

## Removal of Eosin Yellow Dye from Aqueous Solution by Adsorption unto *Musanga cecropioides* Wood Saw Dust: Experimental and Theoretical Study

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This study was designed to investigate the effectiveness of *Musanga cecropioides* wood sawdust as an adsorbent for the removal of eosin yellow dye from aqueous solution. Batch adsorption, FTIR and computational chemistry methods were used. A concentration of the dye was determined by spectrophotometry method. The results obtained confirmed that the wood sawdust is an efficient adsorbent for the removal of eosin dye from aqueous solution. The adsorption capacity of the wood sawdust is a function of concentration, adsorbent dosage, time and temperature. The adsorption isotherms of Langmuir, Freundlich, Temkin and Dubinin-Raduskevich fitted the adsorption data significantly. The fitness of the adsorption data to kinetic models was excellent for pseudo first order and pseudo second order models. FTIR study revealed that the adsorption of the dye is facilitated by some functional groups (that were missing in the original spectrum) while computational chemistry study gave values of electronic parameters that are comparable to those reported for good adsorbents. The molecular orbital, bonds and atoms associated with electrophilic and nucleophilic attacks were also analyzed through frontier orbital theory and Fukui function analysis and the results obtained agreed with each other.

**Keywords:** Water purification, Adsorption, Wood saw dust, Experimental and Theoretical studies

### INTRODUCTION

Global environmental concern places more hope on the provision of portable water that is devoid of all forms of pollutants ranging from physicochemical (including color), organoleptic, heavy metals, etc. [1,2]. One of the major characteristics of portable water is that it must be colorless. Water acquired color when some substances dissolve in it. The textile, paint, leather and tanning industries use dyes of various forms in processing their products [3]. Most often, these dyes find their way into the water bodies (through direct discharge or surface runoff), consequently, the color of the water will be altered. Some dyes are toxic and could therefore be very harmful to aquatic life [4]. Also, the nontoxic dyes can also affect aquatic life because it can obstruct light penetration and consequently retard the primary photosynthesis process [5]. In view of the above listed (and others) impacts of dyes on aquatic system, several researches have been reported on ways of removing dye from water, including adsorption.

Several studies have also been conducted on removal of dyes from aqueous solution using different forms of adsorbents such as natural and artificial polymers, natural and chemical compounds such as limestone, Cao, ZnO, etc. [6] nano materials such as nano carbon tubes, nano graphene oxide [7-9] and plants or animals materials such as plant leaves, stems, etc [10,11]. The use of plant materials offers

sustainable environmental hope because most of them are green and undergo biodegradation at ease. Therefore, the present study is aimed at using wood saw dust obtained from *Musanga cecropioides* wood as an adsorbent for removing eosine yellow dye from aqueous solution. The use of some wood sawdust for the removal of dyes from aqueous solution is not strange. For example, scientists found that [12] found that *Tectonagrandis*, *Ceiba pentandra* and *Terminalia superbasawdusts* were good adsorbents for the removal of dyes from aqueous solution. Scientists [13] investigated the capacity of Beech wood sawdust for the adsorption of some textile dyes (direct orange 26, acid orange 7 and acid green 20). The wood sawdust was an effective adsorbent for the removal of the studied dyes from aqueous solution [14]. Also found that some textile dyes can effectively be adsorbed

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by wood sawdust. The adsorption fitted pseudo first order, pseudo second order, Langmuir, Freundlich and Temkin adsorption models. Adsorption is a surface phenomenon that operates through mechanism of charge transfer or electron transfer. Charge transfer is native for physisorption mechanisms while the transfer of electron from the adsorbate to the adsorbent or vice versa is in accord with the mechanism of chemical adsorption which is more sensitive to temperature and physisorption [15-17].

## MATERIALS AND METHODS

The IUPAC name of the dye (eosin yellow) is sodium 2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl) benzoate. The dye and all other reagents were supplied by the Chemistry departmental store, Akwa Ibom State University. Wood saw dusts were produced from *Musanga cecropioides* wood. Experimental components of the work included batch adsorption experiment, spectrophotometric determination of concentration and FTIR analysis of functional groups. The theoretical components included semiempirical calculations and Fukui function analysis. calculations.

### Batch adsorption experiment

Batch adsorption process as reported elsewhere was used to study the effect of concentration, contact time, adsorbent dosage and temperature of the adsorption of the dye unto the wood saw dust [11]. Amount of dye adsorbed at equilibrium 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.

### Spectrophotometric determination of dye concentration

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

### FTIR analysis

FTIR analysis of the dye, adsorbent (before and after adsorption) was carried out using Agilent FTIR spectrophotometer (Located in Chemistry Department of the Bayero University, Kano, Nigeria). The samples were prepared with KBr powder and the scan range was 650 to 4000  $\text{cm}^{-1}$ . The system status was good while the Apolization was Happ-Genzel. The Agilent Technologies

software also provided provision for display of analytical output.

### Computational chemistry calculations

All computational calculations were performed with a Hewett Parker (HP) core i4 laptop having with processor speed and hard disc capacity of 8 GB and 1 TB respectively. Computational chemistry calculations were performed using DFT and ab initio methods in hyperchem package. Full geometry optimization was achieved using the same software. ChemBio 2018 was used to develop molecular graphic and input files for ORCA package Semiempirical parameters were calculated using molecular orbital package (WinMOPAC).

