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Kinetic study and sorption mechanism of methylene blue and methyl violet onto mansonia (*Mansonia altissima*) wood sawdust

Augustine E. Ofomaja*

Department of Industrial Chemistry, Faculty of Physical Science, University of Benin, Ugbowo-Lagos Road, Benin City, Edo State, Nigeria

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Abstract

Batch sorption kinetic experiments were performed to study the adsorption of methylene blue and methyl violet dyes from aqueous solution using mansonia wood sawdust as adsorbent. Operating variables studied include solution pH and particle size of sawdust. Maximum dye removal was observed at a basic pH 10 for both dyes. Sorption kinetic data was fitted to both pseudo-first and pseudo-second-order kinetic models. The experimental data were found to deviate from the straight line of the pseudo-first-order plots after 30 min for the methylene blue and after 15 min for the methyl violet sorption. The pseudo-second-order kinetics was found to fit the experimental data and was able to consistently predict the amount of dye adsorbed over the sorption period and for the range of sawdust particle size used.

The process mechanism was found to be complex, consisting of both mass transfer and intraparticle diffusion. Analysis of the sorption data using the Boyd's plot confirms mass transfer as the dominant mechanism for both methylene blue and methyl violet sorption. Mass transfer mechanism was more predominant in the methyl violet sorption and became more dominant as the particle size of the sawdust material increased. This was confirmed by the values of effective diffusion parameter D_i, which were found to be higher for methylene blue, and reduced with increasing sawdust particle size. The molecular sizes of the basic dyes and the stability of the positive charge on the dyes played a significant role in their sorption onto the sawdust material.

Keywords: Mansonia wood sawdust; Kinetic models; Sorption mechanism; Methylene blue; Methyl violet

1. Introduction

Surface water contamination by pollutants is common in highly industrialized countries due to direct discharge of industrial effluents in to water bodies or by precipitation of air borne pollutants in to surface waters. Of the pollutants released along with industrial effluents, dyes are the most easily detected since dyes are inherently highly visible, meaning that concentrations as low as 0.005 mg/l will capture the attention of the public and the authorities [1].

Apart from the aesthetic problems caused by dyes, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria to levels insufficient to biologically degrade impurities in the water [2]. Colored effluents can cause problems in several ways: dyes can have acute and chronic effects on exposed organisms depending on the exposure time, and dye concentration; dyes absorb and reflects sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants [3]. Majority of these dyes are synthetic in nature and are usually composed of aromatic rings in their structures, which makes them carcinogenic and mutagenic [4], inert and non-biodegradable when discharged in to waste streams [5].

Several techniques are available for the treatment of industrial wastewaters. Among these methods, adsorption technique for wastewater treatment has become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods. Adsorption can produce high quality water while also being a process that is economically feasible [6]. Some adsorbents and their capacities for Methylene blue and methyl violet removal are shown in Tables 1a and 1b. To effectively apply an adsorbent for a particular pollutant removal from aqueous solution, it is important to study the kinetics and mechanism of the sorption process so as to ascertain the applicability of the choice of sorbent and to optimize the process design.

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* Tel.: +234 08028715034.
E-mail address: aus_ofomaja@yahoo.com.

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Table 1a
Comparison of sorption capacities of various adsorbents for and methyl violet

Adsorbent	Methyl violet capacity (mg/g)	Reference
Cellulose-based wastes	11.50	[7]
Bagasse fly ash	26.25	[8]
Crosslinked amphoteric starch	333.33	[9]
Sepiolite	2.60	[10]
Sepiolite	2.33	[11]
Mansonia Sawdust	16.11	This study

Table 1b
Comparison of sorption capacities of various adsorbents for and methylene blue

Adsorbent	Methylene blue capacity (mg/g)	Reference
Cereal chaff	20.3	[12]
Rice husk	40.60	[13]
Raw beech sawdust	9.78	[14]
Raw *P. oceanica* fibres	5.56	[15]
Palm Kernel fibre	223.43	[16]
Mansonia sawdust	28.89	This study

Methylene blue and methyl violet are two basic dyes, which have been shown to have harmful effects on living organisms on short periods of exposure. Ingestion of methylene blue through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia. While inhalation of methyl violet may cause irritation to the respiratory tracks, vomiting, diarrhea, pain, headaches and dizziness. Long-term exposure may cause damage to the mucous membranes and gastrointestinal tract [17].

This study seeks to examine the applicability of a new adsorbent, Mansonia wood sawdust for the sorption of methyl violet and methylene blue dyes from aqueous solution and to investigate the kinetics and mechanism of the sorption process. The system variables studied include pH, particle size.

2. Materials and methods

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: 150–300, 150–400, 150–500 and 150–600 μm. The sieved sawdust was then stored in an airtight container.

The basic dyes, Methylene blue and methyl violet were used without further purification. The stock solution of 1000 mg/l was prepared by dissolving accurately weighed amounts of Methylene blue and methyl violet in separate 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary (Fig. 1).

2.2. Methods

The proximate composition of the mansonia wood sawdust was determined using methods of the Association of Official Analytical Chemist (AOAC) [18]. The IR spectra of the mansonia wood sawdust sample were recorded using KBr disk in conjunction with a PerkinElmer infrared spectrophotometer. KBr disk 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.

2.2.1. Effect of solution pH

An accurately weighed amount (0.4 g) of mansonia sawdust was added to ten 250 ml beakers containing 100 ml of 120 mg/dm^3 of the various dye solutions each adjusted to pH of 3.12, 4.34, 4.92, 5.48, 6.34, 7.66, 8.61, 9.94, 10.00 and 11.31 using ether HCl or NaOH solutions. The solutions were stirred at 200 rpm for 2 h at 299 K. The mixture was centrifuged and the clear supernatant was analyzed for the residual concentration of methylene blue ($\lambda_{max} = 665$ nm) and methyl violet ($\lambda_{max} = 580$ nm) left in aqueous solution spectrophotometerically.

