INTRODUCTION:

Dyes are organic compounds that represent an important group of pollutants. They are used in various areas, such as the textile, plastics, rubber, leather, cosmetics and paper industries, with highly toxic components and serious environmental impacts. It is believed that the dyeing industry is responsible for releasing 100 tons of dyes per year into the environment, contaminating rivers and springs (Ramaraju et al. 2014 and Vieira et al. 2012). Of these dyestuffs, 5–10% is lost in industrial effluents, and consequently, wastewater treatment is one of the biggest problems of today (Ebrahimim et al., 2013). Once the dyes are exposed to water, they are difficult to remove, as they are of synthetic origin and have a very complex molecular structure, with stability designed to withstand degradation by light, chemical, biological and other factors. This makes them very difficult to degrade (Attallah et al., 2013).

Synthetic dyes are resistant to natural degradation and pose numerous environmentally-oriented drawbacks when released into natural water bodies. Rhodamine B dye is a basic dye used extensively in dyeing of various products including cotton, silk, paper, bamboo, wood, straw and leather (Shakir et al. 2010). Basic dyes are also considered as cationic dyes because they form a colored cationic salt when dissolved in water (Ghaly et al. 2014). Cationic dyes are considered more toxic than the anionic dyes, because they can easily interact with the negatively charged surface of cell membranes, and can enter into the cells (Orfanos et al. 2017). Therefore, the treatment of dye-contaminated effluents is of significant environmental and commercial importance (Akar, 2009).

However, Adsorption is one of the most efficient and an attractive method for removing pollutants from wastewater because of it is easy process control, low cost and minimal energy requirements (Yang et al., 2014). Various adsorbents, such as activated bituminous coal (El-Qada et al., 2006), clay (Gurses et al., 2006), leaf powder (Bhattacharyya & Sharma 2005), activated carbon from oil palm wood (Ahmad et al., 2007) etc. have been studied for adsorption of dye from aqueous solutions. Compared to activated carbon, biochar may be utilized as a potentially low-cost and effective adsorbent. The production of activated carbon needs higher temperature and additional activation process. In contrast, production of biochar is cheaper with lower energy requirements (Tan et al., 2015).

Hence, Biochar is generally produced by thermochemical decomposition of biomass (organic matter of living organisms (plants and animal) and their residues) at temperatures of 200–900 °C (Lehmann and Joseph 2009). Traditionally, biochar was produced in earthen charcoal kilns where pyrolysis, gasification, and combustion processes were carried out in parallel (Brown 2009; Duku et al., 2011). Traditional charcoal-making technologies emit considerable amount of smoke, soot and combustible gases to the environment and are energy inefficient (Brown 2009). The biochar, has proven to possess excellent adsorption capabilities to remove impurities from both water and soil (Glaser et al., 2000). A few studies have been reported on removal of dyes on using biochar as adsorbent. Biochar, the carbonaceous by-product obtained by pyrolysis of biomass in absence of oxygen, was recently identified as a ‘supersorbent’ for wide variety of organic and inorganic contaminates due to its porous nature, surface area and abundant functional groups (Qu et al. 2009; Mohan et al. 2014).
Municipal solid waste derived biochar has been well studied for its ability to remove heavy metals, metalloids and organics (Agrafioti et al., 2014; Jin et al., 2014). Biochar has been examined to treat landfill leachate, as permeable reactive membranes and as landfill capping and results have shown promising outcomes. Several other studies have also shown its efficacy to retain nutrients in soil for plant uptake enabling the plants to tap into bioavailable nutrients over longer periods of time (Milla et al., 2013; Liu et al., 2017). Biochar adsorbents have been increasingly concerned due to their widely available biomass material, carbon-negative function, enriched surface functional groups and high-adsorption capacity. And as a relatively simple, inexpensive and robust thermochemical technology, pyrolysis is widely used for transforming biomass into biochar under oxygen limited conditions (Klinghoffer, & Castaldi 2013).

The major goal of this research is to look into the possibility of using such a mixture of waste materials as low-cost source of biochar. Following the charring procedure, the Modified Biochar was chemically activated using KOH as an activating agent and another portion of Biochar left unmodified. The two adsorbents were utilized to remove Rhodamine B dye from synthetic aqueous solutions.

