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Equilibrium sorption of methylene blue using mansonia wood sawdust as biosorbent

Augustine E. Ofomaja

Department of Chemistry, Faculty of Physical Science, University of Benin, Ugbowo-Lagos Road, Benin City, Edo State, Nigeria
Tel. +234 802 871 5034; email: aus_ofomaja@yahoo.com

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ABSTRACT

The potential use of mansonia wood sawdust as low-cost adsorbent for the sorptive removal of basic dye, methylene blue, from aqueous solution has been studied. The effect of sawdust particle size on the equilibrium methylene blue uptake was examined using batch sorption technique. Adsorption isotherm was determined using various particle sizes (150, 250, 350, 450 and 550 μm) of mansonia sawdust at 26 °C and the experimental data obtained were modeled using the Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherms. The results revealed that the sawdust particle size has a strong influence on the percentage dye removal and on the amount of dye adsorbed per gram of sawdust from a 120 mg/dm^3 dye solution. Increasing sawdust particle size from 150 to 550 μm reduced the percentage dye uptake from 93.57% to 29.50 % and amount of dye adsorbed per gram of sawdust from 28.07 to 8.85mg/g. The isotherm data were found to be well described by the Langumir, Tempkin and Dubinin–Radushkevich isotherm models. The monolayer capacity calculated from the Langmuir equation is given as 33.44 mg/g using sawdust of particle size 150 μm. The equilibrium binding constant K_t calculated from the Tempkins was reduced with increasing sawdust particle size from 150 to 550 μm, while the mean free energy of sorption per mole of sorbate calculated from the Dubinin–Radushkevich isotherm was in the range 12.91 to 13.89 mol^2kJ^{-2}, suggesting that the sorption mechanism was by ion exchange. A mathematical relationship was also drawn between the equilibrium sorption capacity and the change in pH (ΔH^+) at the end of the isotherm experiments with varying initial dye concentration, supporting the fact that sorption of methylene blue dye on mansonia sawdust is by ion exchange. Desorption of sorbed dye molecules into solution was achieved at low pH conditions.

Keywords: Mansonia sawdust; Sorption isotherm; Methylene blue dye; Ion exchange; Monolayer capacity

1. Introduction

Dyes impart color to water and make it obvious that water is polluted [1]. Some dyes are reported to cause allergy, dermatitis, skin irritation, cancer and mutations in humans [2,3]. Dyes have been found in waters from the textile, paper, plastic, leather, food, and mineral processing industries [4], and pose serious environmental problems due to their persistent and recalcitrant nature. Dyes can also be problematic if they are broken down anaerobically in sediments as toxic amines that are often produced due to incomplete degradation by bacteria [5].

Removal of dyes from water by adsorption can produce high-quality water while also being a process that is economically feasible [6]. Decoloration is as a result of two mechanisms — adsorption and ion exchange [7]— and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. Activated carbon is the most popular adsorbent and has been used with great success [8]. However, due to the difficulty and expense of regeneration, agricultural wastes are being considered as alternative low-cost adsorbents for dyes from aqueous solution [9–20].

Mansonia altissima is a native wood of West Africa; it is reported to occur in tropical West Africa from the Ivory Coast to Cameroon and is especially found along the coast of southwest Nigeria from the eastern margin of the Dehomey Gap in Benin (0240 E) to the Niger River (0650 E) in the west. Mansonia is classified as hard wood and is generally grayish-brown in color [21]. Mansonia wood is used in many applications due to its high bending strength, low stiffness, medium resistance to shock and high crushing strength. Mansonia is used by the automobile industry for interior applications such as fascias, dashboards and window trims. It is also used extensively in the furniture industry.

Mansonia sawdust is therefore a common waste in sawmills located in major cities of southwestern Nigeria. This study is therefore aimed at investigating the potential use of Mansonia sawdust as a biosorbent for the removal of methylene blue dye from aqueous solution. The system variables studied include particle size and initial dye concentration. Isotherm data were analyzed using the Langmuir, Freundlish, Tempkin and Dubinin–Radushkevich isotherm models. The mechanism of dye sorption and desorption of dye from sorbent was also studied.

2. Experimental procedure

2.1. Materials

The Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with 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 was that retained between the set of sieves: 700–150 μm, 600–150 μm, 500–150 μm, 400–150 μm, 300–150 μm. The sieved sawdust was then stored in an airtight container.