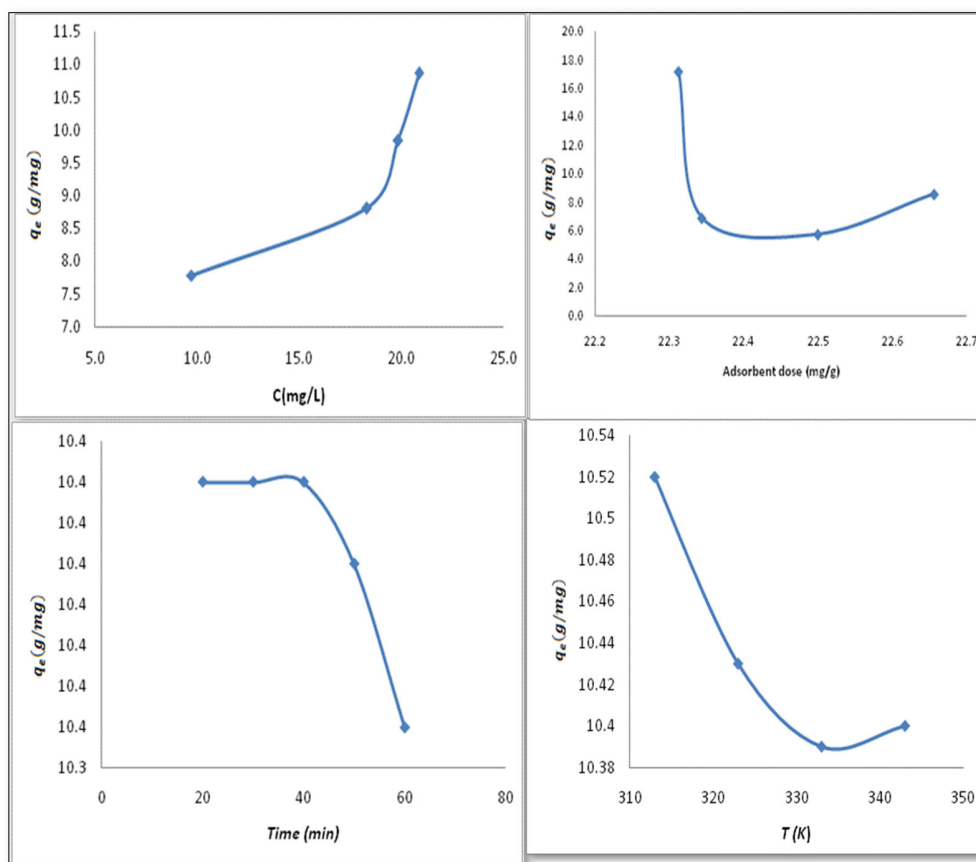
## RESULTS AND DISCUSSIONS

### Batch adsorption study

Beer-Lambert's law of spectrophotometry was applied to convert absorbance measurements to concentrations through extrapolation from the calibration plot. Effect of concentration was studied for various concentrations of EY dye adsorbed under similar experimental conditions (temperature, adsorbent mass, pH, period of contact, etc). **Figure 1** shows plot for the variation of equilibrium amount of dye adsorbed at various concentrations,  $C$  (mg/L), adsorbent mass (in mg), temperatures (in Kelvin) and period of contact (in min).

From **Figure 1**, it is observed that the adsorption of EY dye increases with increase in concentration, which indicate that as the concentration of the dye increases, there is a corresponding increase in the amount of EY dye approaching the adsorption sites of the adsorbent through mass transfer. At low concentration, the mass transfer force is low hence the number of molecules approaching the adsorbent surface is reduced and vice versa. However, the observed steady rate of adsorption above certain concentration suggest that there was an onset of desorption or complete occupancy of all the adsorption sites in the adsorbent. When all the available and activated adsorption sites are occupied, further diffusion of the adsorbate's molecules unto the adsorbent may not increase adsorption [1].

The equilibrium amount of EY dye adsorbed first decreases with increase in the mass of the adsorbent (i.e. adsorbent dosage) before increasing. This implies that, at low adsorbent dose, the adsorption capacity of the adsorbent was not fully explored but as the dosage increases, the adsorption sites and adsorption capacity increase (due to greater accessibility of surface binding sites and interactions). Consequently, the equilibrium amount of EY dye adsorbed increased with adsorbent dosage.



**Figure 1.** Variation of equilibrium amount of EY dye adsorbed (by wood sawdust) with concentration,  $C$  (mg/L), adsorbent dose (mg/g), time (minute) and temperature,  $T$  (K).

Several studies have revealed that increase in concentration can lead to increase in adsorption due to increase in the number of molecules diffusing to the adsorption site. However, the decrease in extent of adsorption is due to desorption of molecules from the adsorption site through thermal or other interferences. In this study, the adsorption of EY dye onto wood saw dust did not display significant changes at various adsorption dosages suggesting equilibration between forces of desorption and desorption [18].

The period of contact between the adsorbent and the adsorbate was also found to be a significant factor that affected the rate of removal of EY dye from aqueous solution. The observed trend (**Figure 1**) revealed a relatively steady rate of adsorption at first before a progressive decrease in the equilibrium amount of EY dye adsorbed (with increasing time). This observation concedes to the fact, that at first, the establishment of adsorption process (hence adsorption equilibrium) between the adsorbate and the adsorbent needed some time. However, once the equilibrium was established, further increase in time resulted in a significant decrease in the amount of EY dye

adsorbed, which can probably be attributed to complete occupation of all the adsorption sites or competition between forces of adsorption and desorption.