2.2.2. Kinetics studies

Kinetic experiments were carried out by agitating 100 ml of 120 mg/l dye solution with 0.4 g of sawdust particle size ranging between 150–300, 150–400, 150–500 and 150–600 μm in a 250 ml beaker at 299 K at an optimum pH of 10 and at a con-

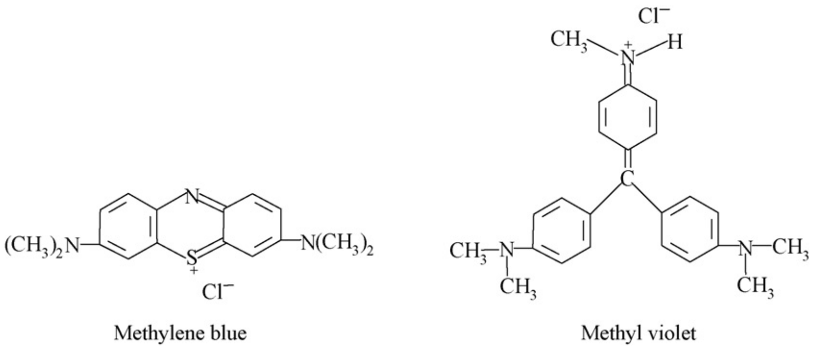

Fig. 1. Chemical structure of investigated dyes.

stant agitation speed of 200 rpm. Samples (3 ml) were pipetted out at different time intervals, centrifuged and the concentration of methylene blue and methyl violet analyzed using UV spectrophotometer.

3. Results and discussion

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution on to an adsorbent.

The pseudo-first-order kinetic model of Lagergren [19,20] for the sorption of the sorption of liquid/solid system based on solid capacity can be expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_\mathrm{t}), \tag{1}$$

where q_t and q_e are the amount sorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo-first-order sorption process. The integrated rate law, after applying the initial conditions of $q_\mathrm{t} = 0$ at $t = 0$ is:

$$\log(q_\mathrm{e} - q_\mathrm{t}) = \log(q_\mathrm{e}) - \frac{k_1}{2.303}t. \tag{2}$$

Plots of log $(q_\mathrm{e} - q_\mathrm{t})$ versus t gives a straight line for pseudo-first-order kinetics, which allows computation of the sorption rate constant, k_1. If the experimental results do not follow Eqs. (1 and 2) they differ in two important aspects: (i) $k_1(q_\mathrm{e} - q_\mathrm{t})$ then dose not represent the number of available sites, and (ii) log (q_e) is not equal to the intercept of the plot of log $(q_\mathrm{e} - q_\mathrm{t})$ against t.

The pseudo-second-order chemisorption kinetics may be expressed as [21,22]

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_\mathrm{e} - q_\mathrm{t})^2, \tag{3}$$

where k_2 is the rate constant of sorption, q_e and q_t have the same definition as above. Separating the variables in Eq. (3) gives

$$\frac{\mathrm{d}q_\mathrm{t}}{(q_\mathrm{e} - q_\mathrm{t})^2} = k_2\mathrm{d}t. \tag{4}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_\mathrm{t} = 0$ to $q_\mathrm{t} = q_\mathrm{t}$ gives:

$$\frac{1}{(q_\mathrm{e} - q_\mathrm{t})} = \frac{1}{q_\mathrm{e}} + k_2 t, \tag{5}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (5) can be rearranged to obtain:

$$q_\mathrm{t} = \frac{t}{(1/k_2 q_\mathrm{e}^2) + (t/q_\mathrm{e})}, \tag{6}$$

which has a linear form of

$$\frac{t}{q_\mathrm{t}} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}}t. \tag{7}$$

If the initial sorption rate is

$$h = k_2 q_\mathrm{e}^2. \tag{8}$$

then Eqs. (6 and 7) becomes

$$q_\mathrm{t} = \frac{t}{(1/h) + (t/q_\mathrm{e})}, \tag{9}$$

and

$$\frac{t}{q_\mathrm{t}} = \frac{1}{h} + \frac{1}{q_\mathrm{e}}t. \tag{10}$$

the constants can be determined experimentally by plotting of t/q_t against t.

Intraparticle diffusion model can be expressed as follows [23]:

$$q_\mathrm{t} = k_i t^{0.5} + C \tag{11}$$

where k_i is the intraparticle diffusion constant (mg/g min$^{0.5}$), and C is the intercept. In this model, due to the porous nature of the adsorbent, pore diffusion is expanded to be surface sorption. Therefore, the rate constant of intraparticle transport (k_i) is estimated from the slope of the linear portion of the plot of amount sorbed (mg/g) against square root of time.

3.1. Some properties of mansonia sawdust

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%.

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. Effect of solution pH

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter in the sorption process [23,24]. The magnitude of electrostatic charges imparted by the ionized dye molecules and the functional groups on the adsorbent surface are primarily controlled by pH of the medium [25]. In aqueous solution basic dyes acquire a net positive charge on ionization and biosorbents containing organic functional groups on their surfaces have also been shown to develop charges on their surface, which are pH dependent [26].

The effect of pH on adsorption of methylene blue and methyl violet dyes on mansonia wood sawdust at temperature of 299 K by varying the initial pH of a 120 mg/l solution of both dye for a fixed adsorbent dose of 0.4 g and particle size of 150–300 μm are shown in Fig. 2. The amount of dye sorbed per unit mass of adsorbent was found to be strongly dependent on solution pH for both methylene blue and methyl violet. At low solution pH, the amount of dye sorbed was found to be low. At pH 3, the amount of dye sorbed was 2.75 mg/g for methylene blue and 0.01 mg/g for methyl violet. The difference in amount of both dyes sorbed on the mansonia wood sawdust may be attributed to the difference in the molecular size of the dyes molecules and the ability of the positive charge on the dye molecules to be stabilized by – I inductive effect of the benzene rings. As solution pH rises to pH 6, the rate sorption increases rapidly for both dyes and

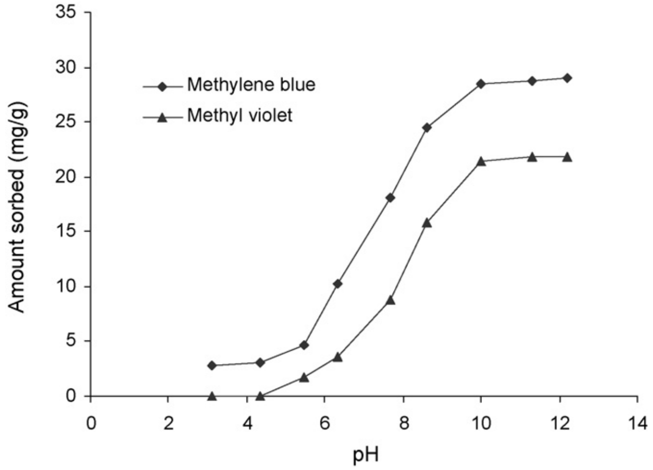

Fig. 2. Effect of solution pH on the uptake of methylene blue and methyl violet dyes onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Particle size: 225 μm; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K.

between pH 6 −9.95, the sorption capacity increases from 10.25 to 28.47 mg/g for methylene blue and from 3.63 to 21.42 mg/g for methyl violet. When solution pH was increased above 9.95, the amount of dye sorbed for both methylene blue and methyl violet did not show any significant increase. Therefore, pH 10 was chosen to carryout further investigations.

