



The Adsorption of Dye Molecules from Aqueous Solution, by Activated Carbon, produced, through Biomass Torrefaction and Pyrolysis

Eseyin, E. Anthonia^{1*}, Egbadekwo, O. Dickson¹, Mamuru, A. Solomon², Ankwai, E. Godwin¹, Mohammed, Ibrahim¹

¹Department of Chemistry, University of Jos, Jos. Plateau State, Nigeria

²Department of Chemistry, Adamawa State University, Mubi, Nigeria

Contact: eseyinae@gmail.com

Abstract The adsorption of methylene blue dye (MBD) on torrefied and pyrolysed corn stalks, from aqueous solutions was investigated under various experimental conditions. FTIR, SEM, ultimate and proximate analyses were used for characterization of various samples. Batch adsorption experiments were conducted on samples to ascertain the best equilibrium conditions for adsorption, by varying activated carbon concentration, dosage, temperature, contact time, pH and agitation speed. Highest % removal was recorded at initial concentration of 10m/L at room temperature. The equilibrium data obtained from the adsorption of methylene blue dye, on activated carbon were better fitted to Langmuir and Freundlich isotherm models. Kinetic studies indicated the Lagergren Pseudo-second order, with a correlation coefficient of 0.983. The thermodynamic data showed that the process was spontaneous, feasible and exothermic in nature. This results shows that torrefaction holds great promise in the preparation of activated carbon with high porosity, for adsorption.

Keywords Adsorption, Methylene Blue Dye, Activated Carbon, Corn Stalks, Thermodynamics

1. Introduction

Water is known to cover 70% of the earth's surface and the easiest means of environmental pollution is through water [1-2]. In recent years, the ecosystem has been highly polluted by industries, through the release of harmful dye effluent and this has attracted worldwide attention, especially the developing countries [3]. Industries have been the major contributor to water pollution because they dispose toxic acidic solid compounds and dye [4]. Currently, dye removal in aqueous solution can be done through physical and chemical processes such as; flocculation, reverse osmosis etc.

This processes mentioned have their challenges, due to their physiochemical properties [5]. Adsorption is the most preferred method for the effective removal of dye [6]. Dyes are found mainly in the effluents of the textile industry and, in a lesser but still significant amount, in the wastewaters of leather, cosmetics, plastics, food, paper and pharmaceutical industries [7]. These types of dyes are non-biodegradable, they are stable, and as such, generate an aesthetic problem. Some of them are even toxic and carcinogenic [8]. Example of dyes are: Methylene Blue, Basic red 18, Brilliant blue, Rhodamine B, Acid red 73, and Reactive red 24 [9].

The research work by Medic *et al*, on the efficiency of activated carbon derived forest and agricultural wastes was reported [10]. In this research, two different biomass wastes were used, and torrefaction was performed at 200 and



250°C at 60 minutes, using closed-lid crucibles in a muffle furnace. It was reported that the efficiency of adsorption by activated carbon was almost 98.5%, signifying high adsorption, and the adsorption process was also fast and reversible. Nevertheless, bio-char presents important physical and chemical characteristics such as low inorganic content, high concentrated carbon, and a non-graphite carbon structure, as a precursor of activated carbon, [11].

The aim of this study is to produce activated carbon, via torrefaction and pyrolysis; optimize the preparation process, through chemical activation with phosphoric acid; using corn stalk as precursor, to deduce the most effective parameter such; as adsorbent dosage, contact time, pH, temperature and agitation speed that has the highest % removal of dye. To investigate the various models such as; isotherm, kinetics and thermodynamics in order to propose the mechanism involved in the adsorption process.

2. Materials and Methods

2.1 Adsorbent Preparation

The corn stalk was chosen for this experiment because of its availability and high carbon content. This agricultural waste was carefully collected from a farm within Jos, Plateau state, Nigeria, washed with deionised water several times, cut into smaller pieces, oven dried for 24 hours and crushed to a mesh size of 2mm. Thermal pre-treatments (torrefaction and slow pyrolysis) were then carried out. The torrefaction process was performed at a temperature of 280 °C and pyrolysis was at 450 °C. The pre-treated sample was chemically activated via a one-step method. The bio-char was mixed with 50% H₃PO₄ (20g sample + 20ml of H₃PO₄, w/v). The sample was placed in an electrical cabolite chamber furnace at ambient temperature, heated to 450°C for one hour and the activated carbon produced was collected and allowed to cool to room temperature. The sample was kept in the desiccator for further use.

2.2 Adsorbent Characterisation

All samples were characterized by ultimate analysis, performed, using an Exerter Analytical Incorporation (EAI CE-440) Elemental Analyzer. Proximate analysis was conducted according to ASTM D 3172e3175 test standards and the results were given as moisture, volatile matter, ash, calorific analysis (high heating value). The HHV of corn stalk was calculated, using the elemental results from Exerter Analytical Incorporation (EAI CE-440) elemental Analyzer, using the Dulong's formula. FTIR spectroscopy, used to define surface functional groups, was conducted at a resolution of 4 cm⁻¹ and 32 scans on a Thermo Nicolet Nexus 670 spectrometer and SEM was conducted on samples to allow for visual analysis of surface structure. Imaging was afforded by an FEI Quanta 200 scanning electron microscope.

2.3 Batch Experiment

Stock solution of dye (1000mg/L) was prepared with 1g of methylene blue dye (MBD). To determine the dye concentration, a stock solution of adsorbate was taken in 250 ml conical flask for batch experiment. In a conical flask, 0.5g of activated carbon was added and agitated with magnetic stirrer on a digital hot plate at 50 rpm. The initial pH of solution was adjusted with 1 M HCl and 1 M NaOH before adding the activated carbon. The batch adsorption experiments were carried out for a wide range of temperatures (30, 40 50, 60 and 70 °C), contact time was for (15, 30, 45, 60 and 75 min), solution pH were (3, 5, 7, 9 and 11) while adsorbent dosages were (0.5, 1, 1.5, 2.5 and 3g).

