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Musanga cecropioides Sawdust as an Adsorbent for the Removal of Methylene Blue from Aqueous Solution

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Abstract *Adsorption is an established method of removing dyes and other pollutants from aqueous solution. The success of adsorption depends on the nature of adsorbent. In this work, saw dust from musanga cecropioides is used for the removal of methylene dye from aqueous solution. Effect of contact time, adsorbent dosage, temperature and concentration of the dye were investigated. The results indicated that* at various adsorption dosage, concentrations, contact time and temperature, the equilibrium amount of dye adsorbed, qe (mg/g) ranged from 1.86 to 5.32, 3.44 to 4.55, 3.73 to 4.58 and from 0.89 to 3.88 respectively. The kinetic of the adsorption was best described by pseudo second order kinetics. The adsorption of the dye on the surface of the wood saw dust was exothermic, spontaneous and favours Langmuir and Temkin isotherm. Based on the observed trend in the variation of extent of adsorption with temperature and calculated values of free energy changes, the adsorption follows both physical and chemical adsorption mechanism. However, physisorption dominated the adsorption at lower temperature. The use of saw dust from *musanga cecropioides* wood is hereby recommended for commercial applications.

Key Words: *Water, contamination, dye, remediation, adsorption, wood saw dust*

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1.0 Introduction

Dyes are used by several industries including textile, paper, food, pharmaceutical, tannery and printing industries (Kee *et al.*, 2016). Consequently, dye rich effluent requires proper treatment before they are discharge to the aquatic or any other part of the environments (Gupta *et al.*, 2016). Dye can impart colour to the water body and can absorbed light, which will ultimately affect the primary productivity of phytoplankton and hence aquatic life (ref). Some dyes are toxic and could even poison aquatic organism (Banerjee and Chattopadhyaya, 2017). Others can interact with some chemical compounds or elements in the water to either mask their usefulness or increase pollution load of the aquatic system (Park *et al.*, 2012). Although there are several options that are available for the removal of dye from aqueous solution, the adsorption method has been widely accepted as one of the best options because it is cheap, easily accessible and ecofriendly method (Odiongenyi and Afangide, 2019, Odiongenyi, 2019). The effectiveness of several adsorbent for the removal of some dyes have been reported for some plant materials (Cardoso *et al*., 2011; Munagapati *et al*., 2018, Odoemelam, *et al*., 2018), nano materials (Odiongenyi, 2019; Sarma *et al*., 2019; Tan *et al*., 2015), animal shells (Odoemelam and Eddy, 2009), plant waste (Okwunodulu and Eddy, 2014; Okwunodulu *et al*., 2018),natural occurring chemical compounds (Sarma *et al.,* 2019;Yagub, *et al.,* 2014), polymeric materials (Sen *et al*., 2018) and others. Wood saw dust has long been discovered to be a good adsorbent for dye removal but little is reported on their usage. For example, badu *et al*. (2014) found that saw dust from *Tectona grandis*, *Ceiba pentandra* and *Terminalia superba* wood are good adsorbent for the removal of Vat Yellow-4, Vat Red-1 and natural dyes in water bodies. M'hamdi *et al*. (2017) reportedly used Beech and red wood sawdust for the removal of methylene blue from aqueous solution and obtained excellent removal efficiencies. Markandeya et al. (2015) obtained maximum adsorption capacity of 76.92, g/g when some wood dusts were used as adsorbents for the removal of methylene blue dye from aqueous solution. Langmuir adsorption isotherm was obeyed by this system. Pimto *et al*., (2020) found that modification of unnamed wood saw dust with succinic anhydride presented it as an excellent adsorbent for the removal of violet Remazol 5R dye from aqueous solution. In Nigeria, wood saw dust are produced in substantial quantity as a waste from timber processing industries. They are normally disposed in a way and manner that they constitute environmental nuisance while other incinerate them without knowledge of the gaseous pollutants that are exhausted to the atmosphere. Resource recovery entails recovery useful components from materials that could have been wasted. Considering their high potential and the existent of research gap on the depth of utilization of wood saw dust, the present study is aimed at investigating the adsorption capacity of *Musanga cecropioides* wood saw dust for the removal of methylene blue from aqueous solution.

