material (0.4 g) used in contact with 120 mg/dm³ methyl violet solution was washed with distilled water at the end of the equilibrium experiment and used for the desorption test. Therefore, 0.4 g of the used biosorbent was suspended in 100 ml of distilled water set at varying pH adjusted to 3.0, 4.0, 5.0, 6.0, and 7.0 using HCl and agitated at 200 rpm at 299 K at the end of 2.5 h; the biosorbent was separated from the solution and analyzed at 580 nm with UV spectrophotometer.

3. Results and discussion

3.1. Some properties of *Mansonia* sawdust

3.1.1. Proximate composition

The percentage proximate composition of *Mansonia* sawdust on dry weight basis was: carbohydrate 71.0%, protein 1.46%, ash 5.88%, fibre 6.15%, lipid 0.49%, and moisture 15.0%.

3.1.2. Infrared analysis

The IR measurement of *Mansonia* wood sawdust showed the presence of the following functional groups: C=O (1682.1 cm⁻¹), COOH (3300–2500, 1111.8 cm⁻¹), –OH (3426.2 cm⁻¹), C–N (1030–1237 cm⁻¹), NH₂ (3400–3500 cm⁻¹).

3.2. Point of zero charge

Point of zero charge determination of biosorbent is important in elucidating biosorption mechanism. Biosorption of cations is favour at pH > pH_{PZC}, while anion biosorption is favoured at pH < pH_{PZC}. The specific

biosorption of cations shifts pH_{PZC} towards lower values whereas the specific biosorption of anions shifts pH_{PZC} towards higher values. The plot of change in solution pH (ΔpH) versus initial pH (pH_i) showed that with increasing initial solution pH, the pH change became more negative and the zero value of ΔpH was reached at pH_i value of 6.91, which is considered as the pH_{PZC} of *Mansonia* wood sawdust.

The result of percentage methyl violet removal with varying solution pH shows that at low solution pH (pH 3–5) only a small percentage of the methyl violet was removed from solution (0.03–0.2%). As the solution pH increased above pH 5 and up to pH 10, the increase in percentage methyl violet removal became more rapid increasing from 3.7% to 40.5%. The increase in percentage removal of methyl violet from solution then slowed down to almost constant value (pH 10–12).

It is clear that there is an observed relationship between cation biosorption and the magnitude of negative charge on the surface of the biosorbent, which is related to the surface functional groups (Selatnia et al., 2004). Ionization of the polar functional groups on the biosorbent surface is brought about by the change in solution pH. For pH values greater than the pK_a of most functional groups on biosorbent surfaces, the sites will be mainly in the dissociated form and can exchange H^+ with cations in solution. pH is also known to affect the structural stability of dyes and therefore its colour intensity (Mall et al., 2005). The biosorption of methyl violet is therefore assumed to follow ion exchange mechanism as shown below



where MS^- and MSH represents the functional groups on biosorbent surface, MV is the methyl violet molecules.

Therefore, at low solution pH, the biosorbent surface associates with H^+ ions and becomes positively charged repelling the positively charged methyl violet cation. As solution pH increases, the functional groups dissociation and becomes negatively charged. At solution pH 6.91, the magnitude of positive and negative charge balances and net charge of the biosorbent surface is zero. Above pH 6.91, biosorbent surface becomes increasing negative; this is revealed in the rapid increase in percentage methyl violet removal observed between pH 6 and 10. Above pH 10, the percentage methyl violet removal becomes negligible.