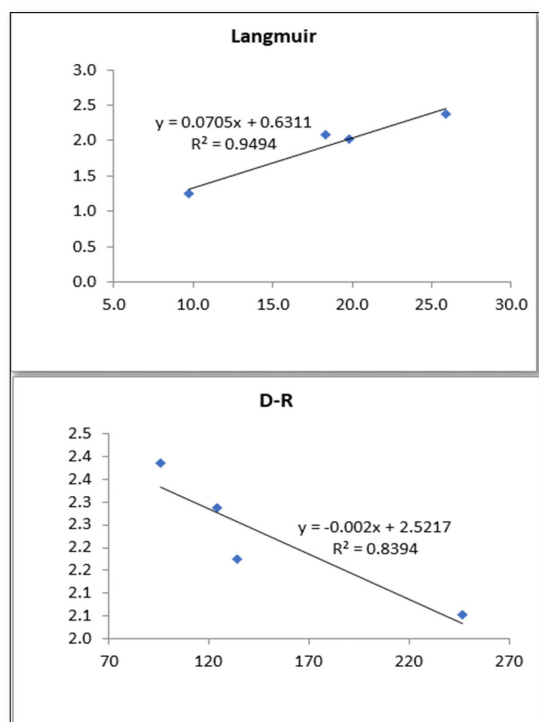
Temperature can affect adsorption of dye in two different ways. In the first case, increase in temperature can activate the adsorption sites and thereby overpopulate the vacant sites leading to increase in adsorption. This will define chemical adsorption mechanism. However, in physical adsorption mechanism, increase in temperature can depopulate the available adsorption sites (due to absence of chemical interaction between the adsorbate and the adsorbent), hence increase in temperature will lead to decrease in the amount of dye adsorbed as observed in this study. Therefore, a physical adsorption mechanism is proposed for the adsorption of EY dye unto wood sawdust. However, the curve seems to present a trend that suggests that the amount of EY dye adsorbed may probably increase if there is further increase in temperature. This trend is not uncommon because prior to chemical adsorption, physisorption must first set in. Therefore, the inception of chemisorptions after initial physisorption process cannot be overruled.

### Adsorption isotherm

The adsorption characteristics of EY dye onto wood saw dust was consistent with the Langmuir adsorption model which can be written according to equation 2 [17].

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

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/g),  $b$  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. From the Langmuir equation, a plot of  $\frac{C_e}{q_e}$  versus  $C_e$  should be linear if the Langmuir assumptions are valid. **Figure 2** presents the Langmuir isotherm for the adsorption of EY dye from aqueous solution onto wood saw dust. Langmuir adsorption parameters calculated from the slope and intercept of the plot were  $q_m = 14.29$  mg/g and  $b = 0.044$ . The calculated  $q_m$  value is comparable to those reported for other dyes. For example, [20] reported  $q_m$  value of 12.83 mg/g for the adsorption of crystal violet dye onto Moroccan pyrophyllite, Banerje and Chattopadhyaya [21] obtained  $q_m$  value of 3.39 mg/g for terazine dye adsorbed on activated carbon, obtained  $q_m$  values of 8.947 mg/g for methyl green adsorbed on regia resin.



**Figure 2.** Langmuir and Dubinin-Radushkevich (DR) isotherms for the adsorption of EY dye unto wood saw dust respectively.

The Langmuir separation factor ( $R_L$ ) defined in equation 3, is a useful index for differentiating between favorable or unfavorable adsorption [22].

$$R_L = \frac{1}{(1 + q_m C_0)} \quad (3)$$

Consequently, if  $R_L$  values lie between 0 and 1, the adsorption is favorable. When  $R_L = 0$  the adsorption is irreversible, when  $R_L$  value is equal to unity, a linear adsorption is favored and  $R_L$  greater than unity indicates unfavorable adsorption [23]. Calculated  $R_L$  values were 0.003088, 0.002561, 0.005933, 0.005933 and 0.005922 for EY dye concentrations of 41 to 51 mg/L respectively. Therefore, the adsorption of EY dye onto wood sawdust is favorable at all concentrations.

The Dubinin-Radushkevich isotherm [24] is significant in describing the adsorption mechanism of an adsorbate onto homogenous and heterogeneous surfaces. The model is expressed according to equation 8.

$$q_e = q_m e^{-\beta \epsilon^2} \quad (8)$$

Mathematical form of applying the above equation is to convert it to a linear model using logarithm function as shown below,

$$q_e = \ln q_m - \beta \epsilon^2 \quad (9)$$

where  $q_m$  is the Dubinin-Radushkevich (D-R) monolayer capacity (mmol/g), and  $\epsilon$  is the polanyi potential defined according to equation 20 while  $\beta$  is a constant that is related to the adsorption energy,  $E$  (equation 11)

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (10)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (11)$$

Adsorption energy less than 8 kJ/mol point toward physical adsorption mechanism while adsorption energy in the range of 8 to 16 kJ/mol indicates that the adsorption is governed by exchange mechanism. However, adsorption energy greater than 16 kJ/mol is consistent with the prevalence or domination of particle diffusion [25]. Calculated value of the adsorption energy (22.36 J/mol) for EY dye indicates that chemisorption mechanism is partly involved in the adsorption of EY dye and also confirms the existence of particle diffusion.

The Gibbs Helmholtz equation can be written as follows [26].

$$\Delta G^* = -2.303RT \log k_c \quad (12)$$

Evaluated values of standard free energy changes from both Langmuir (-13.67 kJ/mol) and Temkin (-16.97 kJ/mol) isotherm constants were comparable and led to the conclusion that the adsorption of EY dye onto wood saw

dust is spontaneous and support the mechanism of physiosorption.

In adsorption study, the equilibrium amounts adsorbed ( $q_e$ ) and equilibrium concentration ( $C_e$ ) are related to the equilibrium constant according to the following equation,

$$k_c = \frac{q_e}{C_e} \quad (13)$$

Also, from thermodynamics,

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

Therefore,

$$-2.303RT \log k_p = \Delta H^* - T\Delta S^* \quad (15)$$

$$-T \ln k_p = \Delta H^* - T\Delta S^* \quad (16)$$

$$\ln k_p = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (17)$$

Therefore, a plot of  $\ln k_p$  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.

The plot obtained (plot not shown) indicated  $R^2$  value of 0.965 while slope and intercept were -0.007 and -0.055 respectively. Estimated values of  $\Delta H^*$  and  $\Delta S^*$  were -0.0582 J and -0.4572 J indicating that the adsorption of EY dye onto the surface of wood saw dust is exothermic and occurs in the direction of increasing degree of orderliness.

