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Wood Saw Dust as Adsorbent for the Removal of Direct Red (DR) Dye from Aqueous Solution

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Abstract: *Current researches in adopting or synthesizing materials for water purification through adsorption are targeted on those ones that are renewable or those that have great potentials of reducing waste in the environment. Attempt was made to utilized wastes from the wood industry (wood sawdust) as adsorbent for the removal of Direct red dye from aqueous solution. The results indicated maximum percentage dye removal approaching 100 %. The adsorption of the dye tends to increase with adsorbate dosage and with increase in the initial dye concentration. The adsorption efficiency also increases with time upto 60 minutes after which, further increase in time did not reflect corresponding increase in time. The mechanism of physical adsorption was established for the adsorption of Direct red dye unto the surface of the wood due to decrease in extent of adsorption with increase in temperature, observed values of standard free energy and heat if been less than the threshold values required for the mechanism of chemical adsorption). Langmuir, Temkin and Dubinin-Raduskevich adsorption models were sufficient to explain the adsorption characteristics of wood sawdust for the removal of Direct dye from aqueous solution. Application of pseudo first order kinetics fails with respect to the adsorption of Direct dye on wood sawdust. However, pseudo second order kinetic was established in addition to the freedom of intra particle diffusion model as a controlling factor*.

Key Word: Water contamination, purification, adsorption, wood saw dust, kinetic, thermodynamic and adsorption modelling

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1.0 Introduction

Dye has the tendency to alter the quality of water through colour presentation and alteration of other physicochemical and organoleptic properties of water (Eddy and Ekop, 2007). Literatures reveal that dye can inhibit the photosynthetic potential of aquatic phytoplankton through its influence on light penetration (Odiongenyi, 2019). Dye can also form complexes with metals and other compounds present in the water and creates toxic effect depending on the type of metal ion and the dye. In view of the aforementioned and other environmental impact of dyes, several studies have been conducted on the application of water treatment technologies for the removal of dye from aqueous solutions. Among all the known and flexible technologies, adsorption is one of the best options. However, some adsorbents are very expensive, unrenewable and can create further disposal problems. Therefore, there are concerted research attention directed towards the implementation of adsorption techniques (using materials of plant origin) for the removal of dyes from aqueous solution.

The use of wood saw dust as adsorbent for the removal of dyes from aqueous solution has been reported by Odiongenyi and Afangide (2019), Odiongneyi (2019), M'hamdi *et al*. (2017), Badu *et al*. (2014), etc. In all these studies, wood saw dusts were found to exhibit excellent removal efficiencies for various dyes. The present study, seek to investigate the adsorption efficiency of wood sawdust for direct red dye from aqueous solution.

2.0 Materials and Methods

The dye was purchased from Sigma Aldrich outlet in Calabar, Cross River State, Nigeria and was used without further purification.

Bath adsorption experiment was carried out as reported elsewhere (Odiongenyi, 2019). The equilibrium amount of dye adsorbed was calculated using the following expression,

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

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.

Spectrophotometric analyses were carried out (at 504 nm, which was the wavelength of maximum absorption of the dye) using 721P/N:A003 UV-visible spectrophotometer

3.0 Results and Discussion

3.1 Calibration curve

The calibration curve developed from the absorbance measurements of various concentration of DR dye is presented in Fig. 1. The curve was developed through the application of Beer-Lambert law which supports a linear relationship between absorbance and concentration as follows,

$$A = \in lC \qquad (2)$$

where A is the absorbance is the absorptivity, l is the path length and C is the concentration of the dye. This plot was a reference to the determination of concentration of the dye through extrapolation.

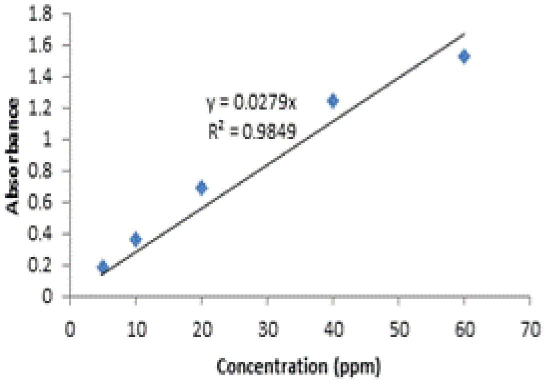

Fig. 1: Calibration curve for DR dye

3.2 Effect of adsorbate dosage

Variation of the percentage amount of dye absorbed with adsorbent dosage (i,e wood saw dust) is presented in Fig. 2. The results reveal that the amount of dye absorbed increases linearly with adsorbent dosage. This may be due to increase in the number of available adsorption sites with increase surface area (Eddy and Odoemelam, 2009; Okwunodulu and Eddy, 2014).