The basic dye, methylene blue (BDH, 85% dye content) was used without further purification. The stock solution of 1000 mg/l was prepared by dissolving 1.127 g methylene blue 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 palm kernel fibre was determined using methods of the Association of Official Analytical Chemists (AOAC) [22]. The IR spectra of the mansonia sawdust sample were recorded using a KBr disk in conjunction with a Perkin–Elmer infrared spectrophotometer. The KBr disk was 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. Effect of sawdust particle size on the uptake of methylene blue from 120 mg/l solution

Accurately weighed amounts (0.4 g) of sawdust material of different particle sizes (150, 250, 350, 450 and 550 μm) were put in contact with 100 ml of 120 mg/l methylene blue solution set at pH 10 (using 0.01 M HCl or NaOH) in a reacting vessel agitated at 200 rpm at 299 K. After 2 h of contact, the solution was centrifuged and the clear supernatant removed for analysis in a UV/visible spectrophotometer at wavelength 665 nm for the methylene blue left. The amount of methylene blue removed was calculated from the difference.

2.4. Equilibrium studies

Accurately weighed amounts (0.4 g) of sawdust material of different particle sizes (150, 250, 350, 450 and 550 μm) were put in contact with 100 ml of methylene blue solutions ranging from 30–150 mg/l and set at pH 10 (using 0.01 M HCl or NaOH) in a reacting vessel agitated at 200 rpm at 299 K. After 2 h of contact, the solution was centrifuged and the clear supernatant removed for analysis in a UV/visible spectrophotometer at wavelength 665 nm for the methylene blue left. The amount of methylene blue removed was calculated from the difference. The solution pH before and after sorption was determined using a pH meter and the corresponding hydrogen ion concentrations calculated.

2.5. Desorption experiment

The sawdust material used in the equilibrium experiment was carefully separated from the solution by centrifugation and decantation. The sawdust was then suspended in distilled water of the same volume with a pH adjusted to 3.0 using HCl. The methylene blue desorbed was analyzed by UV/visible spectrophotometer at wavelength 665 nm.

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 71.02%, protein 1.46%, ash 5.88%, fibre 6.15%, lipid 0.49% and moisture 15.00%.

3.1.2. Infrared analysis

The IR measurement of mansonia 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}), NH_2 (3400–3500 cm^{-1}).

3.2. Equilibrium isotherm

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. The equilibrium study gives the capacity of the sorbent and describes the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. The equilibrium data in this study were analyzed using four different isotherm models.

3.2.1. Langmuir isotherm

Basic forms of the Langmuir isotherm [23] have reasonable agreement with a large number of experimental systems including those which have different interfaces between the two phases [24–27]. Therefore, the Langmuir isotherm is most widely used for the sorption of a solute from a liquid solution assuming the sorption takes place at specific homogenous sites within the sorbent. Furthermore, it also assumes that once a dye occupies a site, on further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ, the rate per unit of surface is:

$$r_a = k_a C(1-\phi) \tag{1}$$

The desorption from the surface is proportional to the amounts of surface covered:

$$r_d = k_d \phi \tag{2}$$

where k_a and k_d are the rate constants, r_a the sorption rate, r_d the desorption rate, C_e the concentration in the solution and ϕ the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

$$\phi = \frac{k_a C_e}{k_d + k_a C_e} \tag{3}$$

and

$$K_a = \frac{k_a}{k_d} \tag{4}$$

Since q_e is proportional to ϕ:

$$\phi = \frac{q_e}{q_m} \tag{5}$$

The saturated monolayer sorption capacity, q_m, can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{6}$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \tag{7}$$

where C_e is the equilibrium concentration (mg/dm^3), q_e the amount of dye sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_a the sorption equilibrium constant (dm^3/mg). A plot of C_e/q_e vs C_e should give a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

3.2.2. Freundlich isotherm

Freundlich presented an empirical sorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multiplayer sorption and is expressed by the equation [28]:

$$q_e = K_F C_e^{1/n} \tag{8}$$

where C_e (mg/dm^3) is the left-out solute concentration at equilibrium, q_e (mg/g) is the amount of lead sorbed at equilibrium, and K_F (mg/g)(dm^3/g)$^{1/n}$ and $1/n$ are the Freundlich constants related to sorption capacity and sorption intensity respectively.