MATERIALS AND METHODS

RAW MATERIALS & PRETREATMENT

Municipal Solid Waste (MSW) was randomly collected from different household wastes. The collected MSW composed mainly of varying quantities of the following materials; Orange peel, Banana peel, Pineapple peel, water melon shell, potato peel, fish bones, animal bones, bread crumbs, chicken droppings and paper scraps. The collected MSW was well-mixed, thoroughly washed under running tap water followed by washing using distilled water to remove any physically adhered materials. Subsequently, the washed sample was oven dried at 110 °C for 24 h.

PREPARATION OF BIOCHAR

The MSW was transferred into a silica crucible and heated in an air-tight furnace (Vecster Ltd, Furnace Division Ecrotherm) operated at 450 °C for 5 minutes. The Obtained biochar were crushed and screened into a particle size of 250 μm and carefully transferred to an airtight container and kept for further treatment.

MODIFICATION ON BIOCHAR

To produce a modified Biochar, 18 g of Biochar were mixed with 500 ml of 2M (KOH) solution and stirred using magnetic stirrer for about 4 hours. The suspension was then filtered and washed with distill water for several times until the pH of the filtrate became nearly to the neutral, the obtained Biochar was dried overnight in an oven at 105 °C, kept in an air tight container for subsequent use, and labeled as Basic Modified Biochar (BMB). While another portion of biochar obtained after pyrolysis was transferred without any modification stored in another separate air tight container & labeled Non Modified Biochar (NMB).

CHARACTERIZATION OF MODIFIED BIOCHAR

The surface morphology and surface characteristics were obtained using a (PHENOM Prox SEM 500-07334) on different magnification. Where the surface functional groups were obtained using VERTEX 70/70V (Agilent Technologies) spectrometer. The value of the pH required to give zero net surface charge, point of zero charge (pHZc) of the Biochar was determined by the pH drift test method described by (Rivera-Utrilla et al., 2001).

PREPARATION OF ADSORBATE

Rhodamine B Dye (C18H13N2O2Cl; with a maximum absorption wavelength 556 nm), analytical grade, which is a cationic dye, were used to investigate the adsorption capability of the prepared Biochar was purchased from (Revertex Chemicals Limited, Abuja Nigeria) without any pretreatment. It is chemical structure is shown in figure 3. A Stock solution of 1000 mg/L Rhodamine-B (RhB) was prepared by dissolving 1g of RhB in 1000 cm3 of distilled water. Hence, other working solutions of lower concentrations were prepared by serial dilution. However, Absorbance measurements were carried out on a T60V PG instrument (United Kingdom).

Figure 1 Chemical Structure of Rhodamine B

BATCH ADSORPTION EXPERIMENT

A series of experiments were carried out in 250 cm3 Erlenmayer flask, containing 50 ml of Rhodamine B dye solution. A weighted amount of modified Biochar was added to the dye solution, with variable parameters (Contact time 20-160 minutes), (Adsorbent Dosage 0.1- 0.5 g), (Initial Concentration 10- 50mg/L) and (Temperature 25° - 60°) used in the study, while others were fixed. The mixture of modified Biochar (Adsorbent) & Rhodamine B dye) solution (Adsorbate) in a conical flask was properly sealed and agitated in a temperature controlled water bath shaker (Flask Shaker Manufactured by Barloworld Scientific limited with a model of ST1505A Uk) operated at 200 rpm. The samples were taken at predetermined intervals, centrifuged and the supernatant were separated from the adsorbent by filtration using Whatman No. 41 filter paper & analyzed for unabsorbed dye using T60 PG instrument (United Kingdom) operated at the maximum absorption wavelength of Rhodamine B Dye (556nm). The removal efficiency of RhB and the amount of dye adsorbed on per weight of modified Biochar, qt (mg g−1) can be calculated using the following equations:

Removal Efficiency (%) = \( \frac{(C_o - C_t)}{C_o} \times 100\% \) (1)

Adsorption Amount (mg g−1) = \( \frac{(C_o - C_t)}{C_o} \times \frac{V}{m} \) (2)

Where, Co (mg g−1) is the initial Rhodamine B concentration (mg/L); Ct (mg/L) is the Rhodamine B concentration at time t (min); And V (L) is the volume of Rhodamine B solution; and m (g) is the weight of Biochar (adsorbent) used (Bordoloi et al., 2017).