At the end of each experiment, small volumes of the solutions were withdrawn at predetermined time and filtered. The concentrations of dye solution in the supernatant solutions before and after adsorption were determined, using a CARY Bio-300 UV-Visible Spectrophotometer (Varion) at 668 nm. The initial and final concentrations of dye were used to calculate % efficiency as follows:

$$\text{Percentage efficiency} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

Where C_i is initial concentration, C_f is final concentration. A linear graph was then plotted to show the effects of the various parameters such as; temperature, contact time, initial concentration, and activated carbon dosage on % dye removal.



3 Results and Discussion

3.1 Characterization of Adsorbent

Table 1: Ultimate analysis, Proximate analysis and HHV of Samples

Sample (cornstalk)	% C	% H	%N	%O	Ash content	Moisture content	Volatile matter	HHV (MJ/kg)
Untorrefied	46.10	5.70	0.35	47.44	5.25	8.10	70.05	31.08
Torrefied	65.15	4.66	0.62	29.57	10.70	5.50	12.40	33.16
Pyrolysed	70.02	3.85	0.95	25.18	12.45	3.15	9.50	33.04

The elemental and ash contents of corn stalk, used in this study are given in table 1 and the trends of the elemental composition in the heating process are also indicated. During the entire torrefaction and pyrolysis processes, the carbon contents increased while the oxygen and hydrogen contents reduced, and the nitrogen contents increased. The ash content indicated a significant rise also, due to increased carbon content. This trend observed in the elemental composition in table 1 is in agreement with different variation in colour change, observed during the entire heating processes.

The change in the moisture contents shows an interesting hygroscopic results. As expected, the untorrefied corn stalk showed higher values of moisture content in comparison to the torrefied and pyrolysed corn stalk samples. Also, the volatile matter decreased rapidly from 70.1% to 12.4% and finally to 9.5%. This was due to the increase in temperature of the torrefaction process at 280 °C, to pyrolysis at 450 °C. The whole process resulted in the concentration of carbon.

Based on the empirical correlation proposed by Dulong, the high heating and lower heating values of samples were calculated from the elemental values in table 1

$$HHV \text{ (MJ/kg)} = \frac{33.5 \text{ wt\%C}}{100} + \frac{142.3 \text{ wt\%H}}{100} + \frac{15.4 \text{ wt\%O}}{100} + \frac{24.5 \text{ wt\%N}}{100} \tag{2}$$

The HHV is mostly dependent on the carbon contents, followed by hydrogen and oxygen. This indicated that torrefaction, as a carbon concentration process, increased the HHV of the torrefied biomass. From table 1 it can be observed that the HHV for torrefied corn stalk is slightly greater than that of pyrolysed corn stalk which is in agreement with previous studies, indicating that torrefaction is most effective in increasing the heating value of biomass [12].

3.2 FT-IR Results

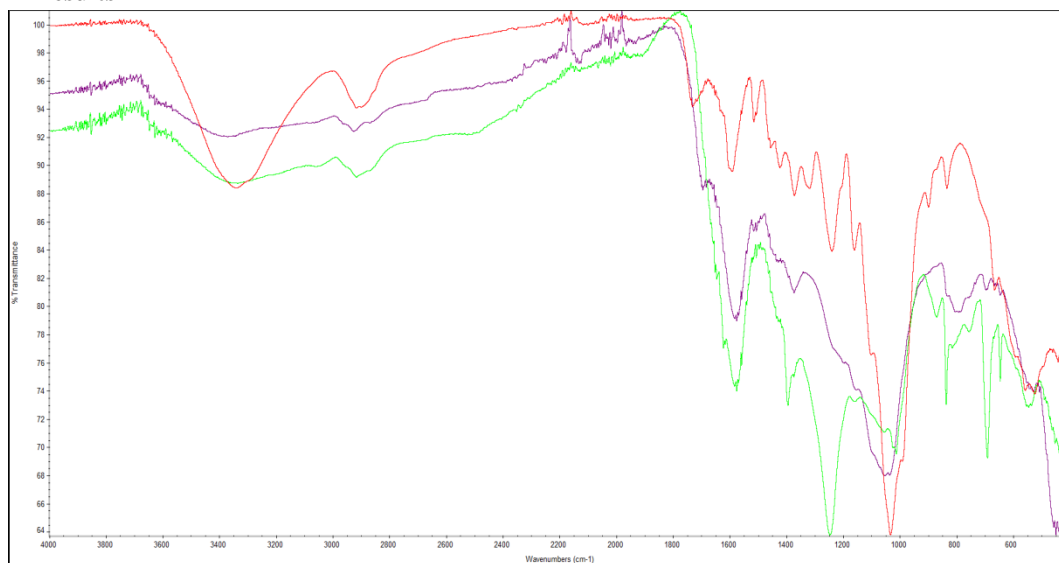


Figure 1: FTIR Results for Untorrefied, Torrefied and Pyrolysed Corn Stalks



The FTIR analysis results for untorrefied, torrefied and pyrolysed corn stalks is shown in figure 1. The bands 3300-3400 cm^{-1} which corresponds to N-H group, has a significant reduction in intensity, due to the torrefaction procedure which includes devolatilization, depolymerisation, and carbonization. Band at 3200-2700 cm^{-1} , corresponds to O-H stretching, suggesting the presence of an alcohol; the signal at 2140-2100 cm^{-1} indicates a C=C stretching of alkynes; the band at 1750-1735 cm^{-1} indicates the presence of C=O stretching of ester; the signals at 1550-1500 cm^{-1} may also be attributed to N=O stretching of nitro compound; the band located at 1600 is a characteristics of C=C stretching α,β unsaturated ketone; another band at 1250-1020 indicates the presence of C-N stretching amine; a band at 1070- 1030 correspond to S=O stretching of sulfoxide; a strong band at 1085- 1050 cm^{-1} indicates a C-O stretching alcohol; and 840-790 cm^{-1} indicates a C=C bending in alkenes.