## Kinetic Study

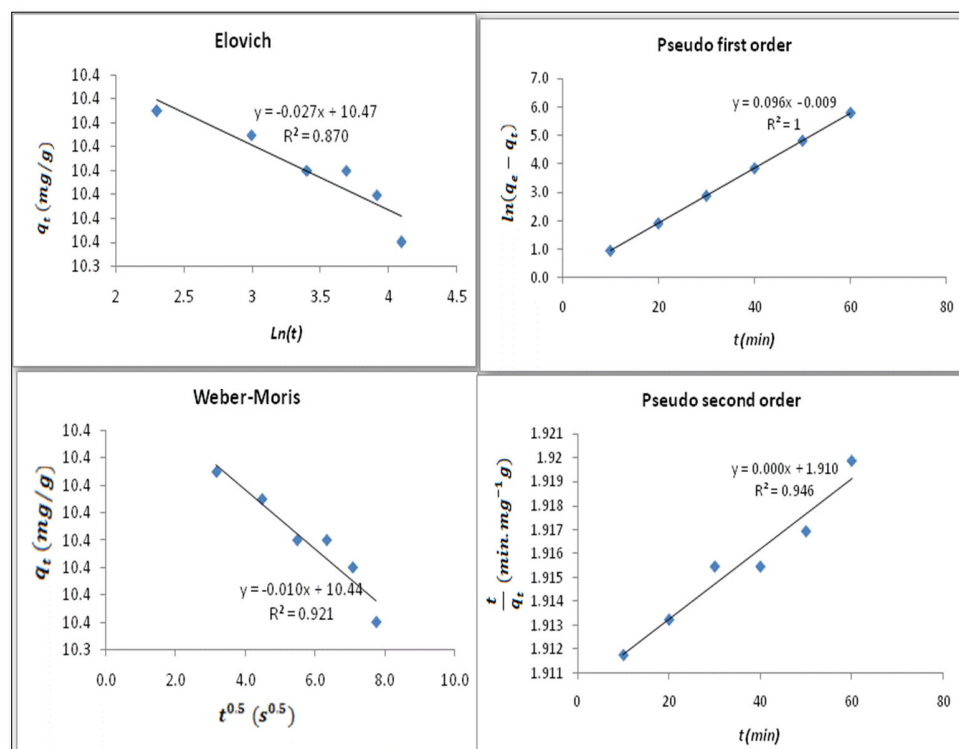
Pseudo first order and pseudo second order kinetics models can be expressed according to equations 18 and 19 respectively [27].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (18)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (19)$$

Agreement of the present adsorption data with pseudo first and second order kinetics was established through linear plots of  $\ln(q_e - q_t)$  versus  $t$  and  $\frac{t}{q_t}$  versus  $t$  for pseudo first and second order kinetics respectively (as shown in **Figure 3**). Calculated adsorption kinetic data (**Table 1**) are  $k_1 = 0.096/\text{m}$  and  $k_2 = 2.3 \times 10^5 / \text{m}$  respectively while  $\ln q_e$  (pseudo first order plot) and  $q_e$  (pseudo second order plots) were 0.009 and 6666.67 respectively. Perfect degree of fitness was obtained for the pseudo first order kinetics ( $R^2 = 1.000$ ) compared to  $R^2 = 0.9462$  obtained for pseudo second order kinetics. Consequently, adsorption of EY dye onto wood saw dust best fitted the pseudo first order kinetics than pseudo second order kinetics. Also, from the pseudo second order kinetic data, the initial adsorption rate (i.e.  $h$ ) and half adsorption time ( $t_{0.5}$ ) were calculated using the formula,

$$h = \frac{1}{k_2 q_e^2} \text{ and } t_{0.5} = \frac{1}{k_2 q_e} \text{ respectively [28].}$$



**Figure 3.** Elovich, Weber-Morris, pseudo first order and pseudo second order kinetic plots for the adsorption of EY dye on wood sawdust.

The Elovich equation is a kinetic model that is most suitable for explaining chemisorptions and for adsorption process that does not approach equilibrium at ease due to low surface coverage. Expression for the Elovich equation [29] can be written as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{k_{Des}} \ln t \quad (20)$$

where  $\alpha$  is the initial adsorption rate in mg/g/min,  $k_{Des}$  is desorption constant and is related to the activation energy of a chemisorption process and the extent of surface coverage. The adsorption of EY dye on the surface of wood saw dust fitted the Elovich adsorption model ( $R^2=0.870$ ) as shown in a linear plot (**Figure 3**) of  $q_t$  versus  $t$ . Therefore, the mechanism of adsorption of EY dye partly involves chemisorptions. Estimated  $\beta$  value was 370.37 while  $\alpha$  was 58.95 mg/g/min. The Weber-Morris adsorption model (expressed as equation 21) is the most useful kinetic model for investigating intra particle diffusion [30].

$$q_t = B + K_{id}\sqrt{t} \quad (21)$$

Kid is the intra particle diffusion constant (mg (g. min<sup>0.5</sup>)) while B is the initial adsorption (mg/g). When B is zero,

intra particle diffusion is the rate controlling step. The Weber-Morris plot for the adsorption of EY dye (Figure 3) indicated a non-zero intercept (i.e. B = 10.44 mg/g) which implies that other mechanism also contributes to the adsorption of EY dye on wood sawdust (in addition to intra particle diffusion). Estimated kid value was 0.010 (mg (g. min<sup>0.5</sup>)).

### FTIR study

FTIR spectra of EY dye and that of the wood saw dust before and after adsorption were analyzed (spectra not shown). Frequencies and intensities of IR adsorption deduced from the FTIR of wood saw dust before and after adsorption of EY dye (spectra not shown) are presented in **Table 1**. The FTIR spectrum of EY dye indicated the presence of OH stretch at 3335 cm<sup>-1</sup> (42.76 %), C=O stretch at 2117 (95.72 %), C=C stretch at 1640 (64.87 %) and C-N stretch at 1242 (88.535 %).

From **Table 1**, it can be deduced that the wood saw dust possess several functional groups that aided the adsorption of EY dye.