3.3. Effect of temperature on equilibrium biosorption

At constant temperature, methyl violet ions held onto the *Mansonia* wood sawdust will be in equilibrium with methyl violet ions in bulk solution. The effect of temperature on the equilibrium isotherm of the biosorption of methyl violet from aqueous solution is shown in Fig. 1. The linear regression was used to determine the best-fitting isotherm. The Langmuir isotherm can be linearized into three different

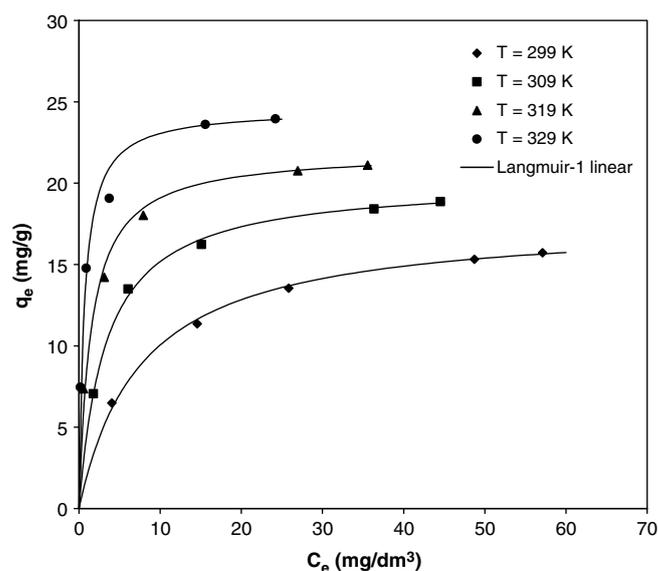


Fig. 1. Langmuir isotherms obtained using the Langmuir-1 linear method for the biosorption of methyl violet onto *Mansonia* wood sawdust at different temperatures.

forms (Table 1) (Persoff and Thomas, 1988), and simple linear regression results in different parameter estimates (Kinniburgh, 1986; Longhinotti et al., 1998). The more popular Langmuir forms used are the Langmuir-1 and Langmuir-2, with the Langmuir-1 most frequent giving the best fit because of the minimal deviation from the fitted equation resulting in the best error distribution (Kinniburgh, 1986). The values of the Langmuir constant, the saturation capacity, q_m , and the biosorption equilibrium constant, K_a , are shown in Table 2 for the biosorption of methyl violet onto *Mansonia* wood sawdust at 299, 309, 319, and 329 K. The values of the coefficient of determination, r^2 , obtained for Langmuir-1 and Langmuir-2 were closer to 1.000 than the other linear form of the Langmuir equation. This indicates that there is strong positive evidence that the biosorption of methyl violet molecules onto *Mansonia* sawdust follows monolayer coverage of methyl violet molecules on the sawdust surface and that the interaction between two methyl violet molecules is negligible. It is also observed in this study that the coefficient of determination for Langmuir-1 is higher than for Langmuir-2.

The monolayer capacity, q_m ; for Langmuir-1 using linear regression was found to increase from 17.7 to 24.6 mg/g and for Langmuir-2 was found to increase from 17.1 to 22.1 mg/g for an increase in solution temperatures from 299 to 329 K. The biosorption constant, K_a ; increases from 0.131 to 1.54 dm^3/mg , using Langmuir-1 form and from 0.150 to 3.15 dm^3/mg , using Langmuir-2 form as temperatures varied from 299 to 329 K. The results reveal that the heat of biosorption largely determines the magnitude of the Langmuir constant, K_a . The increase in K_a values with temperature indicates a higher heat of biosorption with increasing temperature. This means that stronger bonds are formed at

Table 1
Isotherms and their linear forms

Isotherm	Linear form	Plot
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	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} = \frac{1}{\frac{1}{q_m} + \frac{1}{K_a q_m} C_e}$	$\frac{C_e}{q_e}$ vs. C_e
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	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e
Redlich–Peterson	$q_e = \frac{A C_e}{1 + B C_e^g} \ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$	$\ln\left(A \frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$

Table 2
Isotherm parameters obtained using the linear method for the biosorption of methyl violet onto *Mansonia* wood sawdust at different temperatures