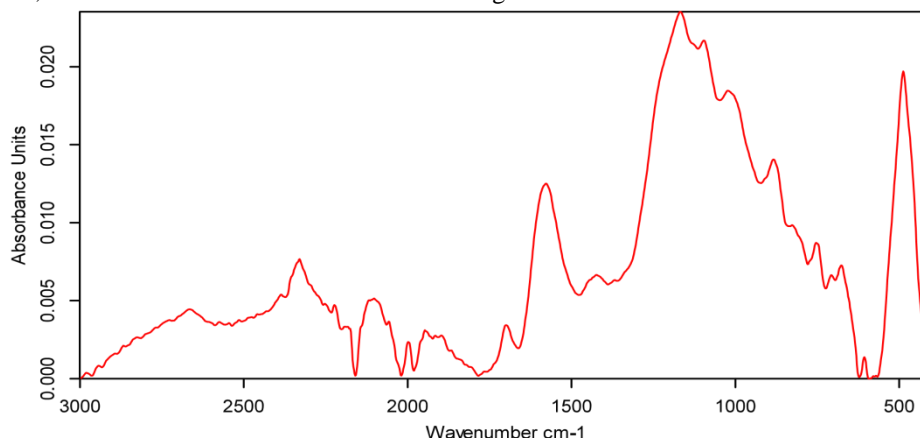
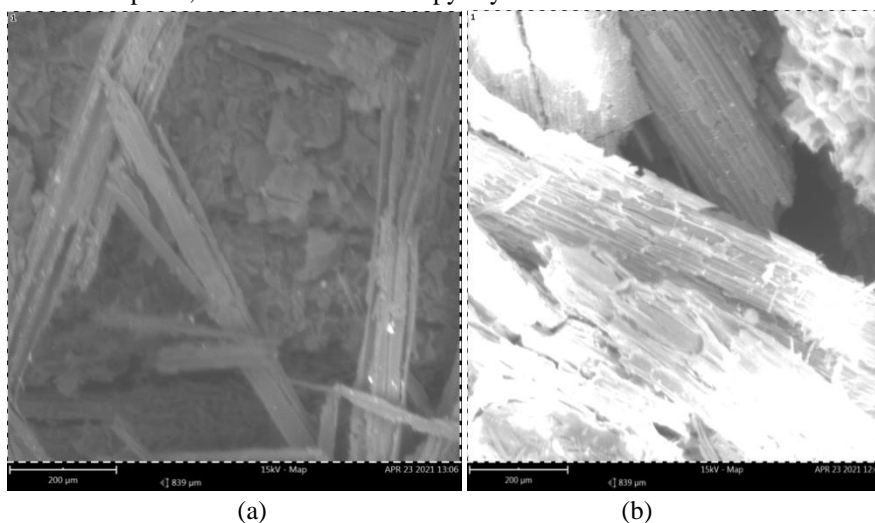


Figure 2: FTIR Results for Activated Carbon

The activated carbon peak is normally, at 3400-3300 cm^{-1} which corresponded to O-H stretching; this is much less prevalent in the activated carbon produced. The reduction of hydrogen bonding shows that the phosphoric acid acts as a dehydrating agent, reacting with the pyrolysed sample as soon as both substances are mixed. The intense band at 2920 cm^{-1} is assigned to asymmetric C-H stretching, which is significantly reduced and this indicates that the activation removed some hydrogen molecules from the sample.

3.3 SEM Results

SEM results of activated carbon, which revealed the presence of abundance of pores with several nanometres in size, occupying a total of 2158.39nm, with area size of 2.135nm, and %area of 11.655nm. These results show differences in the activated carbon surface morphology. A fibre like structure was observed for the untorrefied corn stalks, followed by cracks and little pores, after torrefaction and pyrolysis.



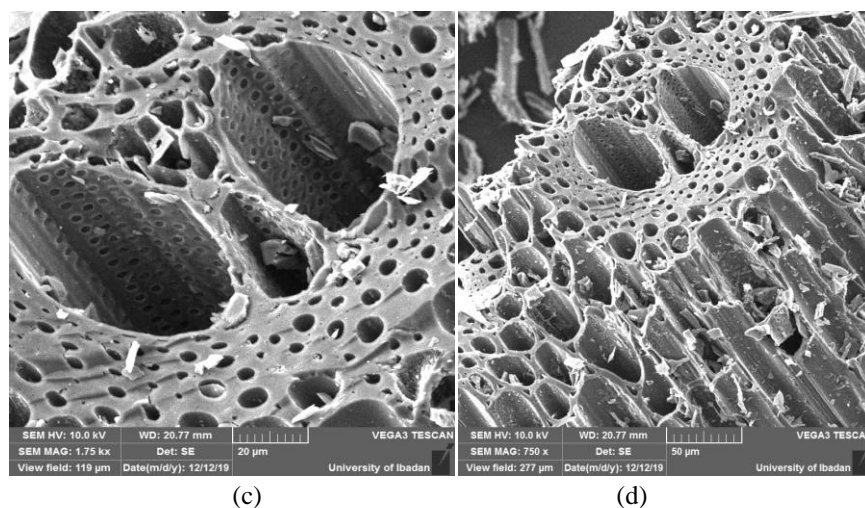


Figure 3: SEM Result (a) Untorrefied (b) Torrefied and Pyrolysed (c) Activated Carbon (d) activated carbon after adsorption

3.4 MBD Adsorption

Different parameters such as dye concentration and dosage, time, temperature, pH, and agitation were used to investigate the adsorption of MBD.