Methylene Blue is a cationic dye mostly used in the textile industry for a variety of purposes. It is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$ and molar mass 319.852g/mol. At room temperature, it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. MB is the most used substance for coloring paper and textiles such as cotton, wool and silk dyeing, as an antiseptic and for other medicinal purposes. The chemical structure of the dye is shown in Fig. 1. According t0 Eddy *et al*. (2011a) adsorption of a molecule is enhanced by the presence of aromatic ring, multiple bonds, hetero atoms, π-electron and other properties. Possession of these properties by methylene blues indicates that its adsorption should be spontaneous.

2.0 Materials and Methods

2.1 Sample Collection and Preparation

Wood sawdust was collected from Ekim Sawmill/Timber market in Mkpat Enin local government area of Akwa Ibom State, Nigeria. The methylene blue dye was supplied by the Chemistry departmental store, Akwa Ibom State University. All reagents used for the study were analytical grades. (Sigma Aldrich, UK) and were gotten from the Chemistry departmental store in the Akwa Ibom State University.

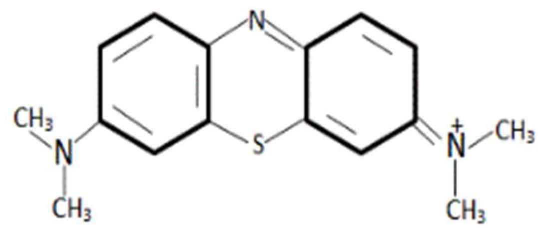

Fig. 1: Chemical structure of methylene blue (MB) dye

The reagent used included methylene blue which is a cationic dye with chemical formula $C_{16}H_{18}N_3SCl$. Stock solution of methylene blue dye was prepared by dissolving 1 g of the dye in 1000 ml of distilled water. From the stock solution, several concentrations of the dye were prepared and used for developing calibration curve and further analysis.

The wood sawdust taken from the mill was rinsed with distilled water and sundried for three (3) days. The sawdust was blended and sieved using 2 mm mesh size sieve and then washed severally using 0.1 M HCl to remove surface ash, followed with hot water and finally with distilled water to remove residual acid. The sample re-dried in the sun for three days before re-drying in the oven whose temperature was set at 120 °C for 24 hours. After oven drying, the samples were stored.

2.2 Batch adsorption experiment

Batch adsorption process as reported elsewhere was used to study the effect of concentration, contact time, adsorbent dosage and temperature (Odoemelam *et al*. 2018). Equilibrium concentration of the dye was calculated using equation 1

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (1)$$

where C_0 is the initial concentration of the dye, C_e is the equilibrium concentration of the dye, V is the volume of solution and m is the mass of the adsorbent.

2.3 Spectrophotometric determination of dye concentration

All spectrophotometric analyses were carried out using 721,P/N:A003 UV-visible spectrophotometer In spectrophotometric analysis, wave length of maximum absorption of EY dye was measured. The measured wavelength was used as a reference wave length for all analysis and determination of the concentrations using extrapolation method according to Beer-Lambert's law of spectrophotometry,

Calibration curve for MB dyes was prepared by measuring the absorbance of serially diluted solutions of the dyes at their wave length of maximum absorption. This is consistent with the Beer-Lambert law of absorption which states that the absorbance of an analyte is proportional to concentration. Therefore, the development of the calibration curve was based on equation 2

$$A = \epsilon l C \quad (2)$$

where A is the absorbance, l is the path length and ϵ is the molar absorptivity. Since ϵ and l is a constant, a linear relationship is expected for the plot of A against C. The slope of such plot gives the product of absorptivity and path length which is a constant. From the calibration curve, concentrations of the respective analytes were obtained through extrapolation. Calibration curve for MB dye is presented in Fig. 2. The plots reveal high values of R^2, which confirm that the solutions obey the Beer-Lambert law.

