FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 5 No. 3, September, 2021, pp 334- 341
DOI: https://doi.org/10.33003/fjs-2021-0503-758

ADSORPTION STUDIES OF RHODAMINE B DYE FROM AQUEOUS SOLUTION USING ALKALINE MODIFIED BIOCHAR & NON MODIFIED BIOCHAR OBTAINED FROM THE PYROLYSIS OF MUNICIPAL SOLID WASTE

[1]Imrana Ibrahim[*], [2]Samaila M. Batagarawa, and [2]Ahmed Salisu

[1]Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto State Nigeria.
[2]Department of Pure and Industrial Chemistry, Umaru Musa Yar'adua University, Katsina State, Nigeria.
[*]*Corresponding email*: imrana.ibrahim@udusok.edu.ng +234 813864 9292

ABSTRACT
The aim of this research is to use Municipal Solid Waste (MSW) prepared from the pyrolysis at 450 ^{o}C for the removal of cationic dye (Rhodamine B) in aqueous solution. The effects of contact time and reaction temperature were studied in a batch setup. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy were used to characterize the modified Biochar and non modified Biochar in order to predict the morphological properties and structural modification respectively. It was found that initial dye concentration (10mg/L), adsorbent dosage (0.3g) and contact time (100minutes) were found to give the highest removal of dye from the adsorbents. Subsequently, it was observed that an increase in the reaction parameters showed an increasing trend for the removal of dye. SEM analysis showed distinct morphology for the fresh and spent adsorbent which was linked to potential clogging resulting from uptake of pore sites by the dyes. The adsorption isotherms showed that the adsorption equilibrium data obeys Langmuir adsorption Isotherm with the maximum monolayer adsorption capacity of 20.30 mg/g and 20.23 mg/g and Pseudo Second Order kinetic model best described the experimental findings for the two adsorbents used in the study. Moreover, thermodynamic study reveals that the adsorption is a spontaneous and exothermic process.

Key Words: Adsorption, Adsorbent, Biochar, Pyrolysis, and Rhodamine B

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 (Ebrahimi *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, weed, 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 (Qiu 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 scrums, 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 ^{o}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 ^{O}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 taken 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 800-07334) 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 ($C_{28}H_{31}N_2O_3Cl$; 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 mgL^{-1} Rhodamine-B (RhB) was prepared by dissolving 1g of RhB in 1000 cm^3 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).

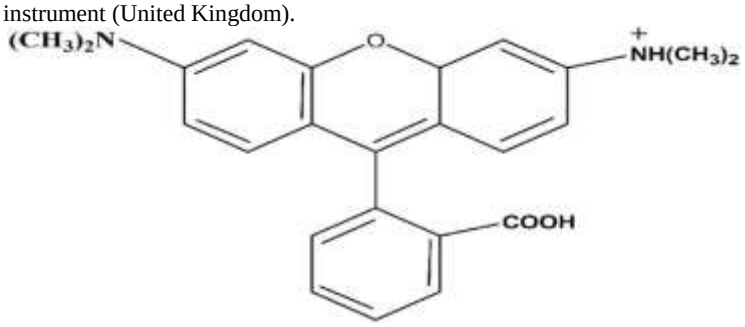

Figure 1 Chemical Structure of Rhodamine B

BATCH ADSORPTION EXPERIMENT

A series of experiments were carried out in 250 cm^3 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- 05 g), (Initial Concentration 10- 50mg/L) and (Temperature 25^0 - 60^0) 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:

$$\text{Removal Efficiency } (\%) = \frac{(Co-Ct)}{Co} \times 100\% \quad (1)$$

$$\text{Adsorption Amount } (\text{mg.g} - 1) = \frac{(Co-Ct)}{Co} \times \frac{V}{m} \quad (2)$$

Where, C_o (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, k_1 (min^{-1}) is the rate constant of the pseudo first order adsorption. The pseudo second-order kinetic model is expressed by the following:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qe} \times t \_\_\_\_\_ (4)$$

Where, k_2 (g/(mg $^{-min}$)) 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 *q*e 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):

$$\frac{Ce}{qe} = \frac{1}{qmKL} + \frac{Ce}{qm} \_\_\_\_\_ (5)$$

Where qe and qm are the corresponding adsorption capacity and maximum adsorption capacity (mg g^{-1}), respectively, Ce 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):

$$\text{Log qe} = \log \text{KF} + \frac{1}{n} \log \text{Ce} \_\_\_\_\_ (6)$$

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,

$$\Delta G° = -RT \ln Kc \_\_\_\_\_ (7)$$

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

$$\ln Kc = {}^{\Delta H°}/_{RT} + {}^{\Delta S°}/_{R} \_\_\_\_\_ (8)$$

Where ΔS^O and ΔH^O 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 ΔS^O and ΔH^O 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 biochars 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.