3.2.3. Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich (D–R) isotherm is generally expressed as follows [29]:

$$q_e = q_D \exp\left(-B_D\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \tag{9}$$

Radushkevich [30] and Dubinin [31] reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant, B_D, is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship [32]:

$$E = \frac{1}{\sqrt{2B_D}} \tag{10}$$

The linear form of the D–R isotherm equation is

$$\ln q_e = \ln q_D - B_D \epsilon^2 \tag{11}$$

where B_D is a constant related to the mean free energy of adsorption per mole of the adsorbate ($\mathrm{mol^2 J^{-2}}$); q_D the theoretical saturation capacity and ϵ is the polanyi potential, which is equal to $RT \ln[1+(1/C_e)]$ where R ($\mathrm{Jmol^{-1}K^{-1}}$) is the gas constant and T (K), the absolute temperature. Hence by plotting $\ln q_e$ against ϵ^2, it is possible to generate the values of q_D ($\mathrm{mol\ g^{-1}}$) from the intercept and the values of B_D from the slope.

3.2.4. Tempkin isotherm

The Tempkin isotherm contains a factor that explicitly takes into account absorbing species-adsorbate interactions. The isotherm assumes that: (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interaction, and (2) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [33]. The Tempkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_t C_e) \tag{12}$$

Eq. (12) can be expressed in its linear form as:

$$q_e = B_1 \ln K_t + B_1 \ln C_e \tag{13}$$

where

$$B_1 = \frac{RT}{b} \tag{14}$$

The adsorption data can be analyzed according to Eq. (13). A plot of q_e vs ln C_e enables the determination of the isotherm constants K_t and B_1. K_t is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and B_1 is related to the heat of adsorption.

The optimisation procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data. In this study, linear coefficient of determination and non-linear Chi-square were examined. The coefficient of determination, r^2, represents the percentage of variability in the dependent variable that has been explained by the regression line. The value of the coefficient of determination may vary from zero to one. A coefficient of determination of one indicates that 100% of the variation of q_e has been explained by the regression equation. The linear coefficient of determination, r^2, found from evaluation of data by linear model, was calculated with aid of the equation:

$$r^2 = \frac{S_{xy}^2}{S_{xx} S_{yy}} \tag{15}$$

where S_{xx} is the sum of squares of X,

$$S_{xx} = \sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i\right)}{n} \tag{16}$$

where S_{yy} is the sum of squares of Y,

$$S_{yy} = \sum_{i=1}^{n} y_i^2 - \frac{\left(\sum_{i=1}^{n} y_i\right)}{n} \tag{17}$$

where S_{xy} is the sum of squares of X and Y, and

$$S_{xy} = \sum_{i=1}^{n} x_i y_i - \frac{\left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_i\right)}{n} \tag{18}$$

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{19}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number.

Therefore, it is necessary to also analyze the data set using the nonlinear Chi-square test to confirm the best-fit isotherm for the sorption system.

3.3. Effect of sawdust particle size

The effect of particle size of mansonia sawdust on methylene blue sorption from a 120 mg/L solution was tested by contacting 0.4 g of each particle size (150, 250, 350, 450 and 550 µm) of the mansonia sawdust in beakers containing 100 ml of 120 mg/L methylene solution agitated at 200 rpm, pH 10 and 299 K. The result of the uptake is shown in Fig. 1. The results revealed that particle size of sawdust had a strong influence on the percentage of methylene blue removed from solution. The percentage of methylene blue removed was found to increase as the particle size of the sawdust material reduced from 550 to 150 µm. When particle size of sawdust was increased (from 150 to 350 µm) the percentage dye removed was reduced by about 50%. The increase in percentage dye removal with decreasing particle size has been observed by several authors using different adsorbents [34–37].

The amount of methylene blue adsorbed per gram of Mansonia sawdust (Fig. 2) was also found to increase with decrease in particle size of the sawdust material. A decrease in sawdust particle size from 550 to 150 µm increased the amount of methylene blue sorbed per gram of sawdust from 8.85 to 28.07 mg/g. The increase in the equilibrium capacity of methylene blue with decreasing particle size can be accounted for by the fact that, as particle size decreases for a given mass of sawdust material, the surface area available for sorption is increased and this leads to an increased number of