3.3 Effect of concentration

Concentration can affect the amount of dye adsorbed at a given temperature through its influence on the amount of dye diffusing from the bulk solution to the adsorption sites (Odoemelam and Eddy, 2009). Variation of equilibrium amount of DR dye adsorbed with concentration is shown in Fig. 3.

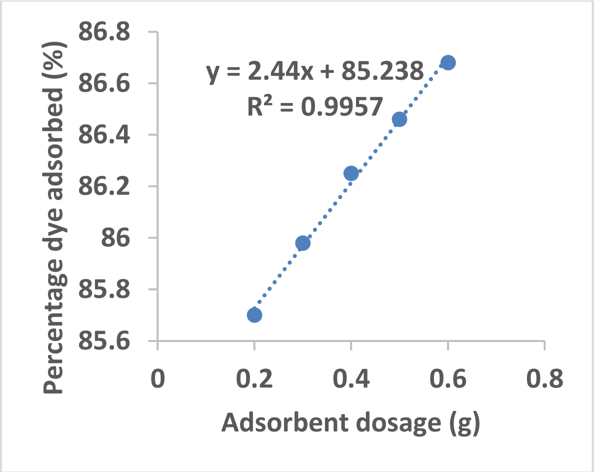

Fig. 2: Variation of amount of dye adsorbed with adsorbate dose

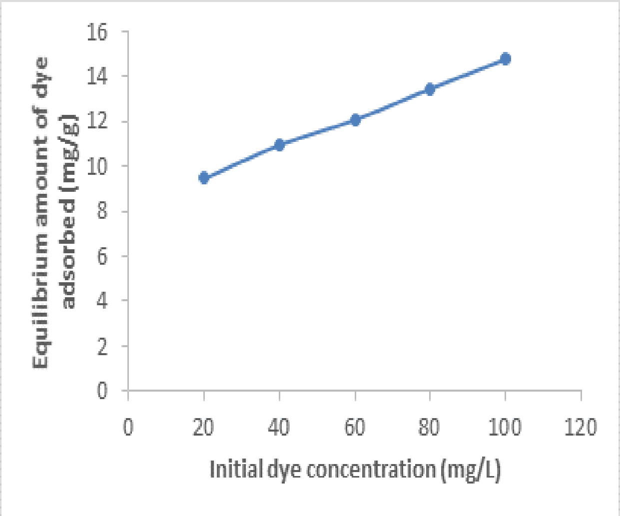

Fig. 3: Variation of equilibrium amount of dye adsorbed with concentration

From Fig. 3, it is evident that the observed variation depicts a linear relationship between equilibrium amount of dye adsorbed and initial dye concentration. This indicates that increase in the initial concentration of DR dye increases, the amount of dye removed from the solution through adsorption also increases. Consequently, increase in concentration might have increase the amount of the dye molecules that migrated to the adsorption sites. Similar observation has been reported for some adsorbent (Ekop and Eddy, 2010).

3.4 Effect of contact time

Contact time may affects the adsorption of dye through the mechanism of adsorption and desorption or through competitive mechanism of the two processes (Odiongenyi, 2019). Fig. 4 shows the variation of equilibrium amount of DR dye adsorbed with the period of contact. It is observed from the plot that the amount of DR dye adsorbed displayed significant dependency on the period of contact. Adsorbed amount of dye was observed to increase as the period of contact increases, suggesting that the adsorption sites might have been increasingly activated or became more porous as the contact time increases (Odoemelam *et al*., 2018). However, after 50 minutes, the amount of dye adsorbed was observed to decrease with time. This may be due to desorption mechanism that succeeded the adsorption process. Continuous contact between the adsorbent and the adsorbate might have led to competition between the adsorbate molecules in the bulk solution and those adsorbed. Once the tendency for desorption outbalances the tendency for adsorption, concentration of the adsorbed dye will start to decrease with time as observed in this work (Odiongneyi and Afangide, 2019).