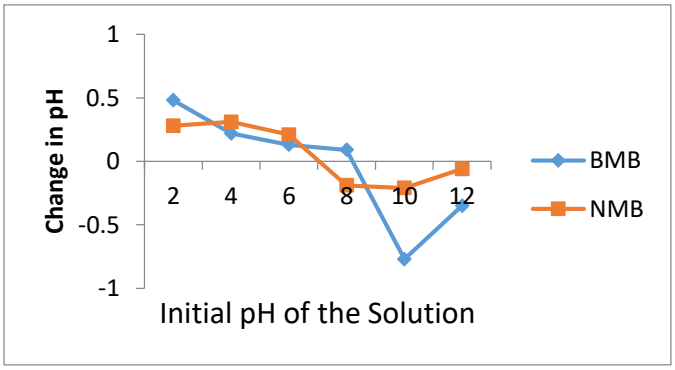

Figure 2. The pH of zero charge of the Adsorbent

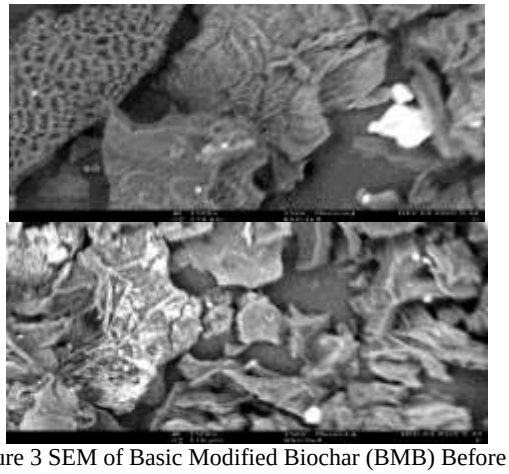

Figure 3 SEM of Basic Modified Biochar (BMB) Before & After Adsorption

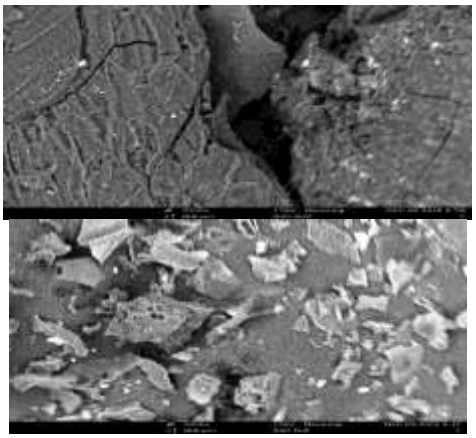

Figure 4 SEM of Non Modified Biochar (NMB) Before & After Adsorption

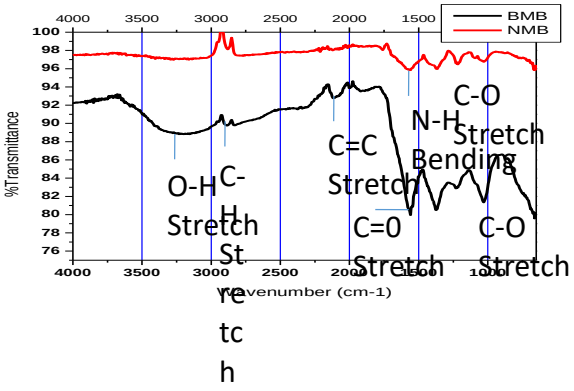

Figure 5 FT-IR Spectrum of BMB And NMB

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 assess 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 from 35% to 70% and 18% to 45% for BMB and NMB respectively. The results indicates that the amount adsorbed at different initial concentration increased rapidly at the beginning of the adsorption, until it reached an equilibrium were it starts to decline, the rapid adsorption of the dye at the start may be as result of the most readily available active sites on the surface of the modified Biochar (Dawood and Sen 2012).