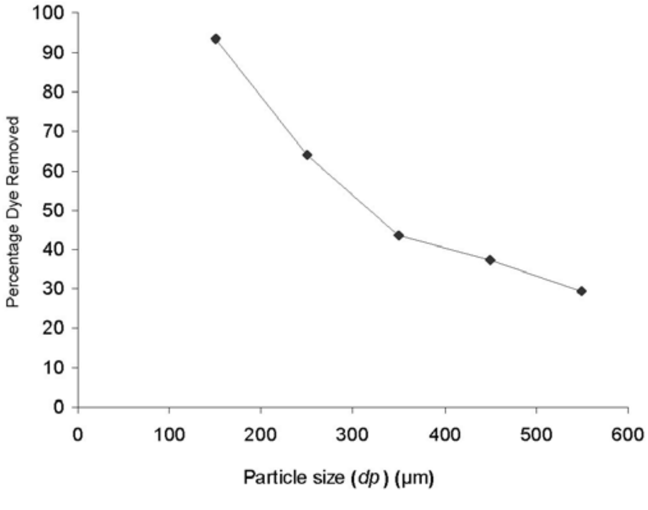

Fig. 1. Effect of sawdust particle size on percent methylene blue uptake from a 120 mg/dm^3 solution. Solution pH: 10; temperature: 26 C; agitation speed: 200 rpm; sorbent mass: 0.004 g/l.

3.4. Equilibrium study

In order to assess the different adsorption isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm are shown with experimental data for the adsorption of methylene blue onto mansonia sawdust (dρ = 150 µm) at a temperature of 299 K (Fig. 3). The plot was made in the form of methylene blue 13 adsorbed per unit mass of sawdust material, q_e, against the concentration of methylene blue remaining in sorption sites. Also, as particle size reduces, inner surfaces become exposed which could not be penetrated by the large dye molecules. Similar effect was observed by Ho et al. [38] in the sorption of Basic Red 13 onto tree fern of various particle sizes.

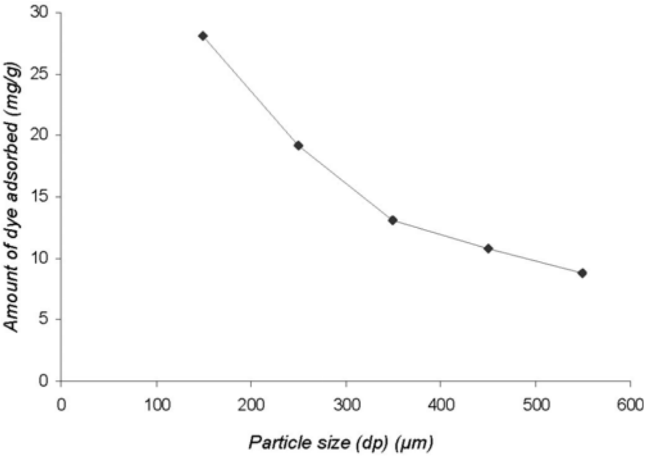

Fig. 2. Effect of sawdust particle size on the amount of methylene blue adsorbed from a 120 mg/dm^3 solution. Solution pH: 10; temperature: 26°C; agitation speed: 200 rpm; sorbent mass: 0.004 g/l.

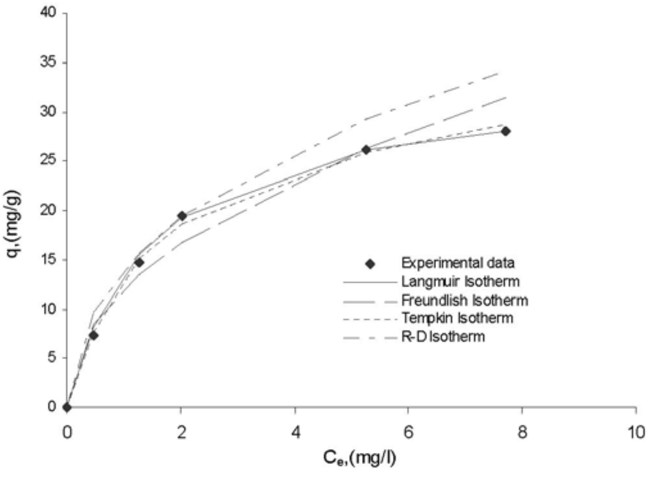

Fig. 3. Comparison of different isotherm models on the sorption of methylene blue from aqueous solution. Solution pH: 10; temperature: 26°C; agitation speed: 200 rpm; particle size 150 µm; sorbent mass: 0.004 g/l.