**Table 1.** Wave number and intensity of IR absorption by wood saw dust before and after adsorption of EY dye.

| Wood saw dust                   |           | Wood saw dust after adsorption  |           | Assignment    |
|---------------------------------|-----------|---------------------------------|-----------|---------------|
| Wave number (cm <sup>-1</sup> ) | Intensity | Wave number (cm <sup>-1</sup> ) | Intensity |               |
| 3320                            | 80.64     | 3339                            | 91.10     | OH stretch    |
| 2988                            | 93.47     | 2895                            | 94.03     | C-H stretch   |
|                                 |           | 2218                            | 97.31     | C=Catretch    |
| 2106                            | 96.13     | 2117                            | 97.10     | C=C stretch   |
|                                 |           | 2009                            | 97.61     | C=C=N stretch |
| 1990                            | 97.40     |                                 |           | C=C=C stretch |
| 1961                            | 96.71     |                                 |           | C=C=C stretch |
| 1905                            | 96.73     |                                 |           | C=C=C stretch |
| 1737                            | 93.71     | 1737                            | 94.40     | C=O stretch   |
| 1655                            | 93.18     | 1640                            | 93.41     | C=O stretch   |
| 1596                            | 91.89     | 1596                            | 92.07     | C=N stretch   |
| 1503                            | 92.92     | 1503                            | 93.19     | C=O stretch   |
| 1482                            | 91.35     | 1482                            | 92.59     | C=C stretch   |
| 1424                            | 90.47     | 1424                            | 90.70     | OH bending    |
| 1369                            | 90.65     | 1369                            | 91.26     | S=O stretch   |
| 1324                            | 89.95     | 1324                            | 90.28     | S=O stretch   |
| 1286                            | 87.80     |                                 |           | C-O stretch   |
|                                 |           | 1235                            | 88.56     | C-O stretch   |
| 1160                            | 87.68     | 1160                            | 88.41     | C-O stretch   |
| 1108                            | 81.75     | 1108                            | 82.22     | C-O stretch   |
| 1033                            | 71.09     | 1033                            | 72.96     | C-OH stretch  |
|                                 |           | 899                             | 88.23     | C-H bend      |
| 836                             | 88.99     | 836                             | 89.94     | C-Cl stretch  |
| 672                             | 81.72     |                                 |           | C-Br stretch  |

After adsorption of ET dye, some functional groups were missing in the spectrum including C-Br stretch, C-O stretch at 1286 cm<sup>-1</sup> and C=C stretches at 1990, 1961 and 1905 cm<sup>-1</sup> respectively. The missing functional groups might have been used for the formation of new bonds [31]. However, new functional groups formed were C=C stretch at 2218 cm<sup>-1</sup>, C=C=N stretch at 2009 cm<sup>-1</sup> and C-H bend at 899 cm<sup>-1</sup>. The OH stretch at 3320 was shifted to 3339 cm<sup>-1</sup> after adsorption of EY dye other included C-H stretch at 2988 shifted to 2895 cm<sup>-1</sup>, C=C stretch at 2106 shifted to 2117 cm<sup>-1</sup> and the C=O stretch shifted from 1655 to 1640 cm<sup>-1</sup>. The shift in frequencies of adsorption indicate that there is interaction between the adsorbent and the adsorbate [15, 16]. Functional groups that witness shift in intensity of adsorption (but not frequency) were C-Cl stretch at 836 cm<sup>-1</sup>, C-OH stretch at 1033 cm<sup>-1</sup>, C-O stretches at 1108 and 1160 cm<sup>-1</sup> respectively, S=O stretches at 1324 and 1369 cm<sup>-1</sup> respectively, OH bend at 1424 cm<sup>-1</sup>, C=C stretch at 1482 cm<sup>-1</sup>, C=O stretch at 1503 cm<sup>-1</sup>, C=N stretch at 1596 cm<sup>-1</sup> and C=O stretch at 1737 cm<sup>-1</sup>. Bathochromic and hypsochromic shifts in intensity confirms that the absorption strength of the adsorbent has been altered by the interaction between the dye and the adsorbent [17].

## COMPUTATIONAL CHEMISTRY STUDY

### Semiempirical parameters

Semiempirical parameters calculated for EY dye were E<sub>HOMO</sub> (-7.787021 eV), E<sub>LUMO</sub> (-1.107504 eV), total energy (-193.1411 eV), binding energy (-4197.2663 eV), isolated atomic energy (-117000.6061 eV), electronic energy (-902517.1837 eV), core interaction (781319.3113 eV) and heat of formation (-10.3993 kCal). The calculated semiempirical parameters are not at variance with those reported for good adsorbent for other dyes. For example [11] reported -8.4071 and -1.6856 eV as values of E<sub>HOMO</sub> and E<sub>LUMO</sub> for methylene blue and malachite green respectively (that were excellently adsorbed on neem leaves). However, their calculated electronic energies were -528,742.2598 and -885,289.2176 eV respectively (which is significantly less than that of EY dye). Other parameters were also relatively comparable [11]. In EY dye, 29%, 25%, 22% and 23% of the HOMO electron population resides in the S, P<sub>x</sub>, P<sub>y</sub> and P<sub>z</sub> orbitals. Adsorption is a surface phenomenon that involves charge or electron transfer or sharing. According to the frontier molecular orbital theory, the formation of adsorption bond (i.e. van der Waal for physical adsorption or chemical bond for chemisorption mechanism) involves interaction between the HOMO and LUMO molecular orbitals and the extent and readiness of the transfer depends on the energy gap [32]. E<sub>HOMO</sub> is an index that reflects tendency toward adsorption while E<sub>LUMO</sub> indicates tendency toward desorption [33,34]. Calculated energy gap is relatively low and suggest ease of adsorption governed by the proposed physical adsorption [34] **Fukui function**.