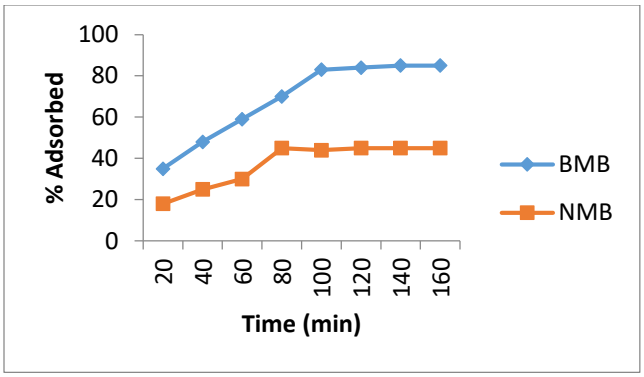

Figure 6 Effect of Contact Time

EFFECT OF ADSORBENT DOSE

The effect of adsorbent dosage was investigated on each adsorbent at different dosage under the following conditions: Initial Concentration 100 mg/l, Contact time 30 minutes and temperature 27°C. Effect of adsorbent dose was presented in figure 7. 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).

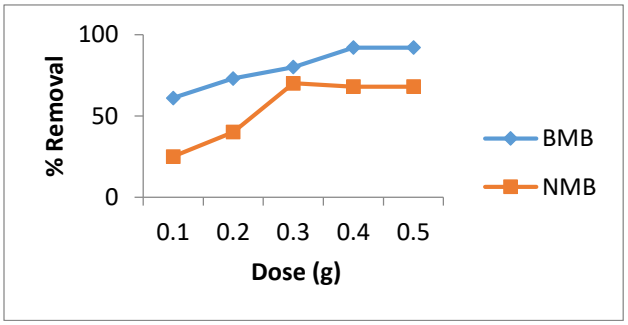

Figure 7 Effects on Adsorbent Dose

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).

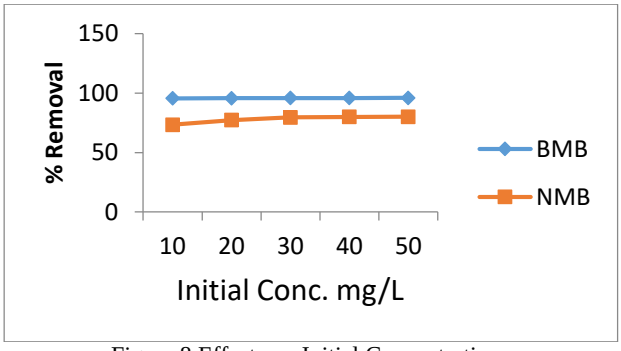

Figure 8 Effects on Initial Concentration

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.

Table 1. Kinetic Model

Kinetic Models	**Constant Values**	BMB	NMB
Pseudo First Order	qe (exp) mg/g	32.97	10.91
	qe (cal) mg/g	1.999	1.2144
	K_1 min^{-1}	0.026	0.005
	R^2	0.636	0.813
Pseudo Second Order	qe (exp) mg/g	5.340	4s.51
	qe (cal) mg/g	5.0251	4.58
	K^2	64.42	0.1159
	R^2	0.999	0.987