KINETICS OF RHODAMINE B ADSORPTION ONTO BIOCHAR

To investigate the mechanism and characteristics of the adsorption of Rhodamine B dye onto Biochar, two kinetics model the pseudo first-order kinetics model of Lagergren, Ho and McKay pseudo second-order were used to test the experimental data. The linear form of the pseudo first-order rate expression is given as;
\[ \ln(qe - qt) = lnqe - k1t \]  
(3)

Where, \( k1 \) (min\(^{-1}\)) is the rate constant of the pseudo first order adsorption. The pseudo second-order kinetic model is expressed by the following:

\[ \frac{1}{qe} = \frac{1}{k2qe2} + \frac{1}{qe} \times t \]  
(4)

Where, \( k2 \) (g/(mg min\(^{-1}\})) is the rate constant of the pseudo second-order model. The validity of the two kinetic models can be checked by their linearized plots. The correlation coefficient \((R^2)\) was used to compare the applicability of different kinetic models in fitting the experimental data. Table 1 shows the corresponding parameters of the two kinetic models under different conditions. Based on \( R^2 \), the pseudo second order kinetic model is well fitted to the experimental data. Furthermore, the \( qe \) calculated from the pseudo second order kinetic model is close to the experimental data.

**ADSORPTION ISOTHERMS**

Adsorption isotherms provide crucial information that reveals the equilibrium relationship between the adsorbate concentration in the liquid phase and the solid phase at a constant temperature. Two isotherm models, Langmuir, and Freundlich, equations, were chosen to describe the equilibrium characteristics in this study. The linear form of Langmuir isotherm is given by the following Eq. (5):

\[ \frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m} \]  
(5)

Where \( qe \) and \( qm \) are the corresponding adsorption capacity and maximum adsorption capacity (mg L\(^{-1}\)), respectively. \( C_e \) is the concentration of the RB solution at equilibrium (mg L\(^{-1}\)), and \( K_L \) is the Langmuir constant (L mg\(^{-1}\)).

The Freundlich isotherm is described by the following Eq. (6):

\[ \log qe = \log KF + \frac{1}{n} \log C_e \]  
(6)

Where, \( KF \) (L g\(^{-1}\)) and \( n \) are the Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively.

**ADSORPTION THERMODYNAMICS**

The effect of temperature is paramount and a major factor influencing the adsorption, the temperature was monitored in the range of (25\(^0\)' - 60\(^0\)'). The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations,

\[ \Delta G^\circ = -RT \ln Kc \]  
(7)

Where \( R \) is the gas constant, \( Kc \) is the equilibrium constant and \( T \) is the temperature According to van't Hoff equation;

\[ \ln Kc = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]  
(8)

Where \( \Delta S^\circ \) and \( \Delta H^\circ \) are change in entropy and enthalpy of adsorption respectively. A plot of in \( Kc \) versus \( 1/T \) is linear as shown in Figure (13 & 14) Values of \( \Delta S^\circ \) and \( \Delta H^\circ \) were evaluated from the slope and intercept of van't Hoff plots.

**RESULT AND DISCUSSION**

**CHARACTERIZATION**

The pHzpc of solid surface is the pH values at which the amount of acidic and basic functional groups is equal. Adsorption of cationic is favoured at pH > (pHzpc) while anion adsorption is favoured at pH < pHzpc. Thus the surface zero-point charge (pHzpc) of the adsorbents used was found to be; 8.70 and 7.01 for BMB and NMB respectively, as clearly shown on figure 2. The surface morphology of modified Biochar was shown on (figure 3 and 4) before and after adsorption respectively. A physical change was recorded on the surface structures of the Biochar before and after adsorption, it can be seen clearly that the SEM image of biochar showed a smooth surface with distinct pores prior to adsorption, while after adsorption showed a rough texture. This is as a result after adsorption of RhB dye; the pores on the biochar surface become clogged with dye particles causing the surface to become uneven (Mahvi 2004).