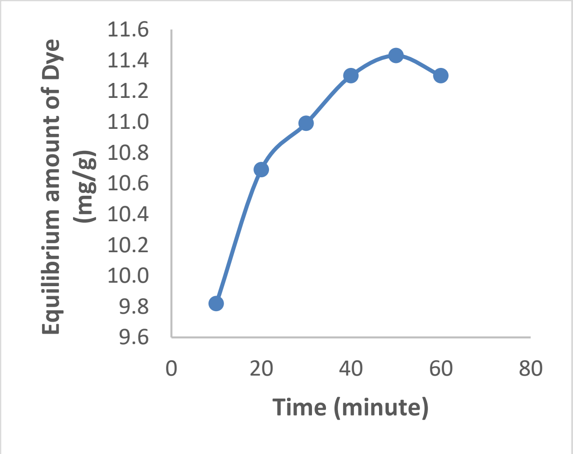

Fig. 4: Variation of amount of dye adsorbed with time

3.5 Effect of temperature

Temperature can affect extent and rate of adsorption through activation or deactivation of the available adsorption sites or through its effect on diffusion. In order to investigate the effect of temperature on the adsorption of DR dye, the batch experiments were carried out at various temperature. The results obtained are presented in Fig. 5. The plot reveals that the amount of DR dye adsorbed decreases with increase in temperature, which suggested that the adsorption is majorly controlled by physisorption mechanism because the extent of adsorption decreases with temperature (Meena *et al*., 2008). At high temperature, the adsorption sites may not present thermodynamically favorable conditions for adsorption and this effect can increase as the temperature increases (Kumar *et al*., 2013).

3.6 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 an adsorbate on the surface. Best suited adsorption models for the removal of DR dye from aqueous solution were selected based on the values of R^2 obtained from the respective model plots. Consequently, the adsorption of DR dye unto wood saw dust obeyed Langmuir, Temkin and Dubinin-Raduskevich isotherms.

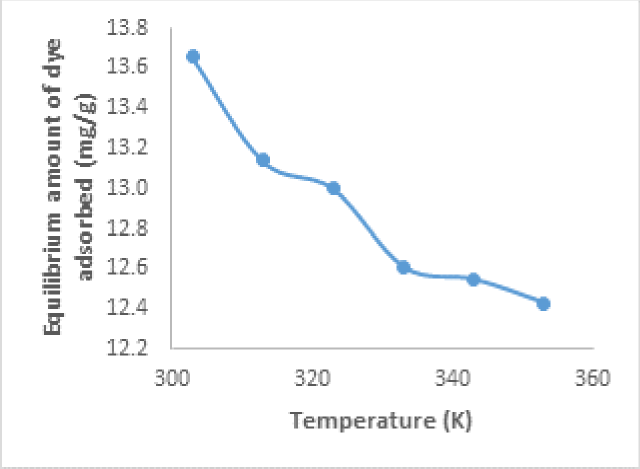

Fig. 5: Variation of amount of dye adsorbed with temperature

Obedient of the adsorption data to the Langmuir isotherm was established through a high degree of linearity of a plot of C_e/q_e versus C_e which gave R^2 value of 0.9387 as shown in Fig. 6. The Langmuir isotherm can be expressed according to equation 3 (Adedirin *et al*., 2012, 2011a-d)

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

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 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. The results indicates that the theoretical adsorption capacity and the Langmuir constant of wood saw dust for DR dye is 1.7212 mg/g which is lower than the maximum equilibrium value obtained from experiment. The discrepancy maybe attributed to slight deviation from the ideal Langmuir isotherm, which is expected to give q_m value of unity. According to Odoemelam *et al.* (2018), an ideal Langmuir isotherm represent a monolayer adsorption with slope value of unity. Consequently, since the dominant adsorption mechanism for DR dye unto wood saw dust is physisorption, then the variation could be due to slight deviation.