Table 1
A comparison of Chi-square and coefficient of determination for four isotherms

Particle size (µm)	Freundlich		Langmuir		Tempkin		D–R	
	χ^2	r^2	χ^2	r^2	χ^2	r^2	χ^2	r^2
150	0.2227	0.9473	0.0138	0.9995	0.0160	0.9947	0.1600	0.9616
250	0.1247	0.9324	0.0003	1.0000	0.0217	0.9805	0.0946	0.9517
350	0.0810	0.8911	0.00003	0.9999	0.0387	0.9354	0.0601	0.9156
450	0.0342	0.9418	0.0016	0.9997	0.0127	0.9715	0.0055	0.9608
550	0.0154	0.9621	0.0002	0.9999	0.0044	0.9864	0.0107	0.9755

solution, C_e. A comparison of coefficient of determination and the Chi-square error analysis for the four adsorption isotherms was made and is listed in Table 1. It can be seen from Table 1 that the Langmuir isotherm was best fitted to the experimental data since it had the highest values for the correlation coefficient and also the least values for the non-linear Chi-square χ^2. The Langmuir isotherm is the most suitable of the four isotherm models applied to the adsorption system. The Langmuir isotherm assumes monolayer coverage of the adsorbent surface by the adsorbate molecules and that the surface is completely uniform and energetically homogeneous.

The Tempkin and D–R isotherms also have fairly good degrees of fitness to the experimental data with relatively high values of coefficient of determination, r^2 and low values for the non-linear Chi-square, χ^2. The good fit may be due to the fact that Tempkin's isotherm assumes that adsorption is characterized by a uniform distribution of binding energies, while the D–R isotherm assumes that some fraction of the surface is uniform and energetically homogeneous.

The linear form of the Langmuir isotherm was used to determine the effect of particle size of sawdust on the methylene blue capacity of various methylene blue/mansonia sawdust systems. The isotherms were determined using five particles size range of mansonia sawdust (150, 250, 350, 450 and 550 µm) in contact with methylene blue for 6 h. Fig. 4 shows the plot of the Langmuir isotherm along side the experimental data at different sorbent particle sizes. The Langmuir isotherm model was found to fit closely with the experimental data, as seen from the coefficient of determination in Table 1. The Langmuir isotherm model assumes a monolayer sorption of dye molecules on the sorbent surface and has also been successfully applied to other dye/sawdust systems such as metal complex blue on pine sawdust onto pine sawdust [39].

The isotherm constants q_m and K_a are presented in Table 2. The monolayer capacity, q_m, increased from 10.32 to 33.44 mg/g as the particle size of mansonia sawdust decreased from 550 to 150 µm. Therefore, for a given mass of mansonia sawdust, smaller particle size increases the number of available sites. The monolayer capacities of other agricultural wastes for dyes from literature are shown in Table 3. The values of particle size of the sawdust material, the monolayer capacity, q_m, and the Langmuir sorption constant, K_a, can be used to derive mathematical relationships. The relationships have coefficients as high as 0.9956 and 0.9937:

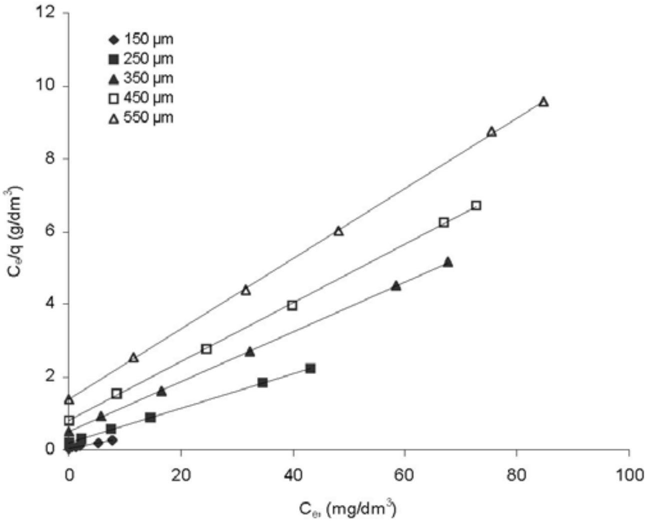

Fig. 4. Langmuir isotherm model for the sorption of methylene blue from aqueous solution. Solution pH: 10; temperature: 26°C; agitation speed: 200 rpm; sorbent mass: 0.004 g/l.