3.4.1 Effect of Initial Concentration

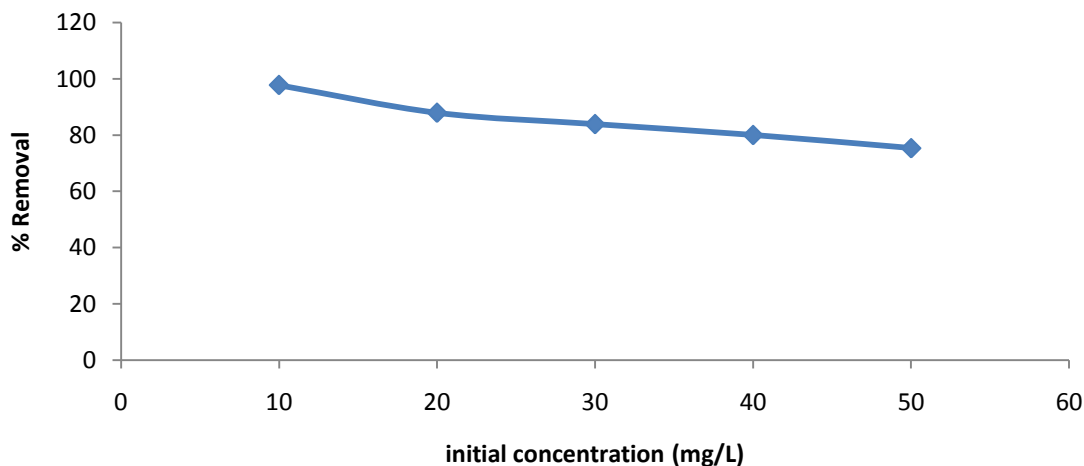


Figure 4: Effect of Initial Concentration on Adsorption of Methylene Blue Dye

The effect of initial concentration of dye (10-50mg⁻¹) was tested with constant dosage of adsorbent. It was observed that the highest % removal (97.8%) was observed at the lowest initial concentration 10mg⁻¹ (Figure 4). However, a reduction was recorded as the initial concentration increased from 20 to 50 mg⁻¹ with % removal of 87.88 to 75.32% respectively. The higher % removal at lower concentration could be related to the ratio of dye molecules to the adsorption sites availability. At lower concentration, the dye has higher affinity to the sites [13]. The results indicate that adsorption of dye is highly dependent on concentration. These observations are in total agreement with that reported by Verma & Mishra, stating that the % removal of dye decreases with increasing initial concentration of dye [14].

3.4.2 Effect of Activated Carbon Dosage

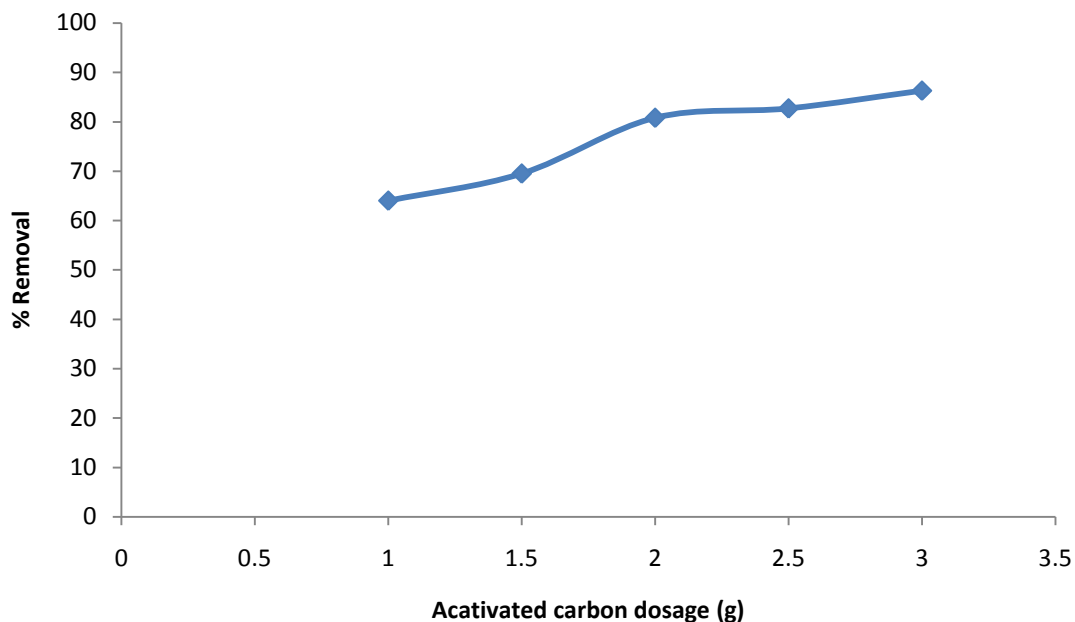


Figure 5: Effect of Activated Carbon Dosage on adsorption of Methylene Blue Dye

The effect of adsorption dosage is considered to be one of the most important adsorption parameters [15]. In this study, the adsorbent dosage was varied from 1-3g/ml of 50ml dye solution, while keeping other parameters constant. This result as presented in figure 5, showed an increased in % removal from 60 % to 86.40 % as the activated carbon dosage increased. This may be due to introduction of more binding sites for adsorption. The result is also in agreement with that reported by Sarioglu & Atay [16].

3.4.3 Effect of Contact Time

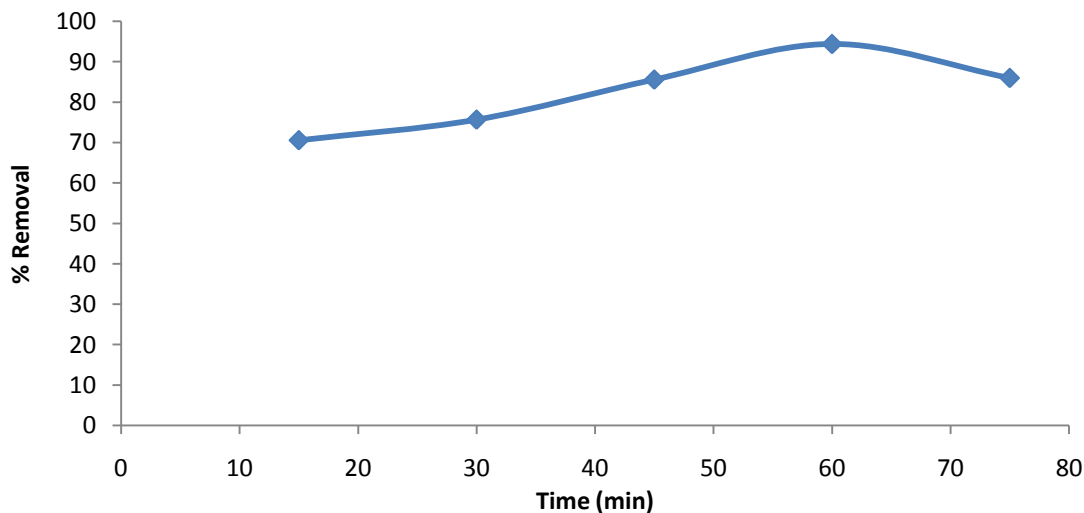


Figure 6: Effects of Contact Time on Adsorption of Methylene Blue Dye

The effect of contact time on the adsorption of MBD on the AC for a fixed initial dye concentration of 10mg/L and other parameters kept constant is shown in figure 6. The study showed that there was a 15min rapid increase in % dye removal which later proceeded at a less rapid manner. At this point, the adsorbed dye molecules are said to be at a dynamic equilibrium. The maximum time of adsorption was recorded under experimental condition. This trend of

rapid rise in temperature was due to the fact that, at the initial stage, more vacant sites were available for adsorption and after some time, lesser vacant site were available, causing AC not to adsorb more dye molecule, thereby causing a form of repulsion between MBD and AC.