3.3. Sorption kinetics

Fig. 3a and b shows the effect of particle size on the percentage methylene blue and methyl violet uptake rate at different contact time from a 120 mg/l solution of methylene blue and methyl violet. It can be observed that the percentage dye uptake increased with contact time, and at some point in time reaches an almost constant value where the amount of dye being removed from aqueous solution onto the mansonia wood sawdust is in a state of dynamic equilibrium with the amount of dye desorbed from the mansonia wood sawdust. For the range of contact time under which the experiments were conducted, the percentage of methylene removed from solution was higher than for methyl violet. Greater percentage of methylene blue and methyl violet dyes were removed from solution for lower sawdust particle sizes than for higher particle sizes. For a time of 140 min, percentage methylene blue removal was 23.8% for particle size range 150–600 μm, 31.39% for particle size range 150–500 μm, 54.04% for particle size range 150–400 μm and 96.59% for particle size range 150–300 μm. The percentage of methyl violet removal was 14.44% for particle size range 150–600 μm, 20.26% for particle size range 150–500 μm, 28.02% for particle size range 150–400 μm and 53.69% for particle size range 150–300 μm.

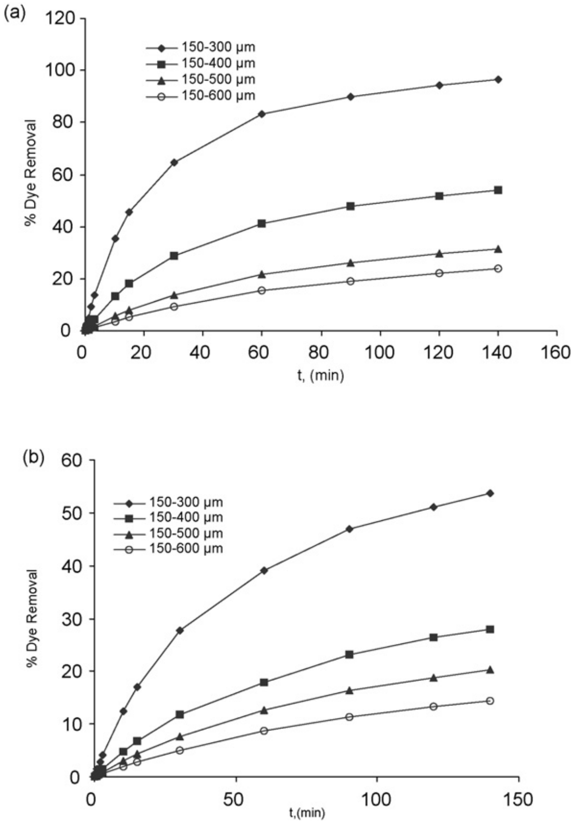

Fig. 3. (a and b) Effect of particle size on the percentage methylene blue and methyl violet removal from aqueous solution at different contact time. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

The sorption reaction at all mansonia wood sawdust particle sizes used for both dyes was found to be extremely rapid at the initial stage and slows down as the sorption proceeds. The sorption rate for methylene blue uptake in the first 30 min was found to be 2.210, 0.984, 0.462 and 0.313 mg/min and then slows down between 60 and 140 min to 0.166, 0.161, 0.123 and 0.104 mg/min for sawdust particle sizes of 150–300, 150–400, 150–500, 150–600 μm. Sorption rate for methyl violet uptake in the first 15 min was found to be 1.142, 0.452, 0.290 and 0.185 mg/min and then slows down between 30 and 140 min to 0.232, 0.148, 0.113 and 0.101 mg/min for sawdust particle sizes of 150–300, 150–400, 150–500 and 150–600 μm. The higher sorption rate at the initial period may be due to a large number of vacant sites available at the initial stage, as a result there exist an increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent surface. The lower particle size presents a larger surface for adsorption, which tends to increase the dye sorption rate at the initial stages. As time proceeds the concentration gradient is reduced due to accumulation of dye particles in the vacant sites, leading to a decrease in sorption rate at the later stage of the sorption. This result reveals that the sorption of methylene blue onto mansonia sawdust of different particle sizes was more rapid than for methyl violet sorption from a solution of the same concentration.

3.3.1. Pseudo-first-order kinetics

The pseudo-first-order constants and correlation coefficient, r_1^2, for the sorption of methylene blue and methyl violet on to mansonia wood sawdust of different particle sizes at 299 K and from a 120 mg/l solution of the dyes were calculated from the plots of $\log(q_e - q_t)$ versus t and are given in Fig. 4a and b Tables 2 and 3. The correlation coefficients, r_1^2, of the pseudo-

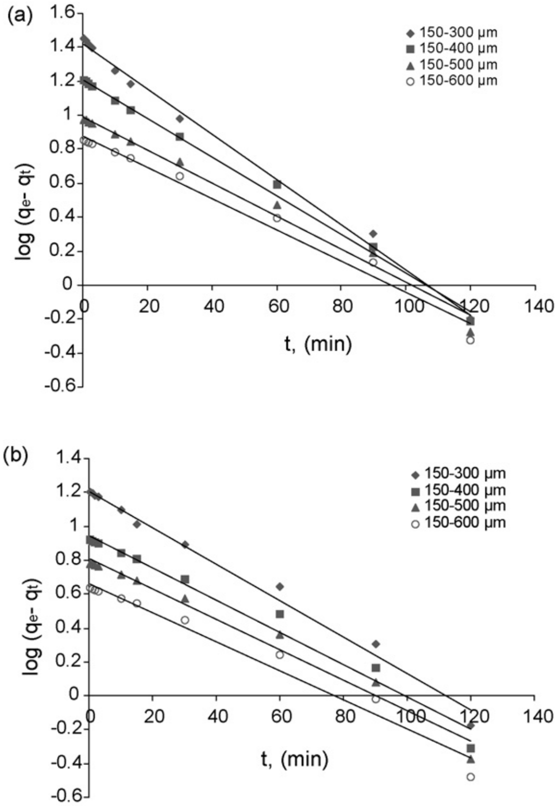

Fig. 4. (a and b) Pseudo-first-order kinetics for the sorption of methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

first-order kinetic model were found to range from 0.9958 to 0.9820 for the methylene blue sorption and from 0.9892 to 0.9731 for methyl violet sorption. The values of correlation coefficient were all greater than 0.97, which are relatively high values. The experimentally determined equilibrium dye sorption was found to decrease from 26.61 to 7.55 mg/g for methylene blue sorption and from 16.25 to 4.63 mg/g for methyl violet sorption as the particle size of mansonia wood sawdust increases. The closeness in the values of experimental and model equilibrium sorption along side the high values of correlation coefficient suggests that methylene blue and methyl violet sorption onto mansonia wood sawdust can be described by the pseudo-first-order kinetic model. Several authors have also shown the applicability of the pseudo-first-order kinetics in describing the sorption of methylene blue and methyl violet on to other adsorbents [23,25,27–28]. The pseudo-first-order rate constant k_1 was found to decrease from 0.0306 to 0.0212 min^{-1} for methylene blue sorption and from 0.0249 to 0.0198 min^{-1} for methyl violet sorption as the particle size of mansonia wood sawdust increases. This indicates that methylene blue dye was sorbed at a faster rate onto mansonia wood sawdust and that the rate of sorption reduces with increase in sawdust particle size.