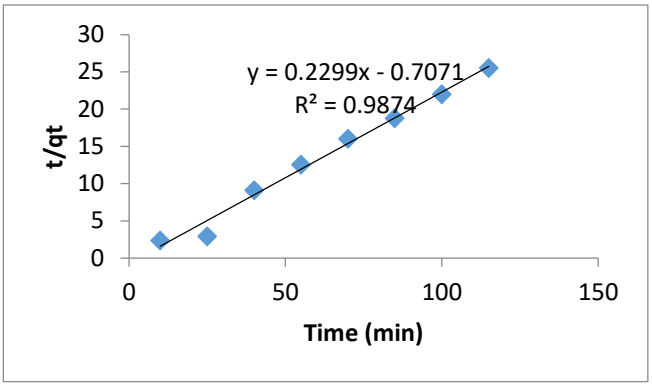

Figure 9 Pseudo Second order kinetics adsorption model of RhB on BMB

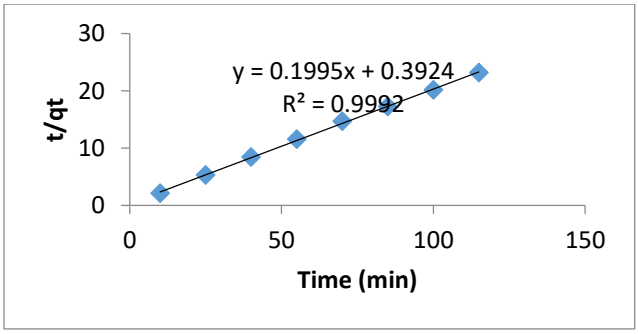

Figure 10 Pseudo Second order kinetics adsorption model of RhB on NMB

ADSORPTION ISOTHERMS

Adsorption isotherms provide vital 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 result of the adsorption Isotherm studies constants for each adsorbent was presented on table 2 below. The table summarized the isotherm parameters of Langmuir and Freundlich adsorption isotherms constants observed on the uptake of RhB dye used in the experiment.

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 R^2 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 (q_{max}) 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 (R^2) of the freundlich model were lower than that of the Langmuir. The K_F value for the

adsorption of RhB was found to be 4.677and 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.

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

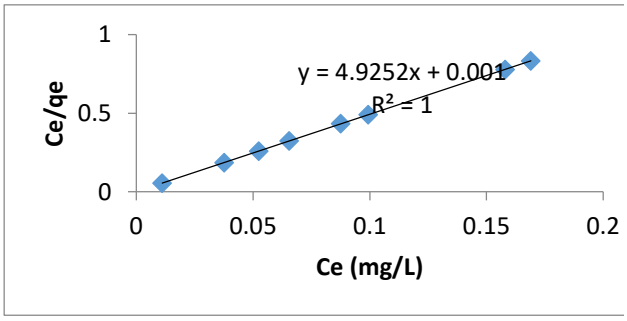

Figure 11 Langmuir Isotherms for BMB

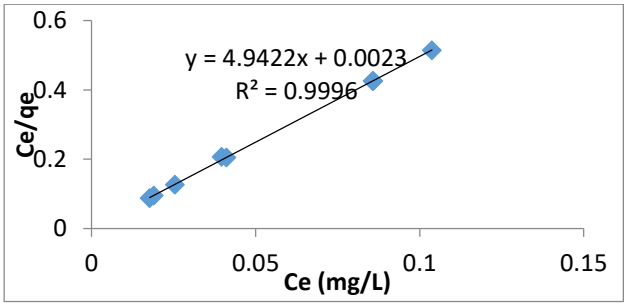

Figure 12 Langmuir Isotherms for NMB

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 values of the thermodynamic parameters are shown on table 3; the values of free energy change (ΔG^0) were negative, indicating the feasibility and spontaneous nature of the adsorption process. Also the more negative the value of ΔG, the more energetically favourable the process is, while the positive value of ΔS^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 ΔH^0 were negative, indicating the process is exothermic in nature. The values of ΔS^0 and ΔH^0 were evaluated from the slope and intercept of van't Hoff plots on figure 13 and figure 14.

Table 3 Thermodynamic Parameters

Adsorbent	ΔH^o (kJ/mol)	ΔS^o (J/K)
BMB	-3.7515	34.57169
NMB	-36.2595	88.79886

Temperature (K)	ΔG^o (kJ/mol) BMB	ΔG^o (kJ/mol) NMB
298	-10.17	-26498.3
303	-10.35	-26942.3
308	-10.51	-27386.3
313	-10.69	-27830.3
318	-10.86	-28274.3
323	-11.04	-28718.3
328	-11.21	-29162.3
333	-11.38	-29606.3

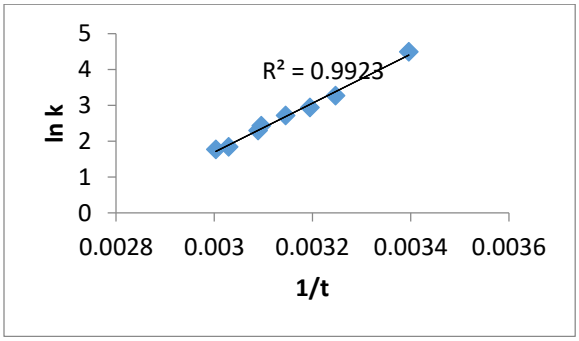

Figure 13 Van't Hoff Plot for Adsorption of RhB onto BMB

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 repectively 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 was 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.