$$q_m = 3.593\times10^3\,dp^{-0.931} \quad (20)$$

and

$$K_a = 1.938\times10^3\,dp^{-1.627} \quad (21)$$

The effect of the isotherm shape can be used to predict whether a sorption system is "favourable" or "unfavourable", both in fixed-bed systems [47] as well as in batch processes [48]. According to Hall et al. [49], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R that is defined by the following

Table 2
Isotherm constants for the adsorption of methylene blue onto mansonia sawdust with various particle sizes

Particle size (μm)	Freundlich		Langmuir		D–R			Tempkin	
	n	K_F (dm^3 g^{-1})	q_m (mol g^{-1})	K_a (dm^3 mol^{-1})	q_D (mol g^{-1})	B_D (mol^2 kJ^{-2})	E (kJ mol^{-1})	B_1 (L mg^{-1})	K_t
150	2.11	11.93	33.44	0.6750	7.9E-04	−3.41E-09	12.91	7.60	5.67
250	2.99	5.95	21.23	0.2228	2.06E-04	−2.59E-09	13.89	7.12	2.87
350	3.39	4.05	14.58	0.1338	1.15E-04	−2.44E-09	14.31	2.08	2.14
450	3.13	2.90	12.31	0.0974	1.08E-04	−2.79E-09	13.39	2.52	1.15
550	3.05	2.15	10.32	0.0698	8.51E-05	−2.86E-09	13.22	2.14	0.80

Table 3
Comparison of monolayer equilibrium capacity of some adsorbents for methylene blue from aqueous solution

Adsorbate	q_m (mg/g)	Reference
Cedar sawdust	142.36	[40]
Wood	84.00	[41]
Raw date peat	80.30	[42]
Peanut hull	68.03	[43]
Indian rosewood sawdust	51.40	[44]
Banana peel	20.80	[45]
Neem leaf powder	19.61	[46]
Orange peel	18.60	[45]
Mansonia wood sawdust	33.44	This study

relationship:

$$K_R = 1/(1 + K_a C_0) \tag{22}$$

where K_R is a dimensionless separation factor, C_0 the initial concentration (mg/dm^3) and K_a the Langmuir constant (dm^3/mg). The parameter K_R values indicate the shape of the isotherm as follows:

- $K_R > 1$: unfavourable
- $K_R = 1$: linear
- $0 < K_R < 1$: favourable
- $K_R = 0$: irreversible

The values of K_R for methylene blue at different particle sizes are shown in Fig. 5. The K_R values indicate that sorption is more favourable for the higher initial dye concentrations than the lower ones. However, the sorption process became more favourable with decreasing particle size of mansonia sawdust. Nevertheless, referring to Fig. 5, it is obvious that mansonia sawdust would be an effective sorbent for removing dye from solution.

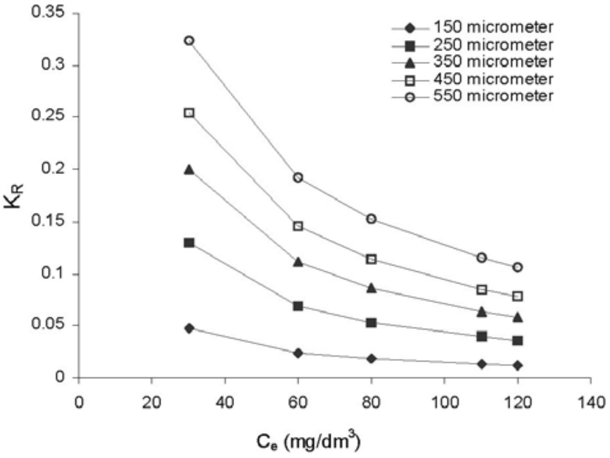

Fig. 5. Values of the separation factor, K_R, for the sorption of methylene blue using mansonia sawdust of various particle sizes.

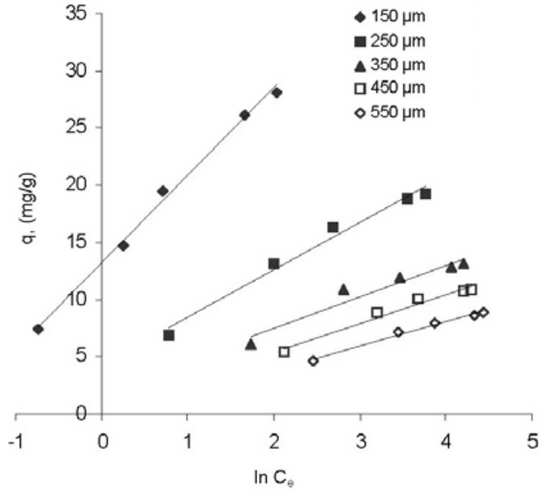

Fig. 6. Tempkin isotherm model for the sorption of methylene blue from aqueous solution. Solution pH: 10; temperature: 26°; agitation speed: 200 rpm; sorbent mass: 0.004 g/l.