A neutral atom having N number of atoms can align in two different ways, either by losing or gaining electron. Such attacks lead to either nucleophilic or electrophilic attack respectively. Losing of one electron leaves the system as N-1 while gaining of one electron changes it to a N+1 system. Apart from variation of electron, there is also variation of charge since donation or acceptance of electron also affects the charge of the molecule. Adsorption occurs via the transfer of charge from charged adsorbate to charge adsorbent surface (physical adsorption) or through the transfer of electron from the adsorbate to the adsorbent and vice versa (chemical adsorption). The Fukui function originates from the concept of considering the reactivity of a molecule in terms of the individual atom as it gains or loses electron. The finite difference approximation defines the three different types of Fukui function [33-35] as follows:

$$f_x^+ = q_{N+1} - q_N \quad (22)$$

$$f_x^- = q_N - q_{N-1} \quad (23)$$

$$f_x^0 = \frac{[(q_{N+1}) - (q_{N-1})]}{2} \quad (24)$$

In analyzing the results obtained from Fukui function calculations, it is necessary to consider the most favorable behavior that will favor each atom on the molecule. The difference between nucleophile and electrophilic Fukui functions (equation 25) is an index that allows the prediction of the location where nucleophilic or electrophilic Fukui function resides [32,36-39]:

$$\Delta f_x = f_x^+ - f_x^- \quad (25)$$

Consequently, if  $\Delta f_x > 0$ , the site is favourable to nucleophilic attack but if  $\Delta f_x < 0$ , the site is favourable to electrophilic attack. Calculated values of  $f_x^+$ ,  $f_x^-$ ,  $f_x^0$  and  $\Delta f_x$  for both Ab initio and DFT levels are recorded in **Table 2**. The results expose various sites with positive values of  $\Delta f_x$  for both Ab initio and DFT calculations. However, highest values of  $f_x^+$  for ab initio (0.0132) and DFT (0.0099) were obtained for O (26) which indicate that nucleophilic attack is likely located in this site [32, 40-43]. The Mayer bond order for this bond is also less than unity. Similarly, both ab initio and DFT predictions for the site for electrophilic attack did not prefer any other side but C(15) which has the highest positive values of  $f_x^-$  and highest negative value of  $\Delta f_x$  for both ab initio and DFT levels of theory. All the valence electron in C (15) are bonded suggesting that the attack will certainly involves a bond or functional group associated with C (15). Also, the total nuclear charge for O (26), Muliken atomic charge, Mayer total valence and Mayer bonded valence (Table 2) are 8.0, -0.617, 1.9961 and 1.9961 respectively. This also suggests that nucleophilic attack will preferably involves a bond or functional group and not the atom alone [44-46].

**Table 2.** Ab initio Fukui function for adsorption of EY dye.

| Atom/No | Ab Initio |         |                 | DFT     |         |                 |
|---------|-----------|---------|-----------------|---------|---------|-----------------|
|         | $f_x^+$   | $f_x^-$ | $f_x^+ - f_x^-$ | $f_x^+$ | $f_x^-$ | $f_x^+ - f_x^-$ |
| 1 C     | -0.0009   | -0.0073 | 0.0064          | -0.0013 | -0.0046 | 0.0033          |
| 2 C     | -0.0005   | -0.0111 | 0.0106          | -0.0054 | -0.0248 | 0.0194          |
| 2 C     | 0.0027    | -0.0116 | 0.0143          | 0.0033  | -0.0058 | 0.0091          |
| 4 C     | -0.0031   | -0.0150 | 0.0119          | -0.0064 | -0.0426 | 0.0362          |
| 5 C     | 0.0034    | -0.0102 | 0.0136          | 0.0038  | 0.0016  | 0.0022          |
| 6 C     | -0.0019   | -0.0232 | 0.0213          | -0.0037 | -0.0511 | 0.0474          |
| 7 C     | 0.0015    | -0.0078 | 0.0093          | 0.0023  | -0.0194 | 0.0217          |
| 8 C     | 0.0008    | -0.0204 | 0.0212          | -0.0024 | -0.0530 | 0.0506          |
| 9 C     | -0.0047   | -0.0114 | 0.0067          | -0.0014 | -0.0067 | 0.0053          |
| 10 O    | 0.0007    | -0.0144 | 0.0151          | 0.0010  | -0.0176 | 0.0186          |
| 11C     | -0.0022   | -0.0128 | 0.0106          | -0.0044 | -0.0049 | 0.0005          |
| 12 C    | 0.0033    | -0.0097 | 0.013           | 0.0026  | -0.0284 | 0.031           |
| 13 C    | -0.0011   | -0.0027 | 0.0016          | 0.0013  | -0.0117 | 0.013           |
| 14 C    | 0.0046    | -0.0151 | 0.0197          | 0.0021  | -0.0205 | 0.0226          |
| 15 C    | -0.0009   | 0.0066  | -0.0075         | -0.0010 | 0.0213  | -0.0223         |
| 16 C    | -0.0003   | 0.0043  | -0.0046         | -0.0018 | 0.0029  | -0.0047         |
| 17 C    | -0.0035   | -0.0068 | 0.0033          | -0.0098 | -0.0154 | 0.0056          |
| 18 C    | -0.0033   | -0.0066 | 0.0033          | -0.0077 | -0.0171 | 0.0094          |
| 19 C    | -0.0005   | -0.0039 | 0.0034          | 0.0003  | -0.0074 | 0.0077          |
| 20 C    | 0.0014    | 0.0008  | 0.0006          | 0.0056  | 0.0001  | 0.0055          |
| 21 Br   | -0.0147   | -0.1215 | 0.1068          | -0.0109 | -0.1008 | 0.0899          |
| 22 Br   | -0.0242   | -0.1043 | 0.0801          | -0.0183 | -0.0837 | 0.0654          |
| 23 Br   | -0.0061   | -0.0611 | 0.0550          | -0.0091 | -0.0434 | 0.0343          |
| 24 Br   | -0.0162   | -0.0977 | 0.0815          | -0.0119 | -0.0775 | 0.0656          |
| 25 O    | -0.0161   | -0.0760 | 0.0599          | -0.0172 | -0.0900 | 0.0728          |
| 26 O    | 0.0132    | -0.0572 | 0.0704          | 0.0099  | -0.0694 | 0.0793          |
| 27 Na   | -0.5207   | -0.0876 | -0.4331         | -0.5237 | -0.0806 | -0.4431         |
| 28 C    | -0.0051   | 0.0010  | -0.0061         | -0.0080 | -0.0001 | -0.0079         |
| 29 O    | 0.0030    | -0.0035 | 0.0065          | 0.0016  | -0.0061 | 0.0077          |
| 30 O    | 0.0058    | -0.0223 | 0.0281          | 0.0035  | -0.0242 | 0.0277          |
| 31 Na   | -0.3660   | -0.0525 | -0.3135         | -0.3687 | -0.0480 | -0.3207         |