The FT-IR spectrum of the biochars used in this study was presented on figure 5, the presence of a broad band in the region 3300 cm\(^{-1}\) is assigned to the vibration of O-H while peak at 2850 cm\(^{-1}\) indicates the presence of C-H aliphatic stretching vibration. The band appears in the region 2140 cm\(^{-1}\) indicates C=C stretching, another peak was observed at the region of 1665 cm\(^{-1}\) which indicates the presence of C=O stretching vibrations, and C-O stretching was also observed at the region of 1050 cm\(^{-1}\). Moreover, N-H bending was observed on NMB at 1641 cm\(^{-1}\), another functional group of C-O stretching were seen on the region of 1225 cm\(^{-1}\) all these changes to the modification effect and role of these groups in adsorption of the dyes.
EFFECT OF CONTACT TIME
The effect of contact time was determined in batch adsorption process at different time interval (20 to 160 minutes) with the same initial concentration of (100 mg/l) fixed adsorbent dosage of (0.1 g) and at room temperature of 27°C. Contact time was assessed as an important parameter affecting the adsorption capacity of an adsorbents. The results of the effect of contact time adsorbed amount of RhB onto the Modified and non-modified Biochar used as adsorbents was given in figure (6).

The result shows that the amount adsorbed increases with increasing adsorbent from 61% to 72% and 25% to 68% as dose increases from (0.1- 0.5 g) for the two adsorbents BMB and NMB. The removal efficiency (amount adsorbed) of Rhodamine B was initially increasing with the increase in dosage of the produced biochar until it reached a stage after which insignificant increases were noticed, Subsequently, a negligible increase was observed when dosage was further increased.

However increase in available surface adsorption site enhances Rhodamine B removal when adsorbent dosage were increased (Angin D, 2014) subsequent saturation of adsorption sight as well as over layer of adsorbent may have resulted in removal equilibrium/reduction in percentage removal (Pirbazari A.E., et al., 2014). Moreover it is well understood that the number of available adsorption sites & the surface area increase by increasing the adsorbent dose and it therefore, result in the increase in amount of adsorbed dyes (Malik et al., 2007).

EFFECT INITIAL CONCENTRATION
The effect of initial concentration was evaluated under different initial concentration (10 – 50 mg/L) with the following condition: Adsorbent dose (0.1 g), Contact time of 30 minutes and temperature of 27°C. The effect of initial concentration was given in (figure 8) the results shows that the amount adsorbed was decreased from 87% to 19% and 96.32% to 30.21% for the adsorbents used in this study, This may be due to the fact that
biochar produced at higher temperature is rendered highly absorptive in nature (Mohan et al, 2014), when exposed to water solutions containing dye molecules with the surface component in the adsorbate, such dehydrated biochar quickly absorbs water, resulting in rapid adsorption of synthetic dyes.

Furthermore, an increase in the initial dye concentration led to an increase in the adsorption uptake of dye, and so was the equilibrium time. This is because a higher initial concentration increased the number of collisions between dye molecules and enhanced the driving force between the solution and solid phases (Wang et al, 2010).

Figure 8 Effects on Initial Concentration

KINETICS STUDIES

The adsorption kinetics and parameters gives important information for designing and modeling the adsorption processes. The parameters of kinetic model of RhB Adsorption onto the adsorbents used were presented on the table 1. Correlation coefficient for the first order model was found to be low with the value of (0.636 and 0.813) the experimentally obtained quantities adsorbed at equilibrium (qe(exp)) compared with calculated (qe(cal)) values for pseudo first order kinetics vary greatly, hence adsorption of Rhodamine B on the BMB failed to fit the first order kinetics.

The coefficient for pseudo second order model was found to be higher than that of the first order the values obtained are (0.999) for BMB and (0.987) for NMB table 1, it is calculated adsorption capacity values closely fitted the experimental values both the values obtained are in close agreement with each other hence the adsorption of Rhodamine B dye follows a second order kinetics.

The Langmuir isotherm model assumes that maximum adsorption correspond to a saturated monolayer of adsorbate molecules on adsorbent surface with no lateral interaction between the adsorbed molecules (Dey & Mukhopadhyay 2015) The results presented on table 2, shows that the adsorption of Rhodamine B on the adsorbent used follows the Langmuir isotherm for recording higher values of R² 1.00 for BMB and 0.999 for NMB, these higher values for the regression coefficient confirms that the adsorption follows the Langmuir model. The maximum adsorptive capacity (qmax) was 20.30 mg/g and 20.23 mg/g for BMB and NMB respectively. It can also be seen from the table that, the value of RL was in the range of 0-1 which confirms the favorable uptake of RhB. While, the Freundlich isotherm model describes the heterogeneous adsorption process, it can be seen from the result presented on table 2, the regression coefficient (R²) of the freundlich model were lower than that of the Langmuir. The KF value for the