The isotherm plot according to the Tempkin isotherm model is shown in Fig. 6 where the isotherm constants B_1 and Kt were calculated and shown in Table 2. The value for the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, K_t, was found to decrease with increasing particle size of mansonia sawdust. This is the same trend as the equilibrium sorption constant or binding constant, K_a, obtained from the Langmuir isotherm. This supports the fact that sorption of dye on to sawdust of smaller particle size is more favourable than for larger particle sizes. The constant B_1, which relates to heat of adsorption, was also found to decrease with sawdust particle size.

The isotherm plot according to the D–R isotherm model is shown in Fig. 7. The parameter E provides information about the adsorption mechanism as chemical ion-exchange or physical adsorption. In the present study, the magnitude of E fell within the range of 12.91 to 14.31 kJ/mol (Table 2) for the sorption of methylene blue onto mansonia sawdust. According to Onyango et al. [50], mean free energy values greater than 8–16 kJ/mol corresponded to adsorption processes controlled by a chemical ion-exchange mechanism. The values obtained in this study were greater than 8 and less than 16 kJ/mol for the adsorption of methylene blue onto mansonia sawdust when sawdust particle size varied between 150 to 550 µm and solution temperature was 299 K.

3.5. Mechanism of methylene blue uptake

The cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds [51]. These compounds are known to exhibit ion-exchange properties. Therefore, the methylene blue cation may attach itself to hydroxyl groups or oxyl groups on the mansonia sawdust surface, displacing H^+ ions into solution. The role played by ion exchange in the sorption process was therefore investigated by determining the influence of the change in hydrogen ion concentration when initial methylene blue is increased, on the equilibrium sorption capacity of the sorbent. Table 4 shows the change in hydrogen ion concentration for each methylene blue initial concentration used and the equilibrium sorption capacity obtained. The results revealed that as the change in hydrogen ion (ΔH^+) concentration increases, the equilibrium sorption capacity increases. This suggests that as more methylene blue cation is sorbed onto the mansonia sawdust surface, more hydrogen ions are released from the mansonia into solution. Consequently, the pH of the reaction mixture decreases.

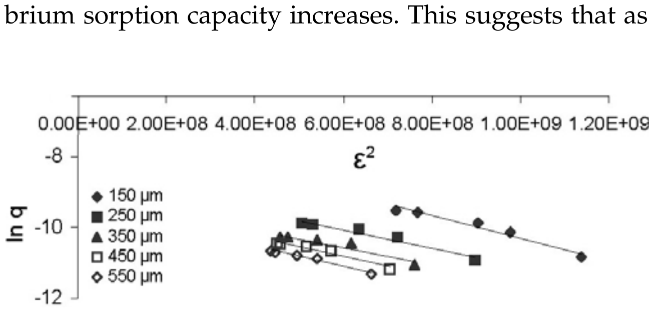

Fig. 7. Dubinin–Radushkevich isotherm model for the sorption of methylene blue from aqueous solution. Solution pH: 10; temperature: 26°C; agitation speed: 200 rpm; sorbent mass: 0.004 g/l.

The corresponding linear plots of ΔH^+ against q_e (Fig. 8) were regressed to obtain an expression for these values in terms of ion exchange with a high coefficient of determination. Therefore, it is further considered that q_e can be expressed as a function of ΔH^+ as follows:

$$q_e = 27934\ \Delta H^+ + 7.0567 \qquad (23)$$

When the sorption system of initial and equilibrium hydrogen ion concentration showed no changes ($\Delta H^+ = 0$), the equilibrium capacity obtained from the intercept of Eq. (23) was 7.0567 mg/g. The ion-exchange rate can be determined from the slope of the straight line in Eq. (23) and is 27,934 mg/g mM of hydrogen ion concentration.

