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Adsorption of Methylene Blue from Aqueous Solution onto *Delonix regia* Pod Activated Carbon: Batch Equilibrium Isotherm, Kinetic and Thermodynamic Studies

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Abstract

Activated carbon was synthesized from Delonix regia pods by impregnation with zinc chloride. The adsorbent characteristics revealed high surface area and porosities. The adsorption of Methylene Blue (MB) from aqueous solution onto *Delonix regia* Pod Activated Carbon (DRPAC) was investigated under various experimental conditions in Batch mode of operation. Effects of adsorbent dose, pH, temperature, and contact time were studied. The optimum conditions of adsorption were found to be: adsorbent dose of 0.6 g, pH of 7, Temperature of 30 ^{o}C and contact time of 40 minutes. At optimum conditions, removal efficiencies (%) were found to be 88.5, 91.2, 96.5, and 100, while adsorption capacity (q_e) was 33.3, 34.3, 36.3 and 37.7 mg/g respectively for the parameters studied. Equilibrium isotherm studies revealed that the adsorption was well described by both the Freundlich and Langmuir models with the Freundlich model exhibiting a better fit (R^2= 0.9102). Kinetic studies showed that the adsorption rate was better described by the pseudo second order model (R^2= 0.999) as compared to the pseudo first order kinetic model (R^2 = 0.969). Thermodynamic parameter estimates showed that MB adsorption on DRPAC is spontaneous, endothermic and feasible. Regeneration and stability of the adsorbent up to five adsorption-desorption cycles was also demonstrated with excellent results. It was concluded that, DRPAC an efficient low-cost adsorbent for the removal of MB from industrial wastewater and hence could generally be used in the treatment of wastewater for colour removal.

1. Introduction

There is a global threat posed to water as one of the most valuable resources on earth. It is the life line of all living organisms and it's constantly depleted by impurities and in many instances has lost its original quality. During the last few decades, the increase in world population as well as industrial revolution has caused serious environmental pollution such that, discharge of inorganic and organic pollutants into water bodies has reduced the ecological balance and caused harmful effects on flora and fauna [1]. Studies undertaken on the toxicity of dyes has shown its negative impact on the ecosystem. These studies show that certain dyes degrade and their derived products can be toxic and carcinogenic even at low concentrations [2], [3]. It's man's responsibility to conserve water and reduce its toxicity by treating industrial effluent before disposal or recycling.

Most industries especially textiles, paper, plastics, leather, food, cosmetics etc, use dyes to give their final products the desired colour [4], [5]. Such extensive use of dyes poses problems in form of coloured wastewater which require pretreatment for colour removal prior to disposal into receiving water bodies. This is because, the dye-bearing wastewater impart toxic substances to aquatic life and damage the

composition of receiving water bodies. Once released into water bodies, dyes not only produce toxic amines by the reductive cleavage of azo linkages which causes severe effects on human beings by damaging the vital organs such as the brain, liver, kidneys and reproductive systems and also prevent photosynthetic activity in aquatic life by reducing light penetration [6], [7], [8]. Many of the dyes used in industries are not reactive with light and/or oxygen and so they are considered as non-oxidizable substances because of their complex structure and large molecular size [9], [10]. This toxic nature of dyes has brought about the urgent need for its removal in coloured water (wastewater) before discharging into receiving surface water bodies.

Methylene blue has wider applications in paper, temporary hair colorant, dyeing cottons, wools, etc. It is a basic dye, with the molecular formula $C_{16}H_{18}N_3SCl$ (molecular weight 373.91g/mol). The chemical structure of the dye is shown in Figure 1 below. It has been reported to cause various health effects on humans and animals, ranging from eye irritation, nausea, vomiting, gastro-intestinal tract disorders and skin irritation among others [11]. MB is widely studied because of its strong adsorption potentials onto solid materials, and is regularly employed as a model compound for removing organic contaminants and colour from aqueous solutions [12].

Adsorption is an age-long technology that has been widely and efficiently utilized for the removal of pollutants including colour from aqueous solutions. It is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. Adsorption occurs naturally, but industrialists and scientists have perfected adsorption methods to clean up hazardous waste or purify drinking water. Adsorption occurs in many natural, physical, chemical and biological systems is widely used in several industrial application such as in water treatment, air stripping and soil remediation [13]. A large variety of unconventional adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater and have been reviewed extensively [14-18]. Throughout the world, much research is being conducted on the use of waste materials in order to either prevent an increasing toxic threat to the environment or to simplify present waste disposal techniques by making them more affordable. These adsorbents could be produced from many raw materials such as industrial and agricultural wastes [4,5,18,19].