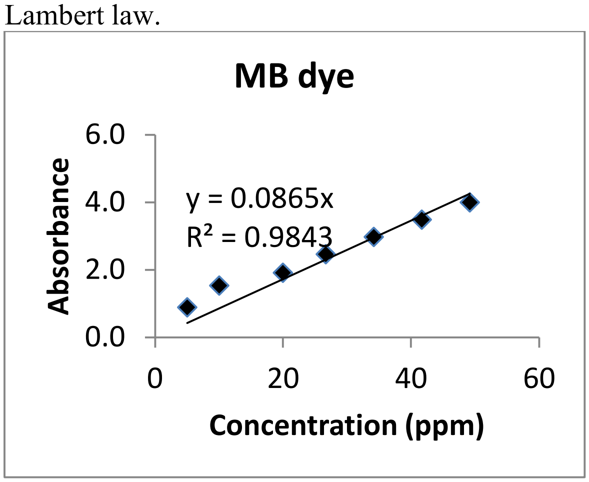

Fig. 2: Calibration curve for methylene blue dye

3.0 Results and Discussion

3.1 Effect of adsorption dosage

Variation of percentage of MB dye adsorbed with adsorption dosage is shown in Fig. 3. The results display slight changes due to increase in adsorbent dosage. Amount of MB dye adsorbed started with a rise and fall before it finally rises. The interruption in trend could be ascribed to competition between adsorption and desorption due to differential levels of activation of the adsorption sites as the dosage changes.

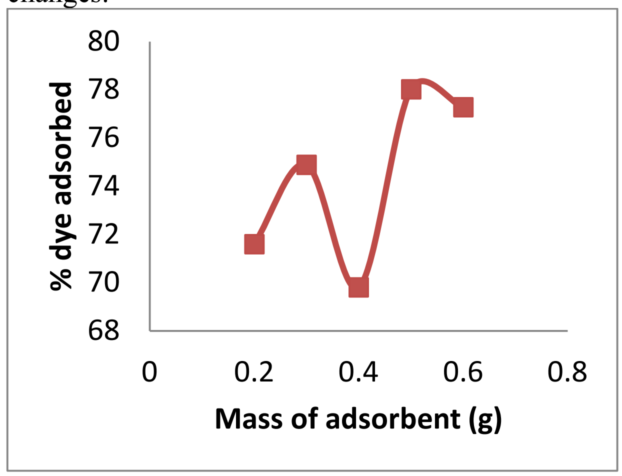

Fig. 3: Variation of percentage MB dyes adsorbed with mass of adsorbent

3.2 Effect of dye concentration

Dye concentration can influence the amount of dye molecule that is adsorbed on the surface of wood saw dust. Effect of dye concentration was investigated using various concentrations of the dye at constant adsorbent dosage and temperature. Fig. 4 shows the variation of percentage MB dye adsorbed with concentration. From the results obtained, the amount of MB dye adsorbed increases with increase in concentration. This is due to increase in the number of molecules approaching the vacant adsorption sites and the consequence increase in sticking probability. Hence, increase in initial concentration of the dye led to increase in extent of adsorption.

3.3 Effect of contact time

Fig. 5 presents a plot obtained with respect to batch experiments that were carried out to investigate effect of contact time on the adsorption of MB dye on the surface of wood sawdust. The plot reveals that increased in the period of contact led to increase in the amount of MB dye adsorbed upto a certain threshold time limit, after which further increase in time led to decreasing adsorption. The observed trend suggest that below the threshold limit, amount of dye adsorbed increases due to increasing strength of sticking probability but as the adsorbate remains on the adsorbent surface with time, forces of desorption tend to decrease the concentration of the dye on the wood surface until an equilibrium is established between forces of adsorption and desorption (Eddy, 2009). Hence in utilizing wood saw dust for adsorption of dyes, adequate considerations must be given to the expected period of contact.