3.4.4 Effect of Temperature

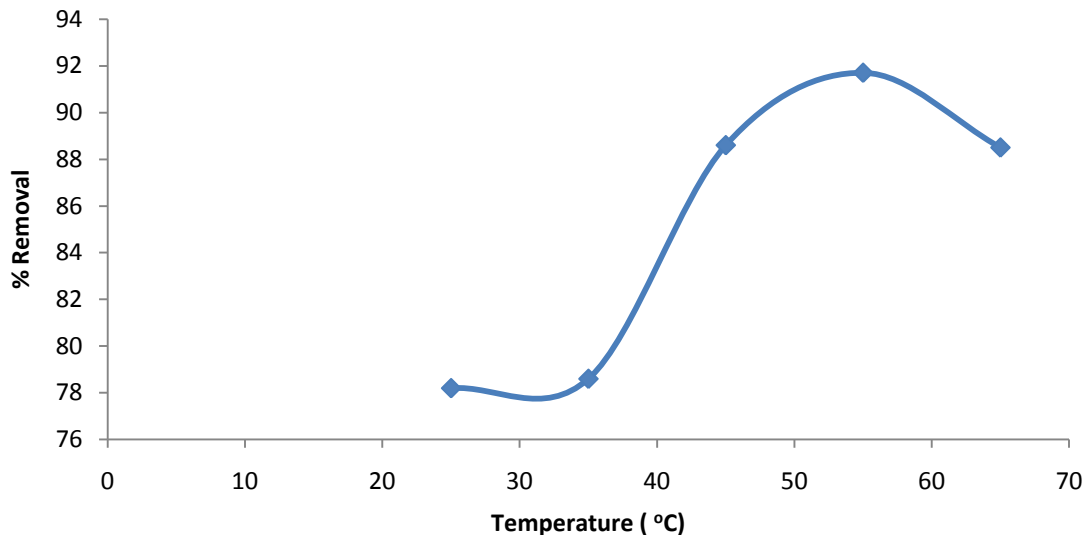


Figure 7: Effect of Temperature on Adsorption of Methylene Blue Dye

Temperature played a vital role in adsorption as it can alter the amount of dye molecule adsorbed on activated carbon. The effect of temperature was investigated at temperatures from 25-65 °C and results presented in figure 7 showed that the % removal increased from 78.2% to 91.7% when the temperature increased from 25°C to 65°C. This rise in diffusion at the external layer of activated carbon binding site may also be due to increase in temperature [17]. An additional rise in temperature may cause an increased surface pore size, causing swelling effect, which can encourage larger molecule to be adsorbed [18].

3.4.5 Effect of pH

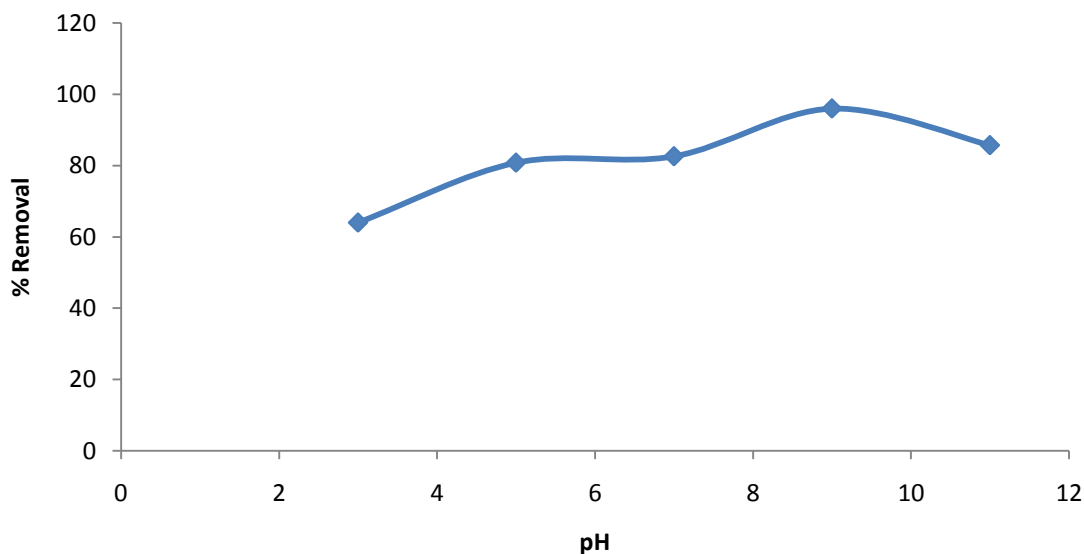


Figure 8: Effect of pH on Adsorption of Methylene Blue Dye



The interaction between MBD molecules was as a result of charges on the dye molecules and the surface of the adsorbent [19]. Results in figure 8 showed that pH had an effect on adsorption of MBD on AC. At pH 9, maximum % removal was recorded. It was evident that increase in pH also increased % removal of dye molecules. The adsorption process was greatly influenced by the surface charge on AC and the pH of MBD [20]. Increased in the negative charge site was as a result of rise in the pH of dye solution, which caused stronger forces of attraction between the positively charged dye molecules, resulting to more favourable adsorption on the negatively charged surface of AC [21].