Among several agricultural wastes studied as adsorbents for the removal of pollutants, delonix regia pod can be of great importance as various parts can be extensively studied as adsorbents for the removal of different types of pollutants using adsorption technology, which will therefore help to contain the problem of sludge disposal and huge energy requirements associated with other wastewater treatment technologies.

Several researchers have used different adsorbents for the removal of methylene blue (MB) and other dyes from waste water [20-23]. Ahsan *et al.*, [3] studied Tuberose sticks as an adsorbent for the removal of methylene blue. It was observed that a greater percentage of methylene was adsorbed as the pH increased. Kavitha and Senthamilsolvi [8] used vitex negundo stem. Results showed that the dye removal increased with increase in the initial dye concentration. Ncibi [24] studied the adsorptive removal of textile reactive dye using *Posidonia oceanica (L.)* fibrous biomass and reported high values of adsorption capacity. Rajappa *et al.*, [25] studied the adsorption of Nickel ion by Delonix regia pod activated carbon. An optimum removal efficiency of 85% was observed at a pH of 6. Rasheed *et al.*, [22] used surface of wool fiber and cotton fiber to investigate methylene blue removal. The result showed that wool fiber had better adsorption capacity as compared to cotton fiber. Mohammad *et al.*, [13] also studied the removal of MB from wastewater using activated carbon prepared from Rice Husk. The column process showed a maximum methylene blue removal efficiency of 97.15% at optimized conditions, inferring that, it is a low cost alternative for wastewater treatment.

Adsorption of MB onto *Delonix regia* pod activated carbon has been studied by a few authors largely as a result of its high propensity to poses sound adsorption properties. For example Ramesh *et al.*, [26] investigated MB adsorption onto microwave assisted zinc chloride activated carbon prepared from *Delonix regia pods*. The results revealed that MB adsorption was endothermic, spontaneous and increased randomly. Similarly, Ho *et al.*, [27] and Vargas *et al.*, [28] investigated MB adsorption onto Delonix regia pod activated carbon and reported varying removal efficiencies and adsorption capacities. Although these studies examined the suitability of *Delonix regia* pod-based activated carbon for removal of MB from aqueous solution in batch mode, the methods of activation (activating agent) of the adsorbents was different for each author. This can be seen from the varying characteristics reported for the adsorbent by the authors, vis-avis the varying removal efficiencies and capacities.

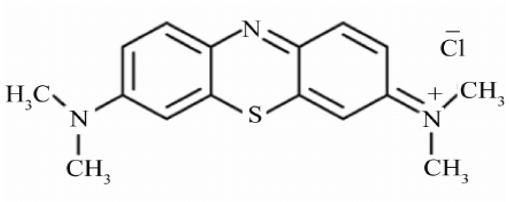

Figure 1: Chemical Structure of Methylene Blue Dye. Source: [29]

It is hypnotized that the method of activation as well as the temperature of activation could play a significant role in improving the quality of the activated carbon for MB adsorption. Furthermore, the authors did not holistically elucidate on the mechanisms involved in MB adsorption onto *Delonix regia* pod activated carbon. For example the work of Ho *et al.*, [27] only elucidated on the adsorption equilibrium isotherms, while that of Vargas *et al.*, [28] and Ramish *et al.*, [26] only considered the adsorption isotherms and kinetics. None of the authors elucidated clearly on the nature of MB adsorption by employing thermodynamic models. Also, the authors did not consider the reusability and stability of the adsorbent in their various studies and also failed to carry-out experiments in involving real wastewater contaminated with MB in order to show its effectiveness for MB adsorption in the presence of other competing pollutants. Lastly, all the afore-mentioned studies have been carried out in different continents of the world, with non from tropical African regions. There is a probability that the biomass (*Delonix regia* pod) could exhibit varying properties when grown under various climatic conditions and agronomic practices. Thus it is suspected that the adsorbent characteristics and performance can vary slightly from region to region.

This study is aimed at evaluating *Delonix regia* pod activated carbon grown under a tropical climate as potential adsorbent for the removal of methylene blue from wastewater using zinc chloride as activating agent. Other specific objectives of this study meant to close the gaps identified in literature include: (i) to evalute the influence of activation temperature and method on the adsorptive characteristics of *Delonix regia* pod activated carbon, (ii) to identify the underlying mechanisms for MB adsorption by the adsorbent by employing kinetics and thermodynamic modeling approaches and (iii) evaluate the reusability potentials of the adsorbent. The novelty of the current work therefore lies in the above listed benign objectives.