## CONCLUSION

The results and findings of this study revealed that wood saw dust from *Musanga cecropioides* is effective in the removal of EY due from aqueous solution. The removal efficiency of the wood saw dust depends on temperature, adsorbent dosage, concentration of the dye and period of contact. The adsorption behavior of the studied system conforms with some kinetic and isotherms models. The adsorption of the dye is spontaneous and exothermic. Quantum chemistry provides good information on the atoms/functional groups associated with the adsorption of the dye. Missing functional groups and the formation of new bonds also confirmed that the dye molecules are removed from the aqueous solution through adsorption.

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## REFERENCES

1. EPA (2018) Drinking water standard and health advisory table. Office of water, US, Environmental Protection Agency, Washington.
2. Odoemelam SA, Eddy NO (2009) Studies on the use of oyster, snail and periwinkle shells as adsorbents for the removal of Pb<sup>2+</sup>. J Chem 6: 213-222.
3. Sciban M, Radetic B, Kevresan Z, Klasnja M (2007) Adsorption of heavy metals from electroplating wastewater by wood sawdust. Resour Technol 98: 402-409.
4. Meena AK, Kadirvelu K, Mishra GK, Rajagopal C, Nagar PN (2008) Adsorptive removal of heavy metals from aqueous solution by treated sawdust *Acacia Arabica*. J Hazard Mater 150: 604-611.
5. Kant R (2012) Textile dyeing industry, an environmental hazard. Nat Sci 22: 26
6. Hassaan MA, ElNemr A (2017) Health and environmental impacts of dyes: Mini review. Am J Environ Sci Eng 13: 64-67.
7. Sdiri A, Higashi T (2012) Simultaneous removal of heavy metals from aqueous solution by natural limestones. Appl Water Sci 3: 29-39.
8. Adhnikan S, Manda S, Sarkar S, Kim D, Madras G (2017) Kinetics and mechanism of dye adsorption on WO<sub>3</sub> nanoparticles. Appl Surf Sci 420: 472-482.
9. Odiongenyi AO (2019) Removal of ethyl violet dye from aqueous solution by graphite dust and nano graphene oxide synthesized from graphite dust. Commun Phys Sci 4: 103-109.
10. Odiongenyi AO, Afangide UN (2019) Adsorption and thermodynamic studies on the removal of congo red dye from aqueous solution by alumina and nano-alumina. Commu Phys Sci 4: 1-7.
11. Bharathi KS, Ramesh ST (2013) Removal of dyes using agricultural waste as low-cost adsorbent: A review. Appl Water Sci 34: 773-790.
12. Odoemelam SA, Emeh NU, Eddy NO (2018) Experimental and computational chemistry studies on the removal of methylene blue and malachite green dyes from aqueous solution by neem *Azadirachta indica* leaves. J Taibah Univ Sci 123: 255-265.
13. Badu M, Boateng I, Boadi NO (2014) Evaluation of adsorption of textile dyes by wood sawdust. Res J Phy Appl Sci 31: 006-014.
14. Rahimi M (2007) Use of beech wood sawdust for adsorption of textile dyes. PJBS 102: 287-293.
15. Pinto T, Bezerra CWB, Silva DS, Filho ECD, Viera AP, et al. (2016) Sawdust derivatives for environmental application: Chemistry, functionalization and removal of textile dye from aqueous solution. An Acad Bras Cienc 883.
16. Eddy NO, Ekwumemgbo PA, Odoemelam SA (2008) Inhibition of the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> by 5-amino-1-cyclopropyl-7-[(3R, 5S) 3, 5-dimethylpiperazin-1-yl]-6, 8-difluoro-4-oxo-uinoline-3-carboxylic acid (ACPDQC). Int J Phys Sci 3: 1-6.
17. Eddy NO, Ameh P, Gimba CE, Ebenso EE (2011) GCMS studies on *Anogeissus leocarpus* (AL) gum and their corrosion inhibition potential for mild steel in 0.1 M HCl. Int J Electrochem Sci 6: 5815-5829.
18. Eddy NO, Ameh P, Gimba EC, Ebenso EE (2012) Chemical information from GCMS of *Ficus platyphylla* gum and its corrosion inhibition potential for mild steel in 0.1 M HCl. Int J Electrochem Sci 7: 5677-569.
19. Okwunodulu FU, Eddy NO (2014) Equilibrium and thermodynamic consideration of Cd<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> removal from aqueous solution onto treated and untreated *Cola nitida* waste biomass. Int J Sci Res 2: 567-569.