The corresponding linear plots of the values of q_e and k_1 against particle size ($d\rho$) were regressed to obtain expressions for these values in terms of particle size for methylene blue and methyl violet dyes and are shown below:

Methylene blue: correlation coefficients: 0.9942 and 0.9882

$$q_e = 2.36 \times 10^7\, d\rho^{-2.529} \tag{12}$$

and

$$k_1 = 1.69\, d\rho^{-0.741} \tag{13}$$

Methyl violet: correlation coefficients: 0.9900 and 0.9655

$$q_e = 7.51 \times 10^6\, d\rho^{-2.417} \tag{14}$$

and

$$k_1 = 0.27\, d\rho^{-0.444} \tag{15}$$

substituting the values of Eqs. (12 and 13) and Eqs. (14 and 15) into Eq. (16),

$$q_t = q_e(1 - e^{-kt}) \tag{16}$$

gives the rate law for a pseudo-first-order reaction and the relationship between q_t, $d\rho$, and t, which is shown in Eq. (17) for methylene blue and Eq. (18) for methyl violet:

$$q_t = 2.36 \times 10^7\, d\rho^{-2.529}(1 - e)^{-1.69 d\rho - 0.741 t} \tag{17}$$

$$q_t = 7.51 \times 10^3\, d\rho^{-2.417}(1 - e)^{-0.27 d\rho - 0.444 t} \tag{18}$$

these equation can be used to derive the amount of methylene blue and methyl violet adsorbed at any given particle size, $d\rho$ and reaction time t.

The plots in Fig. 4a and b show that there is a deviation from the straight line of the pseudo-first-order kinetics in the later stage of sorption. The deviation from the straight line was observed to start after 30 min of sorption in the methylene blue solution and after 15 min of sorption in the case of methyl violet solution. The deviation from the straight line of the pseudo-first-order kinetics was also observed by Kumar et al. [29], in the sorption of methylene blue on to fly ash, Ho and McKay [30],

Table 2
Kinetic values calculated for the effect of particle size on the methylene blue adsorption by Mansonia wood sawdust

Particle Size(μm)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model				Intraparticle diffusion			Mass transfer	
	k_1	$q_{e\,mod}$	$q_{e\,exp}$	r^2	k_2	h	$q_{e\,exp}$	r^2	k_i	C	r^2	k_s	r^2
350–150	0.0306	33.44	26.613	0.9953	0.00140	1.56	28.98	0.9999	0.0725	1.90	0.9790	0.0221	0.9461
450–150	0.0263	21.23	16.346	0.9958	0.00108	0.49	16.21	0.9999	0.0477	0.47	0.9568	0.0098	0.9791
550–150	0.0226	14.60	9.854	0.9867	0.00090	0.19	9.42	0.9999	0.0370	0.13	0.9864	0.0046	0.9916
600–150	0.0212	12.44	7.546	0.9820	0.00078	0.12	7.44	0.9996	0.0311	0.07	0.9917	0.0041	0.9949

$k_1 = \text{min}^{-1}$; $q_e = \text{mg/g}$; $k_2 = \text{g mg}^{-1}\,\text{min}^{-1}$; $h = \text{mg g}^{-1}\,\text{min}^{-1}$; $k_i = \text{mg/g min}^{0.5}$; $k_s = \text{min}^{-1}$.

Table 3
Kinetic values calculated for the effect of particle size on the methyl violet adsorption by Mansonia wood sawdust

Particle Size(μm)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model				Intraparticle diffusion			Mass transfer	
	k_1	$q_{\text{e mod}}$	$q_{\text{e exp}}$	r^2	k_2	h	$q_{\text{e exp}}$	r^2	k_i	C	r^2	k_s	r^2
350–150	0.0249	21.65	16.244	0.9892	0.00095	0.4452	16.11	0.9997	0.0700	0.15	0.9510	0.0114	0.9965
450–150	0.0219	13.48	8.861	0.9795	0.00087	0.1582	8.40	0.9991	0.0443	0.04	0.9712	0.0045	0.9988
550–150	0.0207	10.87	6.449	0.9781	0.00083	0.0982	6.08	0.9999	0.0338	0.02	0.9757	0.0029	0.9991
600–150	0.0198	8.75	4.629	0.9731	0.00080	0.0613	4.33	1.0000	0.0253	0.01	0.9806	0.0019	0.9995

$k_1 = \text{min}^{-1}$; $q_e = \text{mg/g}$; $k_2 = \text{g mg}^{-1}\ \text{min}^{-1}$; $h = \text{mg g}^{-1}\ \text{min}^{-1}$; $k_i = \text{mg/g min}^{0.5}$; $k_s = \text{min}^{-1}$.

in the sorption of Acid Blue 25 and Basic Blue 69 on spruce wood sawdust and Ofomaja [31], in the sorption of methylene blue on to palm kernel fibre. The deviation from the straight line suggests a change in sorption mechanism as the sorption process proceeds.

3.3.2. Pseudo-second-order kinetics

Fig. 5a and b shows the applicability of the pseudo-second-order kinetic model to the experimental data generated for the sorptive removal of methylene blue and methyl violet from aqueous solution using mansonia wood sawdust particles of different sizes. The initial sorption rate, h, pseudo-second-order rate constant, k_2, amount of dye sorbed at equilibrium, q_e, and the corresponding linear regression r_2^2, for methylene blue and methyl violet are given in Tables 2 and 3. From the tables it can be observed that decrease in mansonia wood sawdust particle size caused an increase in the equilibrium sorption capacity, q_e, initial sorption rate, h, and sorption rate, k_2 for both methylene blue and methyl violet sorption. The values of the pseudo-second-order rate constants were higher for the methylene blue sorption than for the methyl violet sorption. It is also observed from the tables, that the values for r_2^2 were all greater than 0.9999, which is much higher than r_1^2 (for pseudo-first order) values. The higher values of r_2^2 and the calculated values of equilibrium sorption capacity, q_e, confirms that the sorption process follows a pseudo-second-order kinetics.