2. Materials and methods

2.1 Materials, Instrumentation and Reagents

Delonix regia pods were collected locally on campus at the Federal University of Agriculture, Makurdi, and the seeds removed from the pods. The pods without seeds were washed with distilled water to remove dirt, dust and impurities, and then was sun dried. The sun dried materials were then ready for carbonization and activation.

All reagents used in the study were of analytical grade. Methylene Blue was purchased from Merck Company Germany. NaOH, NaCl, $ZnCl_2$ and H_2SO_4 were purchased form Pvt Ind. Ltd. India.

2.2 Carbonization and activation process

The two-step activation procedure was employed in the current study. The carbonization process was done using a muffle furnace in the Specialized Nutritional Laboratory at the Department of Animal Nutrition, College of Animal Science, Federal university of Agriculture, Makurdi-Nigeria. The sun dried *Delonix regia* pods were manually broken into pieces using a laboratory mortar and pestle. Table 1 details the instrumentations, laboratory wares and equipment employed in the present study.

Table 1: Materials and instruments used in the study

S/No	Equipment/Instrument	Description	Purpose
1	pH meter	Hanna pH meter-ModelHI98107	ustmentpH adj
2	Crucibles	250ml capacity	Carbonization
4	Measuring Beaker	250ml capacity	
5	Measuring cylinder	100 ml capacity	
8	Isothermal Magnetic shaker	Model HY-2	A gitation of sample solutions
9	Digital Watch		Timing
11	Reagents	Analytical grade	
12	Activated Carbons	DRPAC	Adsorbent
14	Portable Data logging Spectrophotometer	HACH model DR/2000	Determination of methylene blue concentration
15	Thermostatic Water Bath		
16	Digital Analytical Balance	Adam model PW 184	Weighng of samples
17	Murfle furnace	Carbolite Model	carbonization and activation
18	Electric Oven	Model	Drying samples
.19	Electric Milling machine	DFH 48 Model	Shreding of Samples
.20	SEM	JOEL Model JSM 7600F	Sample imaging
.21	FTIR Spectrometer	Nicolet Avarta	umFTIR Spectr
22	BET Surface Area and Porosity Analyzer	Shimadzu, Model SS-100	Determination of BEt surface area and porosities of DRPAC
.23	Set of Sieves		Seiving samples
24	rFlocculato	tuart Scientific Model SW1	Sample agitation
25	Laboratory Flasks	Erlenmeyer	
26	Filter paper	Whatman No 41 and 42	Filtration of samples

Thereafter, they were ready for carbonization and consequent activation. Before selecting the carbonization/activation temperature, a preliminary experiment was conducted to establish the optimum temperature for carbonization that produced the highest estimates of the carbon yield and specific surface area (Sear's method). The temperatures were varied as 400, 500, 600 and 700 ^oC and a residence time of 1 hour was maintained throughout the experiments. Thereafter the temperature of 600 ^oC was found as optimum (Results not presented here).

After carbonization, the sample was allowed to cool at room temperature for 4 hours, passed through a milling machine (Type DFH 48, Number 306961, Upm- 6000) and sieved. The Particles retained on the 300 µm sieve were weighed and taken for activation with Zinc Chloride solution at room temperature in the ratio of 1:2 by weight.

In chemical activation the degree of impregnation ratio plays an important role. It is the ratio of weight of anhydrous activation salt to the dry carbonized material. The effect of the degree of impregnation ratio on the porosity of the resulting product is apparent from the fact that volume of pores increases

with impregnation ratio. Based on the foregoing, the activation solution was produced by dissolving 50g of anhydrous Zinc Chloride in 100ml of distilled water. The *Delonix regia* pod powder was then soaked in the solution of Zinc Chloride ($ZnCl_2$) and left for about 24 hours to enable full activation, after which it was placed in a crucible(s) and heated in a muffle furnace at 600 ^oC for 30 minutes. Thereafter, the samples were removed from the furnace, allowed to cool in a desiccator and washed thoroughly with distilled water until the pH of the supernatant became neutral. The washed samples were then dried for 6 hours in an electric oven set at 110 ^oC. Thereafter, samples were removed from the oven, allowed to cool at room temperature, pulverized and sieved to particle size of 100 – 200 µm to produce *Delonix Regia* Pod Activated Carbon (DRPAC).