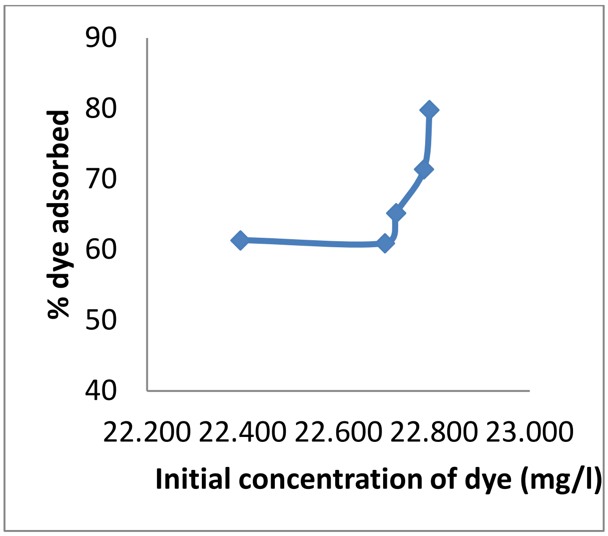

Fig. 4: Variation of percentage dye adsorbed with initial concentration

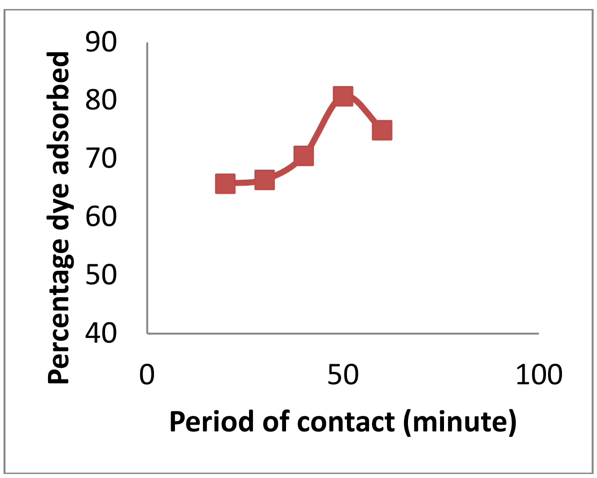

Fig. 5: Variation of percentage MB dye adsorbed with period of contact

3.4 Effect of temperature

Fig. 6 shows plots for variation of percentage dye adsorbed with temperature. The plot reveals that the amount of dye adsorbed generally decreases with increase in temperature upto a certain value after which increase in adsorption with temperature was observed. This indicate that the adsorption of the dye proceeded with physisorption mechanism and was succeeded by chemisorption mechanism.

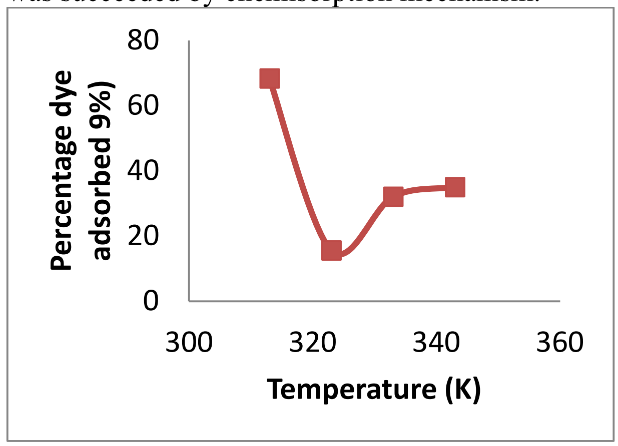

Fig. 6: Variation of percentage dye adsorbed with temperature

Physisorption mechanism is characterized by decrease in extent of adsorption with temperature while chemisorption is characterized with increase in extent of adsorption with temperature (Essien *et al.,* 2020)

3.5 Adsorption isotherm

Adsorption isotherm gives the relationship between the amount of dye adsorbed with concentration at a given temperature. It is a unique factor that can be used to study the adsorption behaviour of dyes and other adsorbates. Attempts to obtained best suited adsorption isotherm through fitting of data led to the conclusion that Langmuir, Temkin and Dubinin-Raduskevich isotherms best described the adsorption behavour of MB dyes.