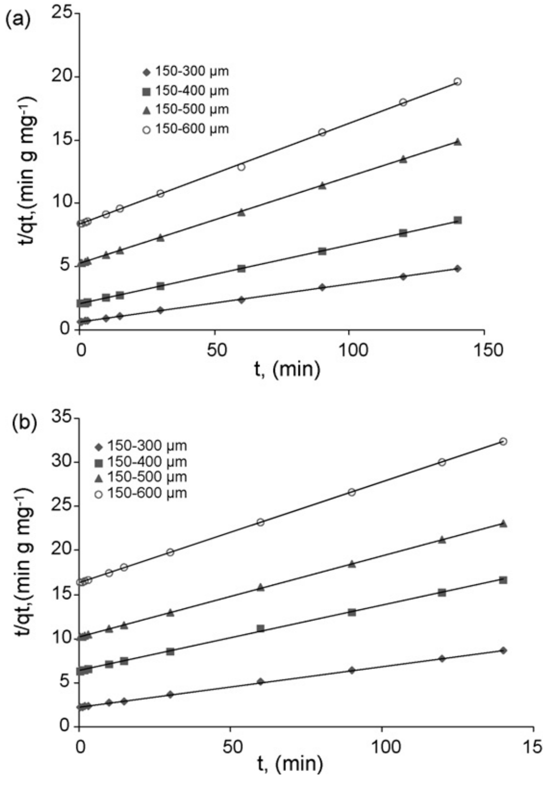

Fig. 5. (a and b) Pseudo-second-order kinetics for the sorption of methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

The corresponding linear plots of the values of q_e, h and k_1 against particle size (dρ) were regressed to obtain expressions for these values in terms of particle size for methylene blue and methyl violet dyes and is shown below:

Methylene blue-Correlation coefficients: 0.9843, 0.9880 and 0.9964

$$q_e = 1.52 \times 10^6\,\mathrm{d}\rho^{-1.986} \tag{19}$$

$$h = 1.64 \times 10^{12}\,\mathrm{d}\rho^{-5.215} \tag{20}$$

and

$$k_2 = 1.47\,\mathrm{d}\rho^{-1.145} \tag{21}$$

Methyl violet-Correlation coefficients: 0.9800, 0.9800 and 0.9822

$$q_e = 2.59 \times 10^5\,\mathrm{d}\rho^{-1.743} \tag{22}$$

$$h = 3.82 \times 10^8\,\mathrm{d}\rho^{-3.817} \tag{23}$$

and

$$k_1 = 5.75 \times 10^{-3}\,\mathrm{d}\rho^{-0.334} \tag{24}$$

substituting the values of Eqs. (19–21) and Eqs. (22–24) into Eq. (25),

$$q_t = \frac{{q_e}^2 k_2 t}{1} + q_e k_2 t \tag{25}$$

gives the rate law for a pseudo-second-order reaction and the relationship between q_t, dρ, and t, which is shown in Eq. (26) for methylene blue and Eq. (27) for methyl violet:

$$q_t = \frac{(1.52 \times 10^6\,\mathrm{d}p^{-1.986}\,t^2)\,1.47\,\mathrm{d}p^{-1.145}}{1 + 1.52 \times 10^6\,\mathrm{d}p^{-1.986}\,1.47\,\mathrm{d}p^{-1.145}\,t} \tag{26}$$

$$q_t = \frac{(2.59 \times 10^5\,\mathrm{d}p^{-1.743}\,t^2)\,5.75\,\mathrm{d}p^{-0.0334}}{1 + 2.59 \times 10^5\,\mathrm{d}p^{-1.743}\,5.75\,\mathrm{d}p^{-0.0334}\,t} \tag{27}$$

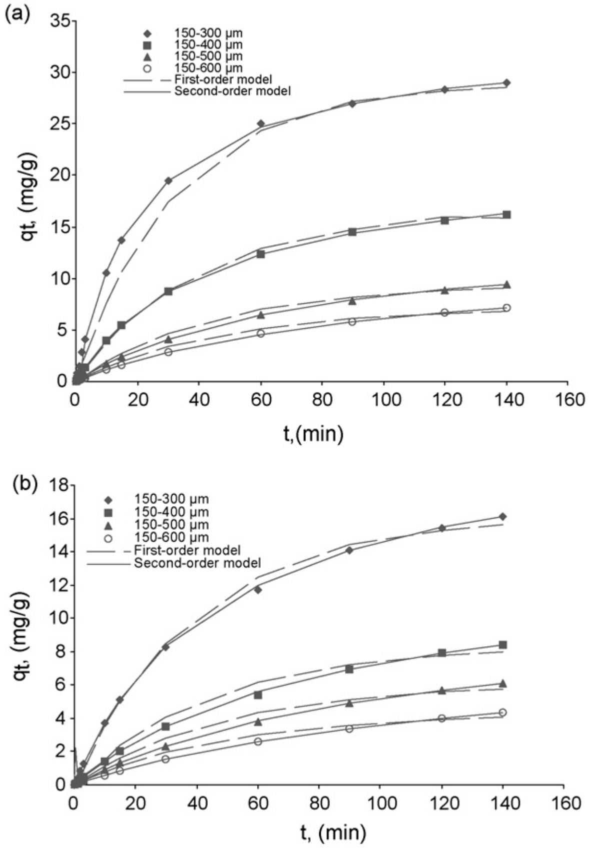

Fig. 6. Comparison of kinetic models in predicting *q* for methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

this equation can be used to derive the amount of methylene blue and methyl violet adsorbed at any given particle size, dρ and reaction time *t*.

Several authors have also reported the applicability of the pseudo-second-order kinetic for modeling the removal of Methylene blue and methyl violet from aqueous solution using other sorbents [32–34].

3.3.3. Comparison of kinetic models

In the present investigation, the pseudo-first-order and pseudo-second-order kinetic were applied to analyze the kinetic data for the sorption of methylene blue and methyl violet from solution. The calculated values of correlation coefficients, r_1^2 and r_2^2, were found to be greater than 0.97, for both dyes which shows the applicability of both kinetic models. The consistency in predicting the amount of dye adsorbed for the entire sorption time and for different particle sizes. The *q* values were predicted by applying the calculated kinetic constants in their corresponding kinetic expressions for methylene blue and methyl violet.