REFERENCE

[1.] Ariyawansha R, Basnayake B, Pathirana K, Chandrasena A (2011) Open dump simulation for estimation of pollution levels

in wet tropical climates. Trop Agric Res 21:340–352. https://doi. org/10.4038/tar.v21i4.3310.

[2.] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

[3.] Agrafioti E, Kalderis D, Diamadopoulos E (2014) Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *J Environ Manag 133:309–314. https://doi.org/10.1016/j.jenvman.2013.12.007*

[4.] ANGIN D. Utilization of activated carbon produced from fruit juice industry solid waste for the adsorption of Yellow 18 from aqueous solution,. Bioresour Technol.**168**, 259, **2014**.

[5.] Bhattacharyya, K. G. & Sharma, A. 2005 Kinetics and thermodynamics of methylene blue adsorption on Neem (Azadirachta indica) leaf powder. Dyes Pigments 65 (1), 51–59.

[6.] Brown R (2009) Biochar production technology. In: Lehmann J, Joseph S (eds) Biochar for environmental management: science and technology. Earthscan, London.

[7.] Inbaraj, B. S. J. T. Chien, G. H. Ho, J. Yang and B. H. Chen, Equilibrium and kinetic studies on sorption of basic dyes by a natural biopolymer poly(gamma-glutamic acid), *Biochem. Eng. J., 2006, 31(3), 204–215.*

[8.] Duku MH, Gu S, Hagan EB (2011) Biochar production potential in Ghana—a review. Renew Sust Energ Rev 15:3539–3551. https://doi.org/10.1016/j.rser.2011.05.010

[9.] Dey, M. D. & Mukhopadhyay, R. 2015 Adsorptive removal of methylene blue by biomass of Aspergillus versicolor: a mechanistic study. *International Journal of Advanced Research in Science and Technology 4 (4), 398–405.*

[10.] Ozmen, E. Y. S. Erdemir, M. Yilmaz and M. Bahadir, Removal of carcinogenic direct azo dyes from aqueous solutions using calix[n]arene derivatives, Clean: Soil, Air, Water, 2007, 35(6), 612–616.

[11.] El-Qada, E. N., Allen, S. J. & Walker, G. M. 2006 Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm. Chemical Engineering Journal 124 (1–3),103– 110.

[12.] Gurses, A., Dogar, C., Yalcin, M., Acıkyıldız, M., Bayrak, R. & Karaca, S. 2006 The adsorption kinetics of the cationic dye, methylene blue, onto clay. *Journal of Hazardous Materials 131 (1–3), 217–228.*

[13.] Jin H, Capareda S, Chang Z, Gao J, Xu Y, Zhang J (2014) Biochar pyrolytically produced from municipal solid wastes for aqueous As(V) removal: adsorption property and its improvement with KOH activation. Bioresour Technol 169:622– 629. https://doi.org/10.1016/j. biortech.2014.06.103

[14.] Anandkumar, J. and B. Mandal, Adsorption of chromium(VI) and Rhodamine B by surface modifed tannery waste: kinetic, mechanistic and thermodynamic studies, *J. Hazard. Mater, 2011, 186(2–3), 1088–1096.*

[15.] Klinghoffer NB, Castaldi MJ (2013) Gasification and pyrolysis of municipal solid waste (MSW). In: Waste to energy conversion technology. Elsevier, pp 146–176

[16.] Wang, L.J. Zhang, R. Zhao, C. Li, Y. Li and C. L. Zhang, Adsorption of basic dyes on activated carbon prepared from Polygonum orientale Linn: equilibrium, kinetic and thermodynamic studies, Desalination, 2010, 254(1–3), 68–74.

[17.] Liu G, Xie M, Zhang S (2017) Effect of organic fraction of municipal solid waste (OFMSW)- based biochar on organic carbon mineralization in a dry land soil. J Mater Cycle Waste Manag 19:473–482. https://doi.org/10.1007/s10163-015- 0447-y

[18.] Lehmann J, Joseph S (2009) Biochar for environmental management: science and technology. Earthscan, Sterling ISBN:9781844076581.

[19.] Malik R., Rnteka D.S and Wte, S.R (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. Waste Management, 27,1129-1138.