The Langmuir adsorption isotherm can be written according to equation 3 (Igwe and Abia, 2007).

$$\frac{C_e}{q_e} = \frac{1}{q_m b_{ads}} + \frac{C_e}{q_m} \qquad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/l), b_{ads} is the Langmuir adsorption constant which is related to affinity between the adsorbate and the adsorbent while q_m is the theoretical monolayer saturation capacity. From the Langmuir equation, a plot of $\frac{C_e}{q_e}$ versus C_e should be liner if the Langmuir assumptions are valid. The Langmuir isotherm for the adsorption of MB dye unto wood saw dust is shown in Fig 7. Values of Langmuir adsorption parameters (deduced from the slope and intercept of the plots) are presented in Table 1.

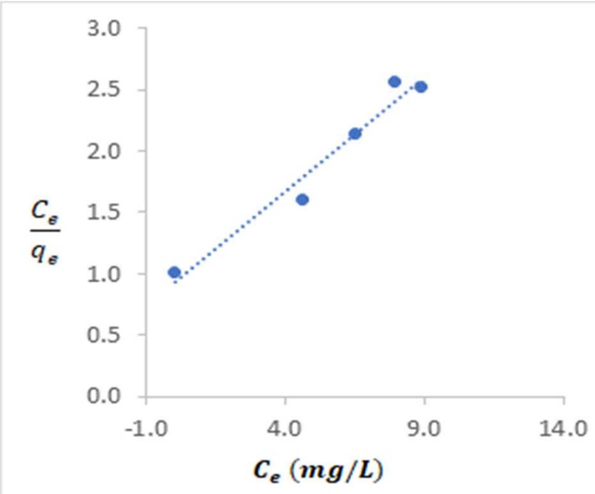

Fig. 7: Langmuir isotherm for adsorption of AB and MB dyes onto wood saw dust

Table 1: Langmuir and Temkin parameters for the adsorption of Mb dye on wood saw dust

Isotherm	lnb_{ads}	B/q_m (mg/g)	ΔG^0_{ads} (J/mol)	R^2
Langmuir	0.6918	2.7100	-1.74272	0.992
Temkin	4.2106	1.709	-24.4284	0.984

**** B is Temkin constant and q_m is Langmuir theoretical adsorption capacity**

The ideal Langmuir model expect the slope value to be equal to unity and this correspond to adsorption where there is no interaction between the adsorbed specie (ref). Slope values greater or less than unity therefore indicate the existent of interaction (Okwunodulu and Eddy, 2014). Hence the existent of interaction between the adsorbed MB dye molecules is indicated by the low free energy associated with the Langmuir isotherm and the exceedingly high value associated with the Temkin (which contain lateral interaction term).

The Linear form of the Temkin isotherm can be written according to equation 4 (Odoemelam *et al.,* 2020)

$$q_e = BlnA + BlnC_e \quad (4)$$

where: A is the Temkin isotherm constant (L/g), B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). Temkin adsorption plots and adsorption parameters are shown in Fig. 8 and Table 1 respectively

The equilibrium constant of adsorption is related to the free energy of adsorption according to equation 5 (Eddy *et al*., 2009)

$$\Delta G^0_{ads} = -RTln(b_{ads}) \quad (5)$$

Calculated free energy of adsorption gave -1.74 and -24.43 kJ/mol using b_{ads} from the Langmuir and Temkin isotherms respectively (Table 1). The observed range signify that why the Langmuir model points toward physisorption, the Temkin points toward chemisorption. According to Eddy *et al.* (2011b) values of free energy upto -20 kJ/mol and above is an indication of the onset of chemisorption mechanism. This suggest that physisorption mechanism was succeeded by chemisorption. The extremely low value obtained for the free energy of adsorption through the Langmuir plot indicate the existent of interaction.