2.3 Adsorbent characterization

The prepared adsorbent (DRPAC) was subjected to some form of characterization in order to give insights on its adsorptive properties and potential adsorption mechanisms. Thus in the current study DRPAC was characterized for SEM, FTIR, BET surface area, porosities, bulk density and moisture content following standard procedures [30].

2.3.1 SEM and FTIR

The adsorbents were characterized using FTIR spectroscopy and Scanning Electron Microscopy (SEM). The IR spectrum of DRPAC was recorded using a Nicolet Avatar FT-IR spectrometer within the range 4000 cm^{-1} and 450 cm^{-1}, with KBr disc as reference. The surface morphology of the adsorbent was observed using Joel Model JSM 7600F Scanning electron microscope at magnifications of 500 × and 1000 ×, resolution of 200 um, 15 kV bright field and pressure of 70 Pa. Samples were coated with gold before being subjected to SEM analysis [30].

2.3.2 BET surface area and adsorbent porosities

The BET surface area, total pore volume and average pore diameter of DRPAC were determined using the BET surface area and porosity analyzer (Shimadzu, Model SS-100) according to the methods described by [31] with slight modifications. The sample was put in the measurement cup and sample thickness determined through a scale on the piston. The sample was then pressed with the piston, while ensuring that the sample thickness was between 5-15 mm and cross sectional area of sample bearing to be 2 cm^2. Nitrogen gas was allowed to pass over the samples at 77 K. The BET surface area and porosities were then estimated from the nitrogen adsorption isotherms following the Braumer-Emmet Teller equation. The total pore volume was taken as the volume of liquid nitrogen corresponding to the amount adsorbed at relative pressure = 0.99, Micropore volume was estimated using the Dubinin-Radushkevich equation, mesopore volume was taken as the difference between the total pore volume and micropore volume. The average pore diameter was estimated by the relationship; 4 (total pore volume)/BET surface area.

2.3.3 Determination of Bulk Density

A measuring cylinder was weighed and then filled with the prepared sample of DRPAC and gently tamped until no change in the level of the sample was observed. The volume occupied by the packed sample was recorded as V_s. If W_c were the weight of empty cylinder and W, the weight of the cylinder and sample, then, weight of the sample W_s was obtained by equation 1 while the bulk density was calculated using equation 2.

$$W_s = W - W_c \quad (1)$$

$$B_d(g|cm^3) = \frac{W_s}{V_s} \quad (2)$$

2.3.4 Determination of moisture content

Activated carbon is generally priced on a moisture free basis, although occasionally, some moisture content is stipulated in the range of 3-10 %. Some adsorbents when stored under humid conditions still adsorb considerable moisture over a period of time. They may absorb as much as 25 to 30 % moistures still look or appear dry. A sample of the DRPAC was weighed as W_1 (g). It was then heated in an oven to a temperature of 105 ^oC for 24 hours and then allowed to cool. It was weighed again to determine the final weight as W_2 (g). The moisture content was calculated using equation 3.

$$\% \text{ Moisture content } = \frac{W1-W2}{W1} \text{ X } 100 \% \quad (3)$$

2.4 Preparation of stock solution and batch adsorption experiments

A stock solution of methylene blue dye was prepared by dissolving 16 mL of the dye in 1 liter of distilled water. The stock solution prepared was tested for methylene blue concentration which was determined to be 226 PtCo.

Batch studies on methylene blue adsorption onto DRPAC were conducted. The study was based on the effect of contact time, adsorbent dose, temperature and pH at constant concentrations of methylene blue solution in the simulated wastewater. Solutions with initial concentrations of 226 PtCo were placed in Erlenmeyer flasks to which a particular mass (0.2 – 1.0 g) of the produced activated carbon (DRPAC) was added and kept in a flocculator (Stuart Scientific model SW1) at a constant speed of 99 rpm at different temperatures considered for the stated duration to reach equilibrium. Temperature variations were carried out by placing the flocculator with content in a variable temperature water bath. All samples were filtered with a Whatman filter No 42 prior to analysis in order to minimize interference of the carbon particles during the analysis.

Direct reading spectrophotometer (DR/2000) manufactured by HACH was used for colour measurements: A programme number of 120 was entered and set at a wavelength of 455nm and the unit PtCo colour was displayed. A blank of 25 mL of deionized water was measured into the sample cell and placed in the cell, while the cell holder light shield was kept closed. The zero key was pressed and the reading displayed (0.00 PtCo) noted. The blank was thereafter removed and 25mL of water sample was measured using the sample cell bottle and placed into the light shield and then closed and the sample colour content was read directly from the display.