20. Nagy B, Manzatu C, Maicananu A, Indolean C, Lucian B, et al. (2017) Linear and nonlinear regression analysis for heavy metal removal using *Agaricus bisporus* macrofungus. *Arab J Chem* 10: S3569-S3579.
21. Miyah Y, Labrichi A, Idrissi M, Boujraf S, Taouda H, et al. (2017) Assessment of adsorption kinetics for removal potential of crystal violet dye from aqueous solution using Moroccan pyrophyllite. *J Assoc Arab Univ Basic Appl Sci* 23: 20-28.
22. Nethaji S, Sivasamy A, Mandal AB (2013) Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass. *Int J Environ Sci Tech* 10: 231-242.
23. Padmavathy KS, Madhu G, Haseena PV (2016) A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium CRVI from wastewater by magnetite nanoparticle. *International Conference on Emerging trends in Engineering Science ICETEST-2015* 24: 585-594.
24. Elsagh A, Moradi O, Fakhri A, Najafi F, Alizadeh R, et al. (2017) Evaluation of the potential cationic dye removal using adsorption by graphene and carbon nanotubes as adsorbents surfaces. *Arab J Chem* 10: S2862-S2869.
25. Bulut E, Ozacar M, Sengil IA (2008) Adsorption of malachite green onto nemtolite: Equilibrium and kinetic studies and process design. *Micropor Mesopor Mat* 115: 234-246.
26. Keskin O (2006) Isotherm models for predicting the dye adsorption potential of coon tail *Ceratophyllum demersum* and water milfoil *Myriophyllum spicatum*. *Keskin/Adsorption Science and Technology* 24: 321
27. Chiban M, Carja G, Lehtu G, Sinan F (2016) Equilibrium and thermodynamic studies for the removal of AsV ions from aqueous solution using dried plants as adsorbents. *Arab J Chem* 9: S988-S999.
28. Zhao D, Zhang W, Chen C, Wang X (2013) Adsorption of methyl orange dye onto multiwalled carbon nanotubes. *Procedia Environ Sci* 18: 890-895.
29. Santhi T, Manonmani S, Vasantha VS, Chang TT (2016) A new alternative adsorbent for the removal of cationic dyes from aqueous solution. *Arab J Chem* 9: S466-S474.
30. Tan KL, Hameed BH (2017) Insight into the adsorption kinetics model for the removal of contaminants from aqueous solutions. *J Taiwan Inst Chem Eng* 15: 1-24.
31. Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solution. *JSED* 89: 31-59.
32. Eddy NO, Odiongny AO (2010) Corrosion inhibition and adsorption properties of ethanol extract of *Heinsiacrinata* on mild steel in H<sub>2</sub>SO<sub>4</sub>. *Pigm Resin Technol* 385: 288-295.
33. Eddy NO, Essien NB (2017) Computational chemistry study of toxicity of some m-tolyl acetate derivatives insecticides and molecular design of structurally related products. *In Silico Pharmacol* 51: 14.
34. Eddy NO, Ita BI (2011) Experimental and theoretical studies on the inhibition potentials of some derivatives of cyclopenta-1, 3-diene. *Int J Quantum Chem* 11114: 3456-3473.
35. Eddy NO, Ita BI (2011) Theoretical and experimental studies on the inhibition potentials of aromatic oxaldehydes for the corrosion of mild steel in 0.1 M HCl. *J Mol Model* 17: 633-647.
36. Eddy NO, Awe FE (2018) Experimental and quantum chemical studies on ethanol extract of *Phyllanthus amarus* EEPA as a green corrosion inhibitor for aluminium in 1 M HCl. *Port Electrochimica Acta* 364: 231-247.
37. Eddy NO, Ameh PO, Essien NB (2018) Experimental and computational Chemistry studies on the inhibition of aluminium and mild steel in 0.1 M HCl by 3-nitrobenzoic acid. *J Taibah Univ Sci* 12: 545-556.
38. Eddy NO (2009) Modeling of the adsorption of Zn<sup>2+</sup> from aqueous solution by modified and unmodified *Cyperus esculentus* shell. *Elec J Env Agricult Food Chem* 8: 1177-1185.
39. Eddy NO, Ita BI, Dodo SN, Paul ED (2002) Inhibitive and adsorption properties of ethanol extract of *Hibiscus sabdariffa* calyx for the corrosion of mild steel in 0.1 M HCl. *Green Chem Lett Rev* 5: 43-53.
40. Eddy NO, Ekwumengbo PA, Odoemelam SA (2008) Inhibition of the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> by 5-amino-1-cyclopropyl-7-[(3R, 5S) 3, 5-dimethylpiperazin-1-yl]-6, 8-difluoro-4-oxo-uinoline-3-carboxylic acid (ACPDQC). *Int J Phys Sci* 3: 1-6.
41. Banerjee S, Chattopadhyaya MC (2017) Adsorption characteristics for the removal.

42. of a toxic dye, tartrazine from aqueous solutions by a low-cost agricultural by-product. *Arab J Chem* 10: S1629-S1628.
43. Bridgeman AJ, Cavglasso G, Ireland LR, Rothery J (2001) The Mayer bond order as a tool in inorganic Chemistry. *J Chem Soc. Dalton Transaction* 14: 2095-2108
44. Pathania D, Sharma S, Singh P (2017) Removal of methylene blue by adsorption onto activated carbon developed from *Ficus caricabast* . *Arab J Chem* 10: S1445-S1451.
45. Stevenson J, Sorenson B, Subtamaniam VH, Raiford J, Khlyabich PP, et al. (2017) Mayer bond order as a metric of complexation effectiveness in lead halide perovskite solutions. *Chem Mater* 29: 2435-2444.
46. Eddy NO, Momoh-Yahaya H, Oguzie EE (2015) Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. *J Adv Res* 6: 203-216.
47. Ameh PO, Eddy NO (2018) Theoretical and Experimental Investigations of the Corrosion Inhibition Action of *Piliostigma Thonningii* Extract on Mild Steel in Acidic Medium. *Commun Phys Sci* 3: 27-42.
48. Amin MT, Alazba AA, Shafiq M (2015) Adsorptive removal of reactive black 5 from wastewater using bentonite clay: Isotherm, kinetics and thermodynamics. *Sustainability* 7: 15302-15318.