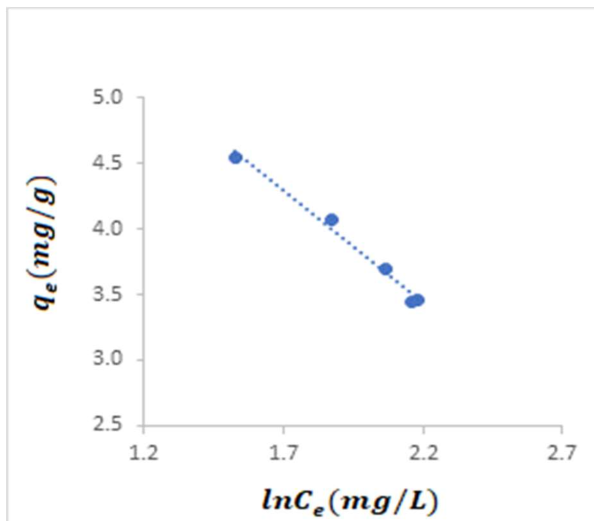

Fig. 8: Temkin isotherm for adsorption of AB and MB dyes on wood saw dust

The Dubinin-Radushkevich (DRK) adsorption model takes the form shown in equation 6 below (Eddy *et al.,* 2008)

$$lnq_e = lnq_m - \beta\varepsilon^2 \quad (6)$$

where q_e is the equilibrium amount of the dye that is adsorbed (mg/g), qm is the theoretical amount of dye adsorbed, β is the activity coefficient which is related to the mean sorption energy and ε is the Polanyl potential and can be expressed as,

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

The value of the adsorption energy can be obtained from the following relation,

$$E_{ads} = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

Application of the DRK equation requires that a plot of lnq_e versus ε^2 gives a straight line with slope equal to β and intercept equal to lnq_m. The DRK plots for the adsorption of MB dye unto wood saw dust are shown in Fig. 9. From the slope of the plots, the adsorption energy for MB dye is 0.5 kJ/mol. Generally, adsorption energy in the range of 1 to 8 kJ/mol point toward physisorption while adsorption energy in the range of 8 to 16 kJ/mol is an indication of chemisorption. Therefore, the adsorption of MB dye is dominantly occurred through physisorption mechanism.

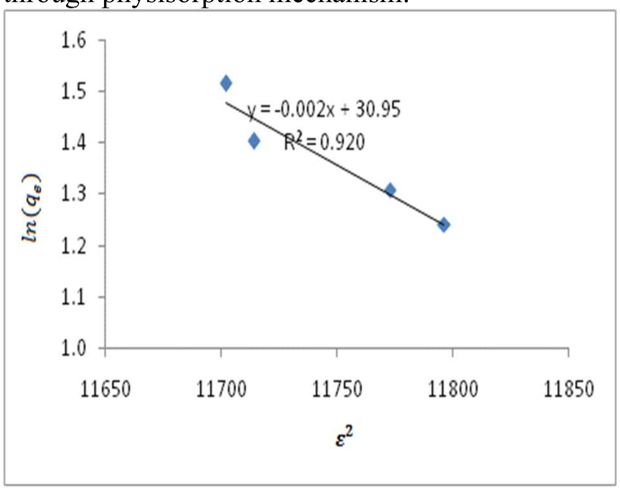

Fig. 9: Dubinin- Raduskevich isotherm for adsorption of AB and MB dyes

3.6 Kinetic study

The expressions for the pseudo first and second order kinetic models are provided in equations 9 and 10 respectively (Okwunodulu *et al.*, 2014,2015)

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Curve fittings to the two kinetic models indicated that the adsorption of MB dyes best fitted the pseudo second order kinetic (i.e. equation 10) than the pseudo first order model. Therefore, plots of $\frac{t}{q_t}$ versus t yielded straight lines for MB dye as shown in Fig. 10. Table 2 shows pseudo second order adsorption parameters for MB dye. From the fitted model, i.e. pseudo second order kinetic data, the initial adsorption rate (i.e. h) and half adsorption time ($t_{0.5}$) (i.e. $h = \frac{1}{k_2 q_e^2}$ and $t_{0.5} = \frac{1}{k_2 q_e}$ respectively) were calculated and are also recorded in Table 2. The results obtained in this study indicated that MB dye has good initial adsorption rate and half adsorption (Odiongenyi, 2019)