3.4.6 Effect of Agitation

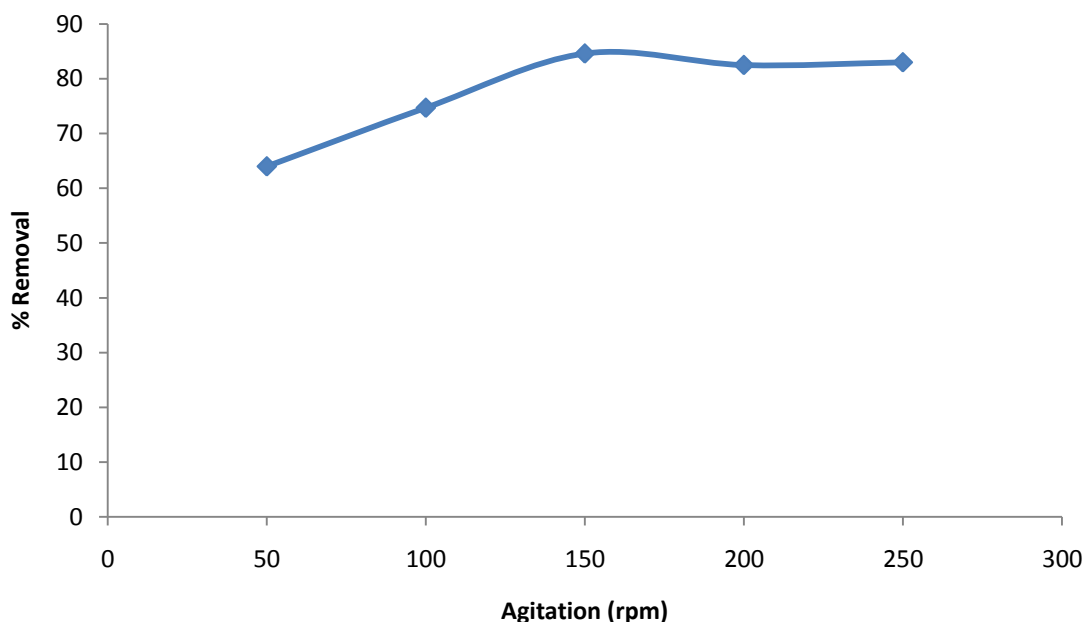


Figure 9: Effect of on Agitation on Adsorption of Methylene Blue Dye

In the course of this study, the agitation was varied to check the vibration of MBD molecules with the adsorption sites of the adsorbent. It was observed that the % removal of the dye was increasing as the agitation was increased. After agitation of 150 rpm the % removal decreased, which signified the state of equilibrium. Here the pores were saturated and no longer adsorbed more MBD molecules.

3.5 Adsorption Isotherm

The adsorption isotherm represents the relationship between the amount of dye molecules adsorbed per unit weight of solid adsorbent and the amount of adsorbate remaining in the solution at equilibrium [22]. The applicability of isotherm equation to the adsorption study is within the experimental conditions of concentration range of 10-50mg/L, activated carbon dosage 3g/L, temperature 35°C, contact time 75 min and stirring speed of 150 rpm was compared by judging the correlation coefficient values.

3.5.1 Langmuir Isotherm Model

The linear form of Langmuir isotherm is given as

$$C_e/q_e = 1/(1+q_m K_L) + 1/q_m \tag{3}$$

Where C_e (mg/L) is the equilibrium concentration of dye, q_e (mg/g) is the amount of dye adsorbed at equilibrium time, q_m (mg/g) maximum adsorption capacity and K_L (L/mg) is the Langmuir isotherm constant. A graph of C_e/q_e against C_e gave a fitted curve, with correlation coefficient, very close to unity, indicating that the adsorption process

did follow the model. Other values like q_m , K_L and R^2 , obtained from the Langmuir graph are given in table 2. The separating constant factor as defined by Ho & McKay [23] as:

$$R_L = 1/(1 + K_L \times C_0) \tag{4}$$

The separation factor is in the range of ($0 < R_L < 1$) and is read as favourable.

Table 2: Parameters for Adsorption Isotherm of MB Dye on Activated Carbon

Isotherm model	Parameter	Activated carbon
Langmuir	q_m (mg/g)	0.2960
	K_L (L/mg)	2.3950
	R_L	0.0075
	R^2	0.9410
Freundlich	N	2.9600
	K_F	1.9140
	R^2	0.9710

3.5.2 Freundlich Isotherm

According to research work by Lafi & Hafiane [24], this isotherm model can be expressed as the linear form of Freundlich equation as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Where q_e (mg/L) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the equilibrium concentration of dye solution, K_F (mg/L) is the Freundlich adsorption constant, related to the adsorption capacity, and n is the constant indicative of intensity of adsorption processes. The value of n is lying in the range of 1 to 10, illustrating that the adsorbate (MBD) is favourably adsorbed on the adsorbent (AC). A plot of $\log q_e$ against $\log C_e$ gives a straight line of slope $1/n$ and intercept $\log K_F$.

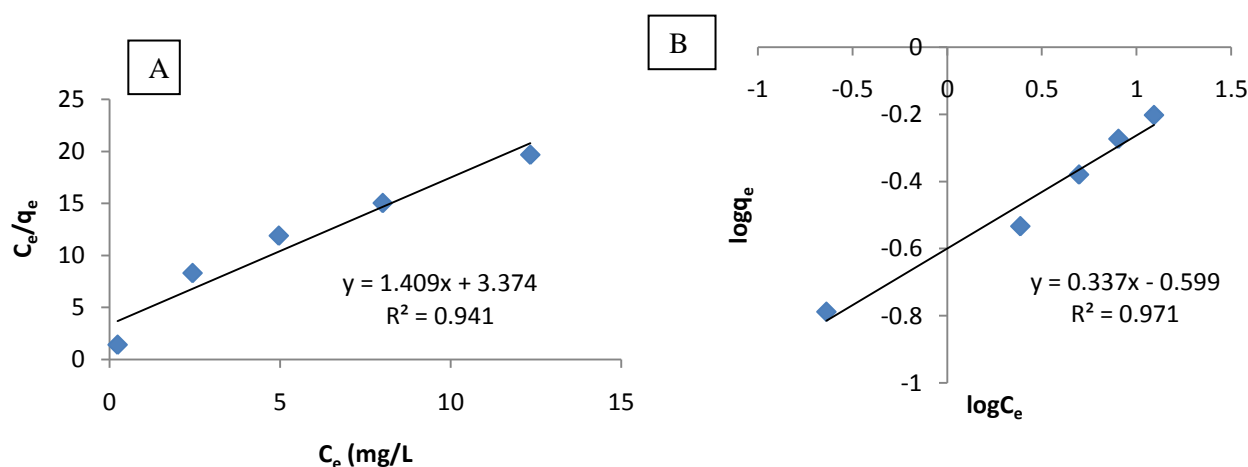


Figure 10: Fitting Adsorption Data with (A) Langmuir isotherm (B) Freundlich Isotherm

3.6 Adsorption Kinetic Study

In order to examine the controlling mechanism of sorption process, several models are employed for this work. Models were compared by the values of correlation constant (R^2).