2.4.1 Effect of adsorbent dose

To determine the optimum adsorbent dose of *Delonix regia* pod activated carbon (DRPAC), the adsorbent was added to the Erlenmeyer flasks in varying amounts (0.2, 0.4, 0.6, 0.8 and 1.0 g), containing 100 mL concentration of Methylene Blue (MB) at a constant pH of 7. The solution in the Erlenmeyer flask was subjected to stirring in a flocculator at a speed of 99 rpm for optimum contact time, filtered and analysed for residual methylene blue concentration. The dosage which gave the minimum residual concentration was chosen as the optimum dosage.

2.4.2 *Effect of solution pH*

The extent of adsorption is strongly influenced by the pH at which adsorption is carried out. The effect of pH on MB adsorption on DRPAC was studied by performing batch adsorption tests at different initial pH values ranging from 4 – 10. The solution pH was adjusted using H_2SO_4 and NaOH as the need arose. The pH at maximum methylene blue removal was taken as the optimum pH.

2.4.3 Effect of contact time

The adsorption is also known to be strongly influenced by the contact time. To study the effect of contact time on MB adsorption on DRPAC, 100mL of 226 (mg/L) concentration of methylene blue solution at

pH 7.0, was mixed with 0.6 g of activated carbon (DRPAC), and stirred at different contact times varied from 10 – 60 minutes. At the end of each contact time, the filtrate was analysed for residual methylene blue concentration using the (DR/2000) HACH spectrophotometer.

2.4.4 Effect of temperature

Temperature has been shown to greatly affect colour removal in wastewater by adsorption technology. In the current study, experiments were carried out at optimum conditions of 40 minutes (contact time), pH of 7 and 0.6 g (adsorbent dosage) at varying temperatures of 20, 30, 40, 50, and 60 ^{o}C respectively, in a variable temperature water bath to elucidate on the effects of temperature on MB adsorption on the newly synthesized adsorbent (DRPAC). The Methylene blue removal efficiency (E) and adsorption capacity (q_e) of the adsorbent were calculated using Equations 4 and 5 respectively.

$$E\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (4)$$

Where

C_o and C_e are the initial concentration of MB in wastewater and the equilibrium concentration of MB in wastewater, respectively.

$$q_e\ (mg/g) = \frac{(Co - Ce)V}{W} \quad (5)$$

Where,

C_o= Initial MB concentration in wastewater before treatment in mg/L

C_e= Equilibrium concentration of MB in wastewater after treatment in mg/L

V = Volume of the solution (L) and

W = Mass of dry adsorbent used (g)

2.5 Equilibrium isotherm modeling

The Langmuir and Freundlich equilibrium isotherm models were adopted to analyze the adsorption data of the current study with a view to elucidate on the type of adsorption responsible for MB adsorption on DRPAC. The Langmuir isotherm model is employed based on monolayer adsorption of adsorbate on homogeneous active sites and thus saturation is attained, beyond which no further attachment of adsorbate on adsorbent takes place. It also operates with the assumption that there is no interaction between the adsorbed molecules on adjacent sites [32]. The linear form of the Langmuir model is presented in Equation 6.

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \quad (6)$$

where, Ce is the equilibrium concentration in liquid phase (mg/L), q_m is the monolayer adsorption capacity (mg/g), q_e is the equilibrium adsorption capacity (mg/g) and k_L is the Langmuir constant related to the free adsorption energy (L/mg). A plot of C_e/q_e vs C_e should yield a straight line from where k_L and q_m can be estimated from the slope and intercept of the plot respectively.

The separation factor (RL) whose value determines the nature of the isotherm shape is an important feature of the Langmuir isotherm. It represents favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible adsorption ($R_L = 0$). The dimensionless parameter is given by equation 7.

$$R_L = \frac{1}{1 + k_L C_o} \quad (7)$$

C_o (mg/L) is the maximum initial MB concentration and k_L (L/mg) is the Langmuir equilibrium constant. The Freundlich isotherm is the oldest known two parameter adsorption model, which is applied for multilayer, heterogeneous adsorption sites and is expressed in its linear form as in equation 8.

$$Log q_e = Log k_f + \frac{1}{n} Log C_e \quad (8)$$

k_f is a constant indicative of the adsorption capacity of the adsorbent (mg/g) and the constant 1/*n* indicates the intensity of the adsorption. Similarly, a plot of $Logq_e$ vs $LogC_e$ should yield a straight line from where the constants could be estimated from the intercept and slope of the line respectively [32].