Table 1. Kinetic Model

<table>
<thead>
<tr>
<th>Kinetic Models</th>
<th>Constant Values</th>
<th>BMB</th>
<th>NMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo First Order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>qe (exp) mg/g</td>
<td>32.97</td>
<td>10.91</td>
<td></td>
</tr>
<tr>
<td>qe (cal) mg/g</td>
<td>1.999</td>
<td>1.2144</td>
<td></td>
</tr>
<tr>
<td>K1 min⁻¹</td>
<td>0.026</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.636</td>
<td>0.813</td>
<td></td>
</tr>
<tr>
<td>Pseudo Second Order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>qe (exp) mg/g</td>
<td>5.340</td>
<td>4.51</td>
<td></td>
</tr>
<tr>
<td>qe (cal) mg/g</td>
<td>5.0251</td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td>K2</td>
<td>64.42</td>
<td>0.1159</td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.999</td>
<td>0.987</td>
<td></td>
</tr>
</tbody>
</table>
adsorption of RhB was found to be 4.677 and 4.5708. However, higher values of $K_F$ indicates an easy uptake of dye from solution (Mahvi et al, 2004).

Table 2 Parameters of Langmuir and Freundlich isotherms.

<table>
<thead>
<tr>
<th>Isotherm Parameters</th>
<th>Constants</th>
<th>BMB</th>
<th>NMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{max}$ (mg/g)</td>
<td>20.30</td>
<td>20.23</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>4926.11</td>
<td>247.57</td>
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<tr>
<td></td>
<td>$R_L$</td>
<td>0.909</td>
<td>0.4546</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>1.00</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>4.677</td>
<td>4.5708</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>0.0263</td>
<td>0.0110</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.149</td>
<td>0.112</td>
</tr>
</tbody>
</table>

Table 3 Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMB</td>
<td>-3.7515</td>
<td>34.57169</td>
</tr>
<tr>
<td>NMB</td>
<td>-36.2595</td>
<td>88.79886</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>$\Delta G^0$ (kJ/mol)</td>
<td>$\Delta G^0$ (kJ/mol)</td>
</tr>
<tr>
<td>298</td>
<td>-10.17</td>
<td>-26498.3</td>
</tr>
<tr>
<td>303</td>
<td>-10.35</td>
<td>-26942.3</td>
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<tr>
<td>308</td>
<td>-10.51</td>
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<tr>
<td>328</td>
<td>-11.21</td>
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</tr>
<tr>
<td>333</td>
<td>-11.38</td>
<td>-29606.3</td>
</tr>
</tbody>
</table>

ADSORPTION THERMODYNAMICS

The effect of temperature is paramount and a major factor influencing the adsorption, the temperature was monitored in the range of 25⁰ - 60⁰. The values of the thermodynamic parameters are shown on table 3; the values of free energy change ($\Delta G^0$) were negative, indicating the feasibility and spontaneous nature of the adsorption process. Also, the more negative the value of $\Delta G$, the more energetically favourable the process is, while the positive value of $\Delta S^0$ indicates the increased randomness at the solid/solid interface during the adsorption of RhB onto the active sites of the adsorbent (Gupta et al, 2011) hence suggesting the good affinity of the dye towards the adsorbent and that significant changes occur in the internal structure of the adsorbent due to the adsorption (Akar et al, 2009). The values of $\Delta H^0$ were negative, indicating the process is exothermic in nature. The values of $\Delta S^0$ and $\Delta H^0$ were evaluated from the slope and intercept of van’t Hoff plots on figure 13 and figure 14.

Figure 11 Langmuir Isotherms for BMB

Figure 12 Langmuir Isotherms for NMB

CONCLUSION

The Experimental results shown that the Biochar prepared from the pyrolysis of municipal solid waste can be used as a low cost adsorbent for the removal of cationic dye (Rhodamine B) the point of zero charge (pHz) was 8.70, 7.01 for BMB and NMB respectively, which indicates the property of adsorption of cationic dye. The surface morphological analysis was characterized using Scanning Electron Microscopy & Fourier Transform Infrared Spectroscopy. The adsorption parameters were investigated using batch experiment, it was evident that the kinetic data obtained follows the Pseudo second order kinetic and Langmuir isothermal model. Thermodynamic parameters indicate that the adsorption of Rhodamine B onto the modified Biochar is primarily Chemisorption with spontaneous & exothermic in nature.