The predicted *q* values from the pseudo-first and pseudo-second-order kinetics for the sorption of methylene blue and methyl violet on to mansonia wood sawdust at different particle size are shown in Fig. 6a and b. From Fig. 6a and b, it was observed that for the entire sorption period, and at all particle sizes used, the pseudo-second-order expression better predicts the sorption kinetics than the pseudo-first order model for the sorption of methylene blue and methyl violet on to mansonia wood sawdust.

3.4. Diffusion processes

Sorptive removal of dyes from aqueous solution involves solute transfer, which is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The sorption process can be described by four consecutive steps:

1. Transport in the bulk of the solution;
2. Diffusion across the liquid film surrounding the sorbent particle;
3. Particle diffusion in the liquid contained in the pore and in the sorbate along the pore walls;
4. Sorption and desorption within the particle and on the external surface.

The sorption systems under investigation were designed to eliminate the effect of transport in the solution by rapid mixing, so that this step dose not become rate limiting. Step 4 is considered to be an equilibrium reaction and is assumed to be rapid and considered negligible. The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion.

To investigate the possibility of dyes being transported within pores of mansonia wood sawdust, the experimental data was fitted in an intraparticle diffusion plot. Fig. 7a and b shows the plot of amount of dye sorbed, q_t (mg/g) versus $t^{0.5}$ (min$^{0.5}$), for the methylene blue/mansonia sawdust system and the methyl violet/mansonia sawdust system. Both plots show that the sorption patterns are similar and the processes tend to follow two distinct phases. This kind of multi-linearity in the shape of the intraparticle diffusion plot has also been observed Waranusantigul et al. [27], in the biosorption of methylene blue by giant duckweed (*Spirodela polyrrhiza*). The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and an intraparticle diffusion stage. The initial curved portion of the plot indicates a boundary layer effect; the second portion is due to intraparticle diffusion. The slope of the second portion of the plot is defined as the intraparticle diffusion parameter k_i (mg/g min$^{0.5}$). On the other hand, the intercept of the plot reflects the boundary layer effect. The lager the intercept, the greater the contribution of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient k_i values were given as 0.0725, 0.0477, 0.0307, and 0.0311 mg/g min$^{0.5}$, for the methylene blue/mansonia sawdust systems and 0.0700, 0.0443, 0.0338, and 0.0253 mg/g min$^{0.5}$, for the methyl violet/mansonia sawdust systems. The results reveal that there is an increase in intraparticle rate constant, k_i, with decreasing sawdust particle size. The presence of a large number of smaller particles provides the sorption systems with a greater surface area available for dye removal. The effect of increasing the surface increases slightly the intraparticle parameter. The intraparticle diffusion rate constants for the methylene

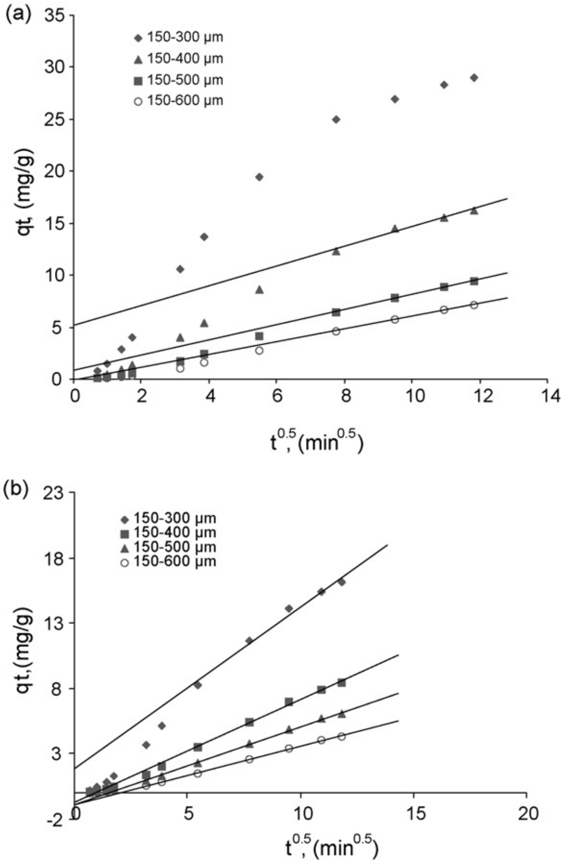

Fig. 7. Intraparticle diffusion plots of the sorption of methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

blue sorption were all higher than for the methyl violet sorption, indicating that methylene blue diffused faster into the pores of the mansonia wood sawdust material. This may be due to the size of the methylene blue molecules being smaller and can easily penetrate smaller pores of the adsorbent material. The rate constant for intraparticle diffusion, k_i, was also found to be correlated with the mansonia sawdust particle size for the methylene blue/mansonia wood sawdust and methyl violet/mansonia wood sawdust systems in these experiments. The corresponding linear plots of the values of k_i against particle size (dρ) were regressed to obtain expressions for these values in terms of particle size for methylene blue and methyl violet dyes and is shown below:

For methylene blue: Correlation coefficient 0.9987

$$k_i = 3.46\,\mathrm{d}\rho^{-0.773} \tag{28}$$

For methyl violet: Correlation coefficient 0.9965

$$k_i = 1.06\,\mathrm{d}\rho^{-0.909} \tag{29}$$

The multiple nature observed in the intraparticle diffusion plots suggest that intraparticle diffusion is not solely rate controlling. External mass transfer of dye molecules on to sorbent particles is also significant in the sorption process, especially at the initial reaction period. The external mass transfer rate is therefore calculated for the initial time intervals using the plot of C/C_0 vs. time, t [35], where C and C_0 represent the concentration at any time (mg/dm^3) and the initial concentration of dye. Fig. 8a and b show the plots of C/C_0 versus time for different initial dye concentrations of methylene blue and methyl violet. The slope of these plots can be calculated either by assuming a polynomial relation between C/C_0 and time or based on the assumption that the relationship is linear for the first initial rapid phase (in the present study the first 30 min for methylene blue systems and 15 min for the methyl violet systems). The later technique has been applied by McKay et al. [35] for the sorption of Basic Blue 69, Basic Red 22, Acid blue 25 and Acid Red 114 on to bagasse pith. In the present study the second technique was adapted by assuming the external mass transfer occurs in the first 30 min for the methylene blue systems and 15 min in the methyl violet systems, thus simply by drawing a tangent to the curve, $C_{30\,\mathrm{min}}/C_0$ versus time for methylene blue and $C_{15\,\mathrm{min}}/C_0$ for the methyl violet system through the origin, S, the rate constant of external mass transfer could be obtained.