[20.] Mahvi, A.H., Maleki, A.,Eslami, A., (2004). Potential of Rice husk ash or phenol removal in aqueous system. *American Journal of Applied Science (4): 321-326.*

[21.] Milla OV, Wang H-H, Huang W-J (2013) Feasibility study using municipal solid waste incineration bottom ash and biochar from binary mixtures of organic waste as agronomic materials. *J Hazard Toxic Radioact Waste 17:187–195*

[22.] Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuel 20:848–889. https://doi.org/10.1021/ef0502397

[23.] Mohan, D., Sarswat, A., Ok, Y. S. & Pittman, C. U. 2014 Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. Bioresource Technology 160, 191–202.

[24.] Maurya, N. S. A. K. Mittal, P. Cornel and E. Rother, Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH, Bioresour. Technol., 2006, 97(3), 512–521.

[25.] Park D, Yun Y-S, Park JM (2006) Comment on the removal mechanism of hexavalent chromium by biomaterials or biomaterial-based activated carbons. Ind Eng Chem Res 45:2405–2407. https:// doi.org/10.1021/ie0509387

[26.] PIRBAZARI A.E., SABERIKHAH E., HABIBZADEHKOZANI S.S. Fe3O4 – wheat straw: preparation, characterization and its application for methylene blue adsorption. Water Resour Ind **7–8**, 23, **2014**.

[27.] Qiu, Y., Zheng, Z., Zhou, Z. & Sheng, G. D. 2009 Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresource Technology 100 (21), 5348–5351.

[28.] Rivera-Utrilla J, Bautista-Toledo I, Ferro-Garcia M A, Moreno- Castilla C, 2001. Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *Journal of Chemical Technology and Biotechnology*, 76(12): 1209–1215.

[29.] Das, S. K. P. Ghosh, I. Ghosh and A. K. Guha, Adsorption of Rhodamine B on Rhizopus oryzae: role of functional groupsand cell wall components, Colloids Surf., B, 2008, 65(1), 30– 34.

[30.] Akar, S. T. A. Gorgulu, Z. Kaynak, B. Anilan and T. Akar, Biosorption of Reactive Blue dye under batch and continuous mode using a mixed biosorbent of macrofungus Agaricus bisporus and Thuja orientalis cones, *Chem. Eng. J., 2009, 148(1), 26 34.*

[31.] Dawood S. And T. K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, Water Res., 2012, 46(6), 1933–1946.

[32.] Gupta, V. K. B. Gupta, A. Rastogi, S. Agarwal and A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye– Acid Blue 113, *J. Hazard. Mater, 2011, 186(1), 891–901.*

[33.] Yang, Y., Lin, X., Wei, B., Zhao, Y. & Wang, J. (2014) Evaluation of adsorption potential of bamboo biochar for metal-complex dye: equilibrium, kinetics and artificial neural network modeling. *International Journal of Environmental Science and Technology 11 (4), 1093–1100.*

[34] Attallah M.F, I.M. Ahmed, M.M. Hamed, Treatment of industrial wastewater containing congo red and naphthol green B using low-cost adsorbent, Environ. Sci. Pollut. Res. 20 (2013) 1106–1116.

[35] Ramaraju B, P.M.K. Reddy, C. Subrahmanyam, Low cost absorbent from agricultural waste for removal of dyes, Environ. Prog. Sustain. Energy 33 (2014) 38–46.

[36] Vieira S.S, Z.M. Magriotis, N.A.V. Santos, M.G. Cardoso, A. A. Saczk, Macauba palm (Acrocomia aculeata) cake from biodiesel processing: an efficient and low cost substrate for the adsorption of dye, Chem. Eng. J. 183 (2012) 152–161.

[37] Ebrahimi A, M. Arami, H. Bahrami, E. Pajootan, Fish Bone as a low-cost adsorbent for dye removal from wastewater: response surface methodology and classical method, Environ. Model.Assess. 18 (2013) 1–10.

[38]Shakir, K., Elkafrawy, A. F., Ghoneimy, H. F., Beheir, S. G. E. & Refaat, M. 2010 Removal of Rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater simulants by ion flotation. Water Research 44 (5), 1449–1461.

[39]Ghaly, A. E., Ananthashankar, R., Alhattab, M. & Ramakrishnan, V. V. 2014 Production, characterization and treatment of textile effluents: a critical review. Chemical Engineering and Process Technology 5 (1), 1–18.

[40] Orfanos, A., Manariotis, I. O. & Karapanagioti, H. K. 2017 bSorption of Methylene Blue onto Food Industry Byproducts. http://www.biochar-international.org/node/7046 (accessed 22 May 2017).