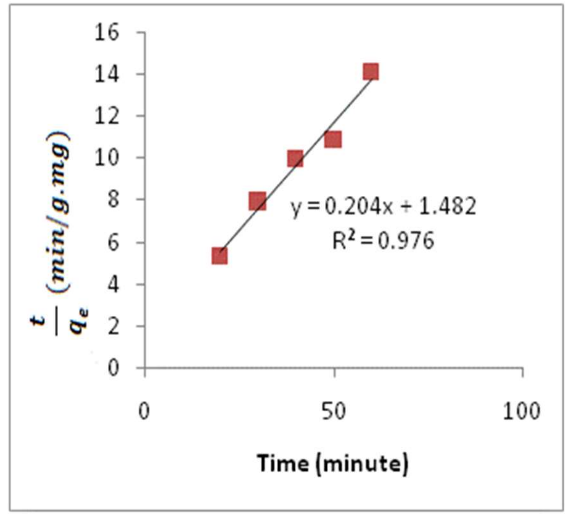

Fig. 10: Pseudo second order kinetic plot for the adsorption of AB and MB dyes on wood saw dust

3.7 Thermodynamic study

According to Odiongenyi (2019), the equilibrium amounts of dye adsorbed(q_e) and equilibrium concentration (C_e) are related to the equilibrium constant according to the following equations,

$$k_c = \frac{q_e}{C_e} \quad (11)$$

Also, from thermodynamics,

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (12)$$

Therefore,

$$-2.303RTlogk_p = \Delta H^* - T\Delta S^* \quad (13)$$

$$-Tlnk_c = \Delta H^* - T\Delta S^* \quad (14)$$

$$lnk_c = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (15)$$

Therefore, a plot of lnk_p $versus$ $\frac{1}{T}$ is expected to be linear with slope and intercept equal to $\frac{\Delta H^*}{R}$ and $\frac{\Delta S^*}{R}$ respectively. This plot is shown in Fig 11. Calculated enthalpy and entropy changes are –0.7086 and 1.9712 J/mol indicating that the adsorption of MB dye onto the surface of the wood saw dust is exothermic and is accompanied by low degree of disorderliness.

Table 2: Pseudo second order kinetic parameters for the adsorption MB dye on the surface of the wood saw dust

Dye	slope	Intercept	qe	K_2	h	$t_{0.5}$	R^2
MB	0.204	1.482	0.675	0.3072	1.482	2.196324	0.975

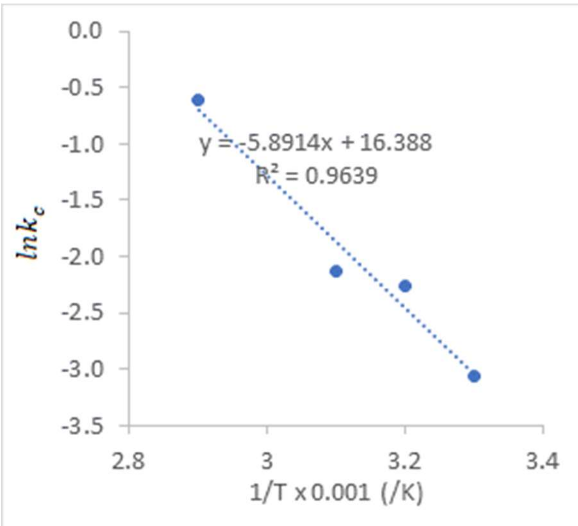

Fig. 11: Transition state plot for the adsorption of MB dye on wood saw dust

4.0 Conclusion

Wood saw dust from *Musanga cecropodies* is a good adsorbent for the removal of methylene blue dye from aqueous solution. The adsorption of dye unto the wood saw dust is exothermic, spontaneous and dominantly followed physisorption mechanism and a pseudo second order kinetics. The adsorption of the dye is sensitive to changes in concentration, adsorbent dosage, period of contact and temperature. Therefore, further investigation on the use of this wood saw dust for decontamination will give a foundation for commercial implementation.

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