The external mass transfer rate constant, k_s, corresponding to the initial rapid phase for both methylene and methyl violet systems were found to decrease with increasing mansonia wood sawdust particle size. This can be explained by the fact that the small particles move faster in solution than larger particles and thus there is more shear on their surface. Hence, boundary layer thickness is thinner than on larger particles, and therefore, k_s increases as particle size decreases. The mass transfer rates for

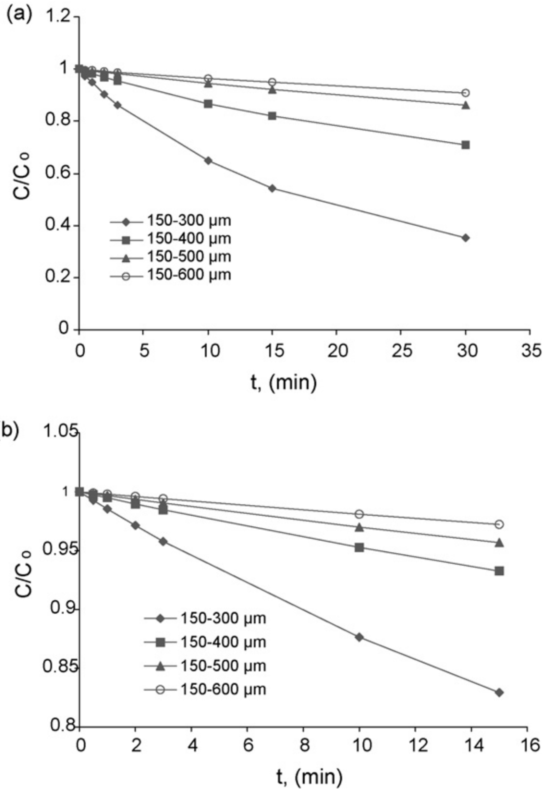

Fig. 8. External mass diffusion plots of the sorption of methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

the methylene blue sorption were all higher than that for methyl violet, this will be so because surface sorption will depend on the molecular sizes and the molecular weights of the dyes [36]. The relationship between k_s and mansonia wood sawdust particle size can be displayed by a straight line curve with correlation coefficient, r_s^2 as high as 0.9748 for methylene blue and 0.9957 for methyl violet mathematically represented as:

$$k_s = 73.198\, d\rho^{-1.622} \tag{30}$$

and

$$k_s = 35.449\, d\rho^{-1.612} \tag{31}$$

It is clear that the sorption of both methylene blue and methyl violet on to mansonia wood sawdust are complex processes involving external mass transfer and intraparticle diffusion in the rate limiting step of the sorption. This can be observed from the high correlation coefficient values of both the intraparticle diffusion and mass transfer plots which were higher than 0.94 in all cases.

In order to characterize what the actual rate-controlling step involved in the dye sorption process is, the sorption data were further analyzed by the kinetic expression given by Boyd et al. [37]

$$F = 1 - \left(\frac{6}{\pi^2}\right)\exp(-\mathrm{Bt}), \tag{32}$$

where F is the fraction of solute sorbed at different times t and Bt is a mathematical function of F and given by

$$F = \frac{q}{q_\alpha}, \tag{33}$$

where, q and q_α represents the amount sorbed (mg/g) at any time t and at infinite time (in the present study 140 min). Substituting Eq. (32) into Eq. (33), the kinetic expression becomes

$$\mathrm{Bt} = -0.498 - \ln\left(1 - \frac{q}{q_\alpha}\right), \tag{34}$$

Thus the value of Bt can be calculated for each value of F using Eq. (33). The calculated Bt values were plotted against time as shown in Fig. 9a and b. The linearity of this plot will provide useful information to distinguish between external transport-and intraparticle-transport-controlled rates of sorption. Fig. 9a shows the plot of Bt versus t for methylene blue systems, which were straight lines that do not pass through the origin indicating that mass transfer is rate limiting. As mansonia sawdust particle size increases the Bt against t plot moves away from the origin indicating that mass transfer becomes more important in the rate determining step. The same effect is seen for the methyl violet systems (Fig. 9b), but that the Bt against t plot were further away from the origin than the methylene blue systems suggesting that mass transfer is more important in the rate limiting step for the methyl violet sorption than for methylene blue. Increase in sawdust particle size also caused an increased importance of mass transfer as the rate limiting step in the methyl violet systems.

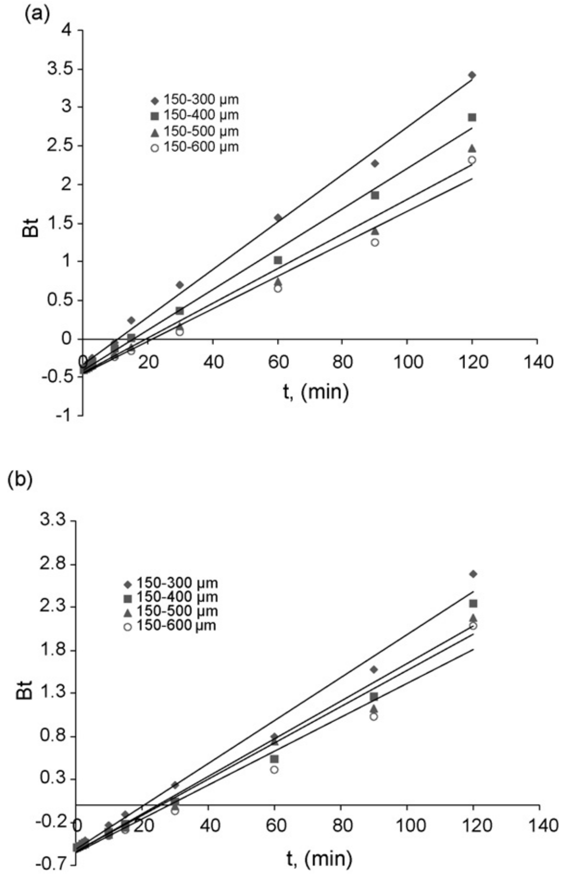

Fig. 9. Boyd expression of the sorption of methylene blue and methyl violet onto mansonia wood sawdust. Conc. of dye solutions: 120 mg/l; Solution pH: 10; sawdust dose: 0.004 g/l; Agitation speed: 200 rpm; Temperature: 299 K. (a) Methylene blue (b) Methyl violet.