2.6 Adsorption kinetic modeling

The linear forms of the pseudo first order (PFO) and pseudo second order (PSO) kinetic models were applied in the current study to give insight into the mechanisms controlling methylene blue adsorption on DRPAC. The linear forms of the kinetic models are presented in equations 9 and 10 for PFO and PSO respectively.

$$Log(q_e - q_t) = Logq_e - k_{ad}t \quad (9)$$

where, k_{ad} is the constant of pseudo-first-order adsorption rate; q_e is the bio-sorption capacity at equilibrium; and q_t is the bio-sorption capacity at time *t*. The adsorption rate (k_{ad}) was calculated from linear regression analysis from the slope of linear plot of experimental data ($Log(q_e - q_t)$ vs *t*).

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

where, k_2 is the constant of pseudo-second-order rate; q_e is the adsorption capacity at equilibrium; and q_t is the adsorption capacity at time *t*. The equilibrium adsorption capacity and the second-order rate constant were estimated from the slope and the intercept of the plot t/q_t against *t*.

2.7 Thermodynamic studies

The data generated from the effects of temperature on MB adsorption was used for thermodynamic modeling of MB adsorption on DRPAC. Thus the thermodynamics parameters of change in enthalpy (ΔH^o), change in entropy (ΔS^o) and change in Gibbs free energy (ΔG^o) were determined using the following equations (11 – 13):

$$\Delta G^o = -RTlnk_o \quad (11)$$

$$k_o = q_e/C_e \quad (12)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (13)$$

Where, k_o is the equilibrium constant, R is the gas constant (8.314 kJ/mol/K) and t is the solution temperature (K). From equation10, the values of ΔS^o and ΔH^o can be determined respectively from the slope and intercept of the plot of ΔG^o vs T [32].

3. Results and discussion

3.1 Characterization of adsorbent

The characteristics of the adsorbent are presented in Table 2, while the results of SEM and FTIR analysis are presented in Figures 2 &3. From Table 2, it was observed that the BET surface area, total pore volume, micro-pore volume, meso-pore volume and average pore diameter of DRPAC were 3943 m^2/g, 2.82 cm^3/g, 1.53 cm^3/g, 1.29 cm^3/g and 3.16 nm respectively. It was generally noticed that DRPAC possessed very high surface area, and porosities, with an almost uniformly distributed micro and meso-pore structure, which makes DRPAC suitable for diverse applications in environmental remediation. This could be attributed to the type and ratio of activation agent used in the current study ($ZnCl_2$) as well as the high temperature of carbonization and activation. At high temperature the pore structures of the adsorbent are better developed and also further enhanced by the type of activating agent employed. The characteristics of the DRPAC reported for the current study are slightly higher than those reported by [28] , probably as a result of the lower carbonization temperature (400 ^oC) employed by the authors as well as the difference in the reactivity of the activation agent (NaOH) used in their study. These findings holds to support the initial hypothesis that both temperature and activation method affect the quality of

the adsorbent even if derived from the same parent materials and also point to the direction that DRPAC is suitable for application in adsorption technologies targeted at both high and low molecular weight compounds such as MB and other micro-pollutants.. The bulk density and moisture content of DRPAC were found to be 0.61 g/cm^3 and 2.73 % respectively (Table 2). This is an indication that the adsorbent is suitable application in a wide range of environmental remediation works including gaseous adsorption systems. The low moisture content points to the fact that the adsorbent has high potentials for storage over a long period of time without adsorbing excessive moisture from the environment. High bulk density shows that adsorbent (DRPAC) also possess high attrition value which guarantees its reusability and stability when in use. SEM image with its 3D projection (Figure 2) shows that DRPAC has well developed pore structure dominated with an almost evenly distributed micro-pore and mesopore structure. This is likely the reason for the high surface area recorded for the adsorbent. As earlier stated, the activation method/ratio used in this study is largely responsible for the well- developed pore structure of DRPAC. The SEM image obtained for the current study is better developed but however comparable with those reported by [27] and [28].

Table 2: Characteristics of DRPAC

S/No	Characteristic	Value
1	Bulk Density (g/cm^3)	0.61
2	Moisture Content (%)	2.73
3	BET Surface Area (m^2/g)	3943
4	Total Pore Volume (cm^3/g)	2.82
5	Micro-pore Volume (cm^3/g)	1.53
6	Meso-pore Volume (cm^3/g)	