3.6. Desorption study

To confirm the presence of ion exchange as a major sorption mechanism and to determine the possibility of

Table 4
Relationship between amounts adsorbed (q_e, mg/g) and changes in hydrogen ion concentration

Particle size (µm)	q_e (mg/g)	pH_0	pH_{240}	ΔpH (mol/dm^3)
150	33.44	10	6.01	0.00095
250	21.23	10	6.33	0.00047
350	14.58	10	6.52	0.00029
450	12.31	10	6.64	0.00023
550	10.32	10	7.05	0.00009

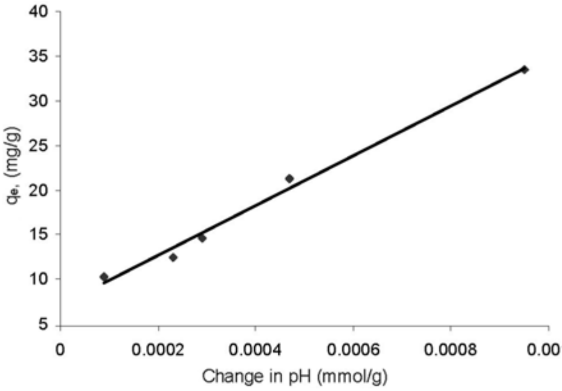

Fig. 8. Relationship between equilibrium sorption capacity and change in hydrogen ion concentration for sorption of methylene blue onto mansonia sawdust. Sorbent mass: 0.004 g/l; sorbate vol.: 100 ml; solution pH: 10; 200 rpm; temperature: 26°C.

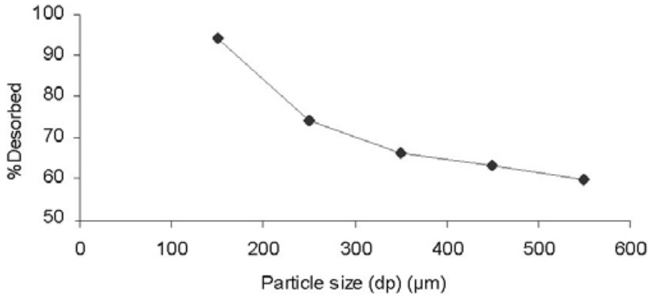

Fig. 9. Desorption of methylene blue dye from mansonia sawdust of various particle sizes. Sorbent mass: 0.004 g/l; sorbate vol.: 100 ml; solution pH: 10; 200 rpm; temperature, 26°C.

reuse, desorption of methylene blue dye already loaded on mansonia sawdust was attempted. It has been shown that cation–H^+ ion exchange is easily reversible, depending upon pH [52]. When the pH of the solution is low enough, the adsorption will go in a reversed manner, that is, cations will be stripped under acidic condition (Fig. 9).

As the particle size of mansonia sawdust increased from 150 to 550 μm, the percentage of dye desorbed from the loaded sorbent (sawdust sorbent of different particle sizes used in contact with 120 mg/dm^3 methylene blue solution) was found to decrease from 94.14 to 59.46% (Fig. 9). When sawdust particle size is reduced, ion-exchange sites within pores, which were blocked or inaccessible to dye cations, becomes expose, and therefore the ion-exchange reaction increases. This accounts for the increase in percentage desorption observed and also the increase in the ion-exchange reaction rate when the particle size of mansonia sawdust in contact with 120 mg/dm^3 of methylene is decreased.

4. Conclusions

Mansonia sawdust, a very abundant agricultural by-product in Nigeria has been shown to be a good sorbent for the methylene blue dye examined in this study and can be suggested for the removal of methylene blue dye from wastewater. Decrease in sawdust particle size results in a higher dye loading per unit weight of the sorbent and increased percentage dye removal. The isotherm data obtained were very well described by the theoretical Langmuir, Tempkin and D–R isotherms.

The equilibrium monolayer capacity of mansonia sawdust for methylene blue was 33.44 mg/g when the temperature was 299 K and sawdust dose and particle size were 0.004 g/dm^3 and 150 μm. The equilibrium binding constant K_t was found to be reduced with increasing sawdust particle size from 150 to 550 μm, while the mean free energy of sorption per mole of sorbate was in the range 12.91 to 13.89 $\text{mol}^2\text{kJ}^{-2}$, suggesting that the sorption mechanism was by ion exchange. A high percentage of the dye adsorbed was desorbed from the dye-loaded adsorbent supporting; therefore, ion exchange is the main sorption mechanism.

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