The calculated B values were used calculate the effective diffusion coefficient, D_i (cm^2/s) using the relation:

$$B = \pi^2\frac{D_i}{r^2}, \tag{35}$$

Where, r represents the radius of the particle calculated by sieve analysis and assuming spherical particles. The calculated D_i values at different particle sizes for methylene blue and methyl violet are shown in Table 4. The effective diffusion coefficient was found to increase as the mansonia sawdust particle size increased from 150–300 to 150–600 μm the methylene blue and methyl violet sorption. The effective diffusion coefficient was higher for methylene blue than for methyl violet for all particle sizes of mansonia sawdust used.

Table 4
Effective diffusion for methylene blue and methyl violet onto mansonia wood sawdust.

Particle size (μm)	Effective diffusion coefficient (cm^2/s)	
	Methylene blue	Methyl violet
150–300	9.88×10^{-08}	8.02×10^{-08}
150–400	1.26×10^{-07}	1.05×10^{-07}
150–500	1.51×10^{-07}	1.41×10^{-07}
150–600	1.88×10^{-07}	1.76×10^{-07}

3.4.1. Possible mechanism

In this study, kinetic data based on the effect of sorbent particle size was applied in the investigation of the kinetics and mechanism of two basic dyes, methylene blue and methyl violet onto mansonia wood sawdust. Two kinetic models (pseudo-first and pseudo-second-order models) and two diffusion models (External mass transfer and intraparticle diffusion models) were applied to analyze the kinetic data.

The kinetics of sorption processes is concerned with forces between sites and dye molecules, and this forms an important area of surface chemistry. The pseudo-first-order plots of the experimental results showed that for both dyes, straight lines were observed with relatively high correlation coefficient. The experimental data was found to follow the straight line at the initial rapid stage of sorption but slightly deviates at the latter stage. The deviation started after 30 min of sorption for the methylene blue systems and after 15 min of sorption for the methyl violet systems. This deviation from the straight line for the pseudo-first order kinetics suggests that a change in sorption mechanism occurred between the two stages of sorption, but it is difficult to access whether the mechanism suddenly changes from first order or the transition is gradual. Atuna and Sismanoglu [38] reported that in the case of two kinetic steps, the first step of sorption was more rapid than the second one and the sorption rate is controlled by either a film diffusion or intraparticle diffusion.

Application of the pseudo-second-order kinetics to the experimental data showed that the pseudo-second-order model accurately fits the experimental data with very high correlation ceofficicints ($r_2^2 > 0.999$). Therefore, the sorption of methylene blue and methyl violet on to mansonia wood sawdust of different particle sizes can be well described by the pseudo-second-order kinetics. The two kinetic models were compared for their consistency in predicting the amount of dye sorbed for the entire sorption period and it was found that for the range particle size used and for a sorption period of 140 min, the pseudo-second-order kinetics was more consistent in predicting the amount of methylene blue and methyl violet sorbed than the pseudo-first-order kinetics.

Mansonia wood sawdust is cellulose based and was analyzed to contain functional groups like carboxylic (COOH), phenolic (Ar–OH), alcoholic (R–OH) and amine ($C–NH_2$). In contact with water and with increasing pH, these groups become negatively charged and are likely sites for chemical reaction to take place on the sawdust surface. These functional groups are responsible for the cation-exchange capacity of the sawdust. Basic dyes on the hand are organic in nature but can ionize in water form a positively charged molecule. The mansonia wood sawdust/dye reaction may be represented in two ways [39] and it seems possible that the basic sorption follow the mechanism below:

$$MS^{-}+BD^{+} \rightleftharpoons MSBD \tag{36}$$

and

$$(BD)_2^{2+} + 2MS \rightleftharpoons (MB)_2MS_2 + 2H^{+} \tag{37}$$

where BD is the basic dyes, MS^- and MSH are polar sites on the mansonia sawdust surface.

These reactions are the basis of the pseudo-second-order model. The pseudo-second-order kinetics assumes that the rate limiting step is chemical sorption or chemisorption involving forces through sharing or the exchange of electrons between sorbent and sorbate as covalent forces.

The sizes of the dye molecules and their ability to form positively charged species would affect their adsorption from solution onto the adsorbent. The positive charge on the methylene blue molecule is carried on the sulphur atom. The positive charge is created by the withdrawal of the lone pair of electrons on the sulphur atom to form a covalent bond with the carbon atom of benzene ring, due to the −I inductive effect of the two benzene rings. While in the case of methyl violet, the −I inductive effect of one benzene ring causes the lone pair of the nitrogen atom to be withdrawn in to the ring thus forming a positive charge on the nitrogen atom. The positive charge on the sulphur atom is therefore more stabilized than the positive charge on the nitrogen atom and will show a higher the affinity for the negative charge on the sawdust. The amounts of dye sorbed and the sorption rate constants for the range of sawdust particle size used were all higher for methylene blue than for methyl violet.

The sizes of the dye molecules were also found to affect the amount of dye adsorbed on the sorbent surface. For example, the amounts of dye needed to occupy a fixed surface are fewer when the size of the dye molecule is larger. This may be the cause of the deviation from one sorption mechanism at 15 min for methyl violet and 30 min for methylene blue to another mechanism. The methyl violet molecule, which is larger, will occupy a fixed surface faster than the methylene blue molecule, which is smaller.

The diffusion modeling of the sorption pf methylene blue and methyl violet on mansonia wood sawdust revealed that the sorption process is complex and may be controlled by both mass transfer and intraparticle diffusion, as seen from the high correlation coefficients for both plots. The predominant mechanism was determined using the Boyds expression. External mass transfer was found to be the dominant mechanism for both methylene blue and methyl violet sorption for the range of sawdust particle size investigated. External mass transfer was more important for the methyl violet sorption than the methylene blue sorption. As the particle size of mansonia sawdust increased, external mass transfer became more predominant in the rate determining step.

4. Conclusion

The present study has examined the kinetics and mechanism of the sorption of two basic dyes, methylene blue and methyl violet onto mansonia wood sawdust. System variables such as pH and mansonia wood sawdust particle size were investigated. Two kinetic models (pseudo-first-order and pseudo-second-order) were employed in modeling the adsorption mechanism of the basic dyes onto mansonia wood sawdust. It was found that the sorption kinetics fitted the pseudo-second-order kinetic better than the first-order kinetics as seen from the higher correlation coefficient and the fact that the pseudo-second-order kinetics described the experimental data in the range of the sorption period and for the range of adsorbent particle size used. Two mechanisms including mass transfer and intraparticle diffusion were found to be involved in the rate determining step of the sorption of the basic dyes from solution. Mass transfer mechanism was found to be the dominant sorption mechanism for both dyes sorption and mass transfer mechanism increases in importance as the dominant mechanism as the particle size of the sawdust material increases. Mass transfer mechanism, was also found to be more dominant for the methyl violet sorption than for the methylene blue sorption.

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