3.6.1 Pseudo-Second-Order

The pseudo-second order model equation can be represented in an integrated linear form as follows:

$$t/q_t = 1/K_2 + 1/q_e \times t \tag{6}$$

Where q_e (mg/g) and q_t (mg/g) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium time and at time t (min). K_2 is the pseudo-second-order rate constant ($g/mg \cdot min$). The equilibrium constants of this model, K_2 and q_e were calculated from the slope and intercept of the plot of t/q_t against t . The R^2 value of the pseudo-second-order model was at 0.983, which can be said that pseudo-second-order model, provided a good correlation for the adsorption of MBD on AC.

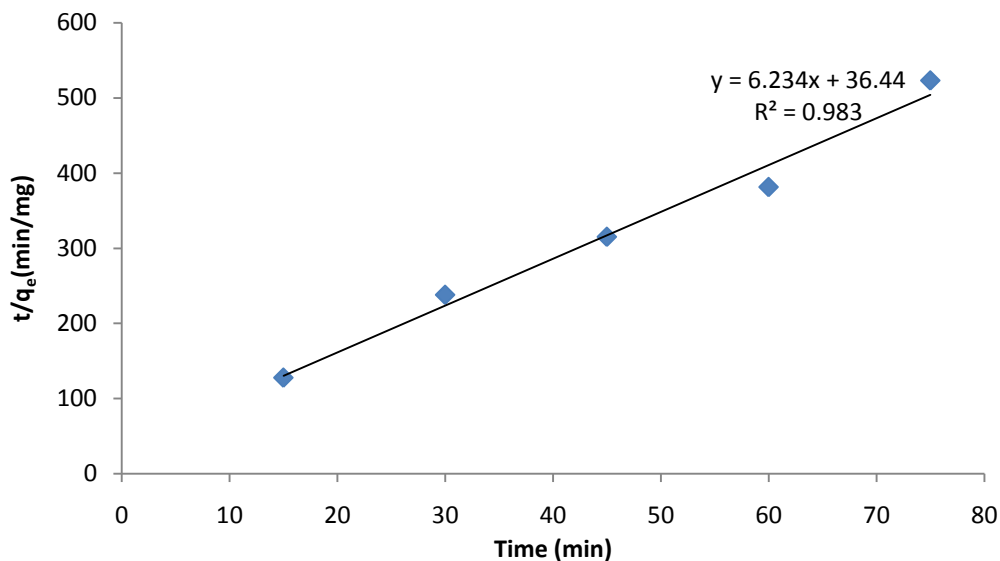


Figure 11: Pseudo-Second-Order Kinetics Model

Table 3: Kinetic Parameters for the Adsorption of MBD

Pseudo-second-order	$q_{e, cal}$ (mg/g)	0.160
	k_2 (g/mg \cdot min)	1.066
	R^2	0.983

3.7 Adsorption Thermodynamics

To evaluate the effect of temperature on adsorption of MBD on activated carbon, the thermodynamic parameters such as the free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined, using the following equations [25].

$$K_c = q_e / c_e \tag{7}$$

$$\Delta G^\circ = -RT \ln K_c \tag{8}$$

$$\ln K_c = -\Delta G / RT = -\Delta H / R * 1/T + \Delta S / R \tag{9}$$

Where K_c is the distribution coefficient of q_e and C_e and are the equilibrium concentration of methylene blue dye on the activated carbon in solution (mg/L) respectively. R is a universal constant T is temperature (K). ΔH and ΔS were calculated from the slope and the intercept of plot $\ln K_c$ against $1/T$.

Table 4 shows the results of all thermodynamic parameters. It was observed that the values of ΔG are all negative; indicating that the adsorptions of MBD onto AC is a feasible and spontaneous physical process. The negative value of ΔH indicated that the adsorption of MBD is exothermic in nature. Also the negative value of ΔS showed that the degrees of freedom increased at the solid-liquid inter-phase during the adsorption of MBD dye onto the activated carbon and reflect the affinity of activated carbon towards MBD ions in aqueous solutions [26].

Table 4: Thermodynamic Parameter for Adsorption of MB Dye onto Activated Carbon

Temperature °C	25	35	45	55	65
ΔG	-7.4	-6.6	-5.1	4.4	-5.5
ΔH		-3.071			
ΔS		-0.007			

4. Conclusion

The % removal of MBD was investigated, and the precursor used in this study (corn stalks), an agricultural waste was modified via torrefaction and pyrolysis respectively and finally activated via chemical means. This led to the change in the surface morphology of the activated carbon, thereby creating various pores, which served as adsorption sites. SEM and FTIR of activated carbon show the morphology of the adsorbent surfaces and the functional groups respectively. The adsorbent showed an improved % removal of MBD from aqueous solutions, and higher (%) removal was recorded at low concentration range of 10mg/L. The effect of pH showed that maximum % removal happened at pH of 9. Temperature study showed that with increase in temperature, dye% removal increased also.

Contact time study showed that maximum % removal was attained within the first 60 min. The adsorbent dosage was a major parameter also. It was observed that % removal of methylene blue dye was increasing with increase in adsorbent dosage. The results of equilibrium adsorption were evaluated by various adsorption models, namely, Langmuir and Freundlich models. Experimental data correlated more reasonably with Langmuir than Freundlich, based on the correlation regression (R^2). A study of the kinetic models on sorption showed that sorption fitted with the pseudo second-order kinetics model.