Isotherm	T (K)	299	309	319	329
Langmuir-1	q_m , mg/g	17.7	20.2	21.9	24.6
	K_a , dm ³ /mg	0.131	0.304	0.671	1.54
	r^2	1.000	1.000	1.000	0.999
Langmuir-2	q_m , mg/g	17.1	20.2	20.5	22.1
	K_a , dm ³ /mg	0.150	0.307	0.989	3.15
	r^2	0.998	0.999	0.991	0.987
Langmuir-3	q_m , mg/g	17.4	20.1	21.1	23.1
	K_a , dm ³ /mg	0.144	0.311	0.896	2.69
	r^2	0.990	0.994	0.962	0.930
Freundlich	1/n	0.333	0.289	0.249	0.224
	K_F , (mg/g)(dm ³ /mg) ^{1/n}	4.31	6.81	9.51	12.9
	r^2	0.969	0.911	0.932	0.931
Redlich–Peterson	g	0.914	1.000	0.914	0.907
	B, (dm ³ /mg) ^g	0.247	0.310	1.57	4.99
	A, dm ³ /g	3.03	6.24	25.2	90.8
	r^2	1.000	1.000	1.000	1.000

higher temperatures supporting the fact that biosorption is endothermic.

On application of the Freundlich biosorption isotherm to analyze the experimental data by plotting $\log(q_e)$ versus $\log(C_e)$, it was observed that the values of coefficient of determination, r^2 , for all three Langmuir isotherm linear forms were higher than the Freundlich isotherm (Table 2), indicating that the biosorption of methyl violet on to *Mansonia* wood sawdust is less likely to be a multilayer biosorption. The Freundlich isotherm constants K_F , $1/n$, and the coefficient of determination, r^2 , are shown in Table 2.

The Redlich–Peterson isotherm constants, A , B , and g as well as the coefficient of determination, r^2 , for the biosorption of methyl violet on to *Mansonia* wood sawdust using the linear regression is shown in Table 2. The values coefficients of determination, r^2 , were as high as those of the Langmuir-1 isotherm form and much higher than for the two other Langmuir equation forms and the Freundlich isotherm. It can be seen that the values of g were close to unity,

which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. Fig. 2 shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich–Peterson isotherm with the experimental data for the biosorption of Methyl Violet onto *Mansonia* wood sawdust at a temperature of 299 K. the values of coefficient of determination for the Redlich–Peterson and the Langmuir-1 isotherm form is the same but the fit of both isotherms to experimental data were different. The use of coefficient of determination of linear regression analysis for comparing the best fit of different linear isotherms was found not to be appropriate (Ho, 2004). Therefore, a further analysis was attempted; a trial and error procedure was used for non-linear method by using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel (Ho, 2006). In this procedure, the application of computer operation was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determi-

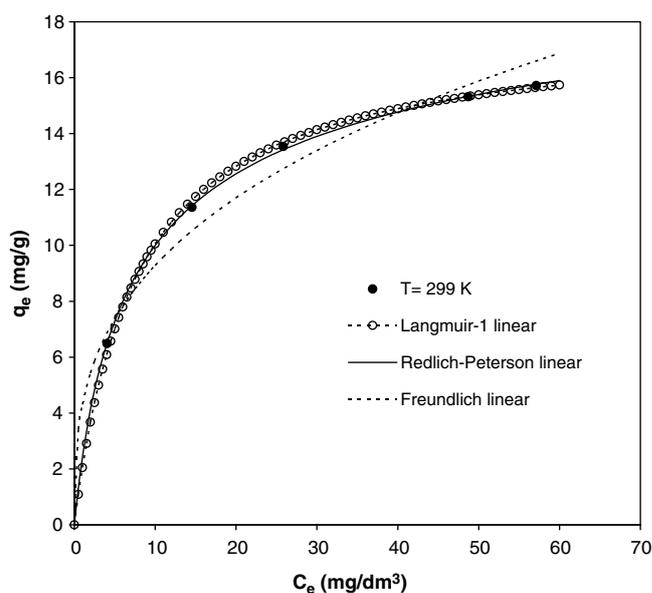


Fig. 2. Isotherms obtained using the linear method for the biosorption of methyl violet onto *Mansonia* wood sawdust at a temperature 299 K.