The significant of the Langmuir adsorption constant is that it can be used to predict the spontaneity of the adsorption process through the standard free energy expressed according to equation 4 (Eddy *et al.*, 2008a,b)

$$\Delta G^0_{ads} = -RTln(b) \qquad (4)$$

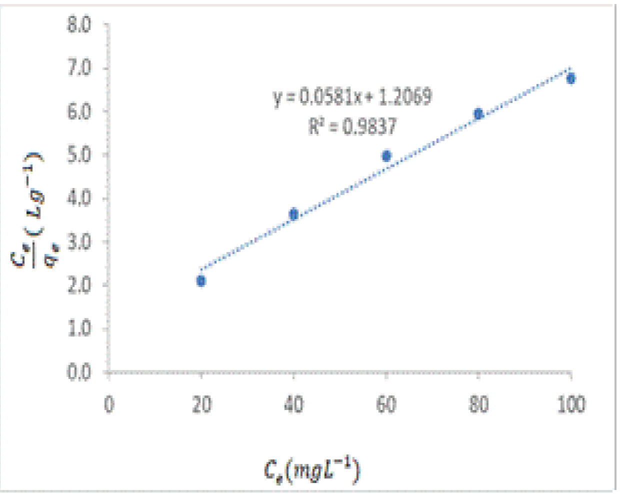

Fig. 6: Langmuir isotherm for the adsorption of DR dye by wood saw dust

Calculated value of ΔG^0_{ads} for the adsorption of DR dye unto the wood saw dust was very low (-6.741 kJ/mol) confirming spontaneous adsorption process and the predominance of physical adsorption mechanism. The fitness of the Temkin isotherm to the adsorption of DR dye unto wood saw dust was also confirmed through a linear plot generated from the plotting of q_e against ln_e (as shown in Fig. 7) according to equation 5 (Eddy and Ekop, 2005, 2009).

$$q_e = BlnA + BlnC_e \qquad (5)$$

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). Evaluated Temkin parameters also confirmed the predominance of physisorption mechanism ($\Delta G^0_{ads} = -2.2111\ kJ/mol$).

The Dubinin-Radushkevich (DRK) adsorption model takes the form shown in equation 6 (Eddy, 2009).

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

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,

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

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

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

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.

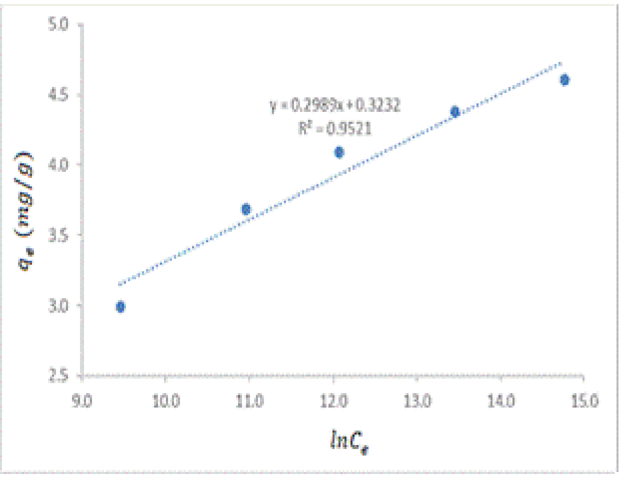

Fig. 7: Temkin isotherm for the adsorption of DR dye

The DRK plots for the adsorption of DR dye unto wood saw dust is shown in Fig. 8. From the slope of the plots, the adsorption energy is estimated as 22.36 J/mol, which is lower than the threshold value of 8 kJ/mol, hence the adsorption of DR dye unto wood saw dust surface aligns with physical adsorption mechanism. Generally, adsorption energy in the range of 1 to 8 kJ/mol point toward physical adsorption mechanism while adsorption energy in the range of 8 to 16 kJ/mol is an indication of chemical adsorption mechanism (Eddy *et al.*, 2010)

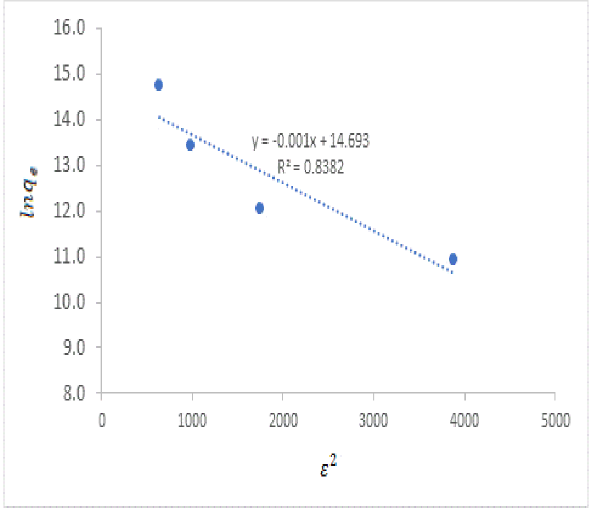

Fig. 8: Dubinin-Raduskevich isotherm for the adsorption of DR dye unto wood saw dust