The negative value of ΔG° confirmed the spontaneous nature of adsorption process. The negative value of ΔS° showed the decrease randomness at the solid-solution interface during adsorption and the negative value of ΔH° indicated the adsorption process was exothermic. Torrefaction and pyrolysis provides suitable means through which cheap biomass could be converted to more efficient activated carbon for adsorption purposes.

References

- [1]. Oki, T., & Kanae, S. (2006). *Global hydrological cycles and world water resources Science*, 313(5790), 1068-1072.
- [2]. Sun, Y., Chen, Z., Wu, G., Wu, Q., Zhang, F., Niu, Z., & Hu, H. (2016). Characteristics of water quality of municipal wastewater treatment plants in China: implications for resources utilization and management. *Journal of Cleaner Production*, 131, 1-9.
- [3]. Safa, Y., & Bhatti, H., N. (2011). Kinetic and thermodynamic modelling for the removal of direct red-31 and direct orange-26 dyes from aqueous solutions by rice husk. *Desalination*, 272: 313-322.
- [4]. Ahmad, M., A. Puad, N. A. A., & Bello, O. S. (2014). Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resource and Industry*, 6 18–35.
- [5]. Pelekani, C., & Snoeyink, V. L. (2000). Competitive Adsorption between Atrazine and Methylene Blue on Activated Carbon: The Importance of Pore Size Distribution. *Carbon*, 38 (1): 1423 - 1436.
- [6]. Su, Y., Zhao, B., Xiao, W., & Han, R. (2013). Adsorption behavior of light green anionic dye using cationic surfactant-modified wheat straw in batch and column mode. *Environmental science and pollution research international*, 20(8), 5558–5568.
- [7]. Uddin, M.T., Rukanuzzaman, M., Khan, M. M. R., & Islam, M.A. (2009). Jackfruit (*Artocarpus heterophyllus*) Leaf Pow-der: An Effective Adsorbent for Removal of Methylene Blue from Aqueous Solutions. *Indian Journal of Chemical Technology*, 16, 142-149.
- [8]. Weng, C.H., Lin, Y., T. Chang C., K. & Liu, N. (2013). Decolourization of direct blue 15 by Fenton/ultrasonic process using a zero-valent iron aggregate catalyst. *Ultrason Sonochem*, 20: 970-977.



- [9]. Zhang, K., Cheung, W. H., & Valix, M. (2005). Roles of Physical and Chemical Properties of Activated Carbon in the Adsorption of Lead Ions. *Chemosphere*, 60 (8): 1129-1140.
- [10]. Malik, R., Ramteke, D.S., & Wate, S.R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Manag* 27, 1129-1138.
- [11]. Marsh, H. & Rodriguez, R. F. (2006). *Activated Carbon. Elsevier Science & Technology Books*, 1st Ed., 536 P.
- [12]. Doddapaneni, T.R.K.C., Konttinen, J., Hukka, T. I., & Moilanen, A. (2016). Influence of torrefaction pretreatment on the pyrolysis of Eucalyptus clone: a study on kinetics, reaction mechanism and heat flow. *Ind. Crop Prod*, 92, 244–254.
- [13]. Eskandarian, L., Arami, M., & Pajootan, E. (2014). Evaluation of adsorption characteristics of multiwalled carbon nanotubes modified by a poly(propylene imine) dendrimer in single and multiple dye solutions: Isotherms, kinetics, and thermodynamics. *Journal of Chemical Engineering Data*, 59(2), 444-454.
- [14]. Verma, V. K., & Mishra, A. K. (2010). Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon. *Global NEST Journal*, 12: 190-196.
- [15]. Ben Hamissa, A., Brouers, F., Mahjoub, B., & Seffen, M. (2007). Adsorption of Textile Dyes Using Agave Americana (L.) Fibres: Equilibrium and Kinetics Modelling. *Adsorption Science & Technology*, 25. 311-325.
- [16]. Sarioglu, M., & Atay, U. A. (2006). Removal of Methylene blue by using biosolid, *Global NEST Journal*, 8(2), 113-120.
- [17]. Dogan, M., Alkan, M., Türkyilmaz, A., & Özdemir, Y. (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Materials*, B109, 141–148J.
- [18]. Çiçek, F., Ozer, D., Ozer, A., & Ozer, A. (2007). Low cost removal of reactive dyes using wheat bran. *Journal of hazardous materials*, 146(1-2), 408–416.
- [19]. Maurya, N. S., Mittal, A. K., Cornel, P., & Rother, E. (2006). Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH. *Bioresource technology*, 97(3), 512–521.
- [20]. Wang, X.S., Zhou, Y., Jiang, Y., & Sun, C. (2008). The removal of basic dyes from aqueous solution using agricultural by products. *Journal of Hazardous Materials*, 157: 374-385.
- [21]. Malik, R., Ramteke, D.S., & Wate, S. R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Management*, 27, 1129-1138.
- [22]. Hu, Z., Chen, H., Ji, F., & Yuan, S. (2010). Removal of Congo Red from aqueous solution by cat tail root. *Journal of hazardous materials*, 173(1-3), 292–297.
- [23]. Ho, Y.S. & McKay, G. (1998). Kinetic models for the sorption of dye from aqueous solution by wood. *Trans. Inst. Chem, Eng. B*, 76: 183-191.
- [24]. Lafi R., & Hafiane, A. (2016). Removal of methyl orange (MO) from aqueous solution using cationic surfactants modified coffee waste (MCWs). *Journal of the Taiwan Institute of Chemical Engineers*, vol. 58: 424-433.
- [25]. Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., & Uddin, M. A. (2004). Low-temperature hydrothermal treatment of biomass: Effect of reaction parameters on products and boiling point distributions. *Energy and Fuels*, 18(1), 234-241.
- [26]. Chen, C., Li, X., Zhao, D., Tan, X., & Wang, X., (2007). Adsorption kinetic, thermodynamic and desorption studies of Th(IV) on oxidized multi-wall carbon nanotubes. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 302: 449–454.