Table 3
Isotherm parameters obtained using the non-linear method for the biosorption of methyl violet onto *Mansonia* wood sawdust at different temperatures

Isotherm	T (K)	299	309	319	329
Langmuir	q_m , mg/g	17.6	20.1	21.6	23.8
	K_a , dm ³ /mg	0.134	0.316	0.731	1.97
	ΔG° , kJ/mol	-9.86	-12.4	-15.0	-18.2
	r^2	0.996	0.997	0.986	0.968
Freundlich	$1/n$	0.311	0.267	0.226	0.202
	K_F , (mg/g)(dm ³ /mg) ^{1/n}	4.64	7.28	10.1	13.5
	r^2	0.966	0.921	0.930	0.943
Redlich–Peterson	g	0.922	0.992	0.926	0.904
	B , (dm ³ /mg) ^g	0.233	0.333	1.39	5.10
	A , dm ³ /g	2.95	6.49	23.3	92.2
	r^2	1.000	0.997	0.998	0.998

nation between experimental data and isotherms. Table 3 shows isotherm parameters obtained by using non-linear method. In the case of Langmuir isotherm, the results for the three Langmuir linear equations were the same. By using non-linear method there was no problem with transformation of non-linear isotherm equation to linear forms, and also they had the same error structures (Ho, 2004). In the case of Redlich–Peterson, the values of g are close to unity, which is the same as the results from linear method and this means the isotherms are approaching the Langmuir but not Freundlich isotherm. The Langmuir constants obtained from the non-linear and linear methods differed even when compared with results of Langmuir-1, which had the highest coefficient of determination for any Langmuir isotherm (Tables 2 and 3). It seems that the best fit was obtained by Langmuir-1 as compared with other Langmuir equations because it had the highest coefficient of determination and the Langmuir constants K_a and q_m were both closer to those obtained using the non-linear method. Fig. 3 shows that the Redlich–Peterson and Langmuir isotherms overlapped, and they seem to be the best-fitting models for the experimental results with the same values of coefficient of determination (Table 3). Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity (Ho, 2003; Ho et al., 2002) and Redlich–Peterson constant B is the same as Langmuir biosorption equilibrium constant, K_a . In addition, it was reported that Freundlich isotherm is a special case of Redlich–Peterson isotherm when constants A and B are much greater than unity (Ho, 2004). Unlike the linear analysis, different isotherm forms would affect r^2 significantly, and impact the final determination of parameters while non-linear methods would prevent such errors.

3.4. Thermodynamic studies

Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° , is an indi-

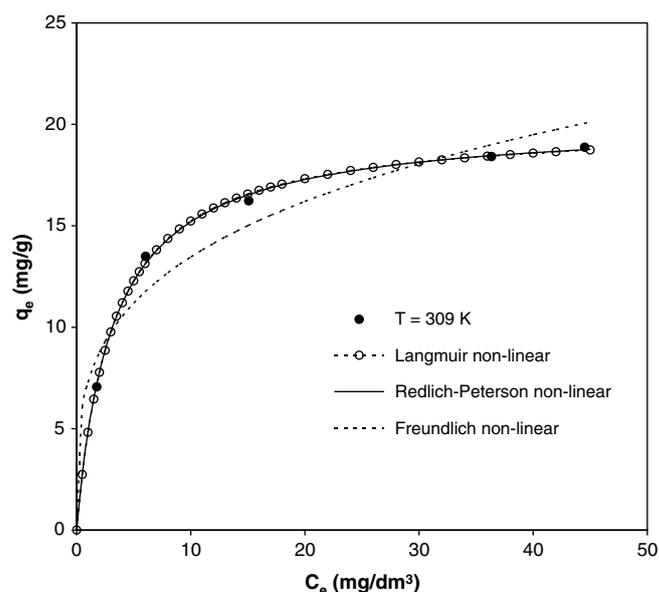


Fig. 3. Isotherms obtained using the non-linear method for the biosorption of methyl violet onto *Mansonia* wood sawdust at a temperature 309 K.

cation of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of a biosorption reaction, considering the biosorption equilibrium constant K_a is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (3)$$

where ΔG° is the standard free energy change, J/mol; R is the universal gas constant, 8.314 J/mol K, and T is absolute temperature, K.