3.7 *Kinetic study*

In kinetic study of dye removal, two significant pseudo-order models are pseudo first and pseudo second order kinetic models. The expressions for the models are provided in equations 9 and 10 respectively (Essien and Eddy, 2015)

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

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

Curve fittings to kinetic models indicated that the adsorption of DR dye best agree with the pseudo second order kinetic (i.e equation 11). Therefore, a plot of $\frac{t}{q_t}$ versus t yielded a straight line as shown in Fig. 9. The kinetic data is seen to fit the pseudo second order model excellently. The initial adsorption rate (i.w 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 comparable to those reported by others.

3.8 *Intra particle diffusion model*

The existent of intra particle diffusion can be established if equation 11 is obeyed (Uchechuku *et al.*, 2015a,b),

$$q_e = k_p \boldsymbol{t^{0.5}} \qquad (11)$$

Consequently, graphs of q_e versus $t^{0.5}$ for the adsorption of DR dye (Fig. 10) consisted of two sessions, which were a slowly rising graph and a linear section. The existent of nonlinear section in the plot indicates that both intra particle diffusion and surface adsorption occur simultaneously (Odoemelam *et al.*, 2018).

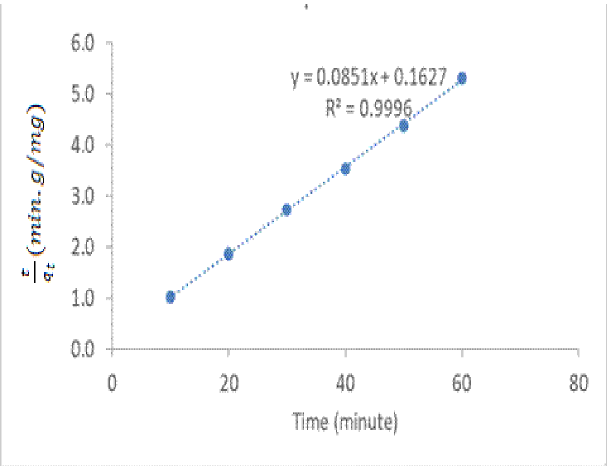

Fig. 9: Pseudo second order kinetic plots for the adsorption of DR dye by wood sawdust

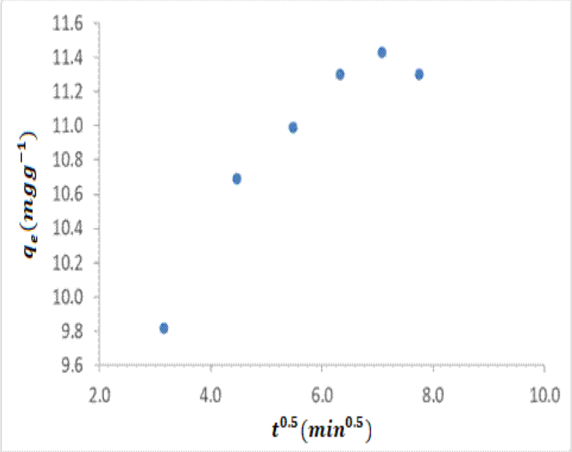

Fig. 10: Intra particle diffusion model plot for the adsorption of NR DR dyes

4.0 Conclusion

Wood saw dust has the potential of serving as a good adsorbent for the removal of DR dye from aqueous solution is the controlling factors (time, adsorbate dosage, initial dye concentration, temperature, pH and contact time) are optimized. The adsorption mechanism favours physical adsorption and accepted the models of Langmuir, Temkin and Dubnin-Raduskevich isotherms. The adsorption is spontaneous, obeys pseudo second order kinetics and is controlled by intra particle diffusion.

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Conflict of Interest

The authors declared no conflict of interest