Considering the relationship between free energy and equilibrium constant, change in equilibrium constant with temperature can be obtained in the differential form as follows (Ho, 2003):

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (4)$$

After integration, the integrated form of Eq. (4) becomes

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + Y \quad (5)$$

where Y is a constant. Eq. (5) can be rearranged to obtain $-RT \ln K_a = \Delta H^\circ - TRY$

Let

$$\Delta S^\circ = RY \quad (7)$$

Substituting Eqs. (6) and (7), the Gibbs free energy change, ΔG° , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

The biosorption equilibrium constant, K_a , obtained from non-linear method were analysis using Eqs. (3) and (8). A plot of Gibbs free energy change, ΔG° , versus temperature, T , will be linear and the values of ΔH° and ΔS° determined from the slope and intercept of the plot. The parameter Gibbs free energy, ΔG° , for the biosorption process using the biosorption equilibrium constant, K_a , from the Langmuir-1 forms is shown in Table 3. The values of Gibbs free energy, ΔG° , calculated using the biosorption equilibrium constant, K_a , from the non-linear method were negative for the biosorption of methyl violet onto *Mansonia* wood sawdust all temperature. The negative values confirm the feasibility of the process and the spontaneous nature of the biosorption. The values of ΔG° , were found to increase -18.2 to -9.86 kJ/mol using the equilibrium constant, K_a , from the non-linear method. The values of ΔH° and ΔS° calculated from the plot of Gibbs free energy change, ΔG° , versus absolute temperature, K , using the biosorption equilibrium constant, K_a , from the non-linear method is given as 67.1 kJ/mol and 0.257 kJ/mol K. The value of ΔH° is positive, indicating that the biosorption reaction is endothermic. The positive value of ΔH° reflects the affinity of the *Mansonia* wood sawdust for methyl violet and suggests some structural changes in the methyl violet/*Mansonia* wood system (Gupta, 1998). In addition, the positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the biosorption of methyl violet on *Mansonia* wood sawdust. Positive values of ΔS° have also reported for the biosorption of some basic dyes on tree fern (Ho et al., 2005), wheat shell (Bulut and Aydin, 2006), and Neem leaf powder (Bhattacharyya and Sharma, 2005). In most cases, the biosorption of basic dyes onto agricultural wastes have been shown to be spontaneous and endothermic (Bhattacharyya and Sharma, 2005; Ho et al., 2005; Bulut and Aydin, 2006).

3.5. Desorption study

The result of desorption showed that more of the biosorbed methyl violet was desorbed at lower pH and that desorption reduced as solution pH increased to pH 7. It has been shown that distilled water at neutral pH will desorb cations that are only weakly attached to biosorbent (Mall et al., 2006). As solution pH is reduced, hydrogen ion (H^+) concentration increases in solution, which then displaces biosorbed dye cations into solution. Increase in hydrogen ion concentration caused an increase in the displacement of dye cation from the biosorbent. Biosorption mechanism of methyl violet on to *Mansonia* wood sawdust may likely be due to ion exchange mechanism between methyl violet cation and acidic functional groups on *Mansonia* wood sawdust surface.

4. Conclusion

Biosorption of methyl violet from aqueous solution by *Mansonia* wood sawdust is a spontaneous and endother-

mic process. The saturated monolayer biosorption capacity of the *Mansonia* wood sawdust for methyl violet at 329 K was calculated to be 24.6 mg/g. The biosorption process is pH dependent and maximum percentage removal of methyl violet from aqueous solution occurred above the pH_{PZC} of the sawdust material. Desorption of biosorbed methyl violet dye increased with increasing HCl concentration suggesting that biosorption mechanism is by ion exchange. Non-linear method of error analysis could be a better way to compare isotherm fitting. Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity. Both two-parameter Langmuir and three-parameter Redlich–Peterson isotherms were the best-fitting models for the biosorption of methyl violet on *Mansonia* wood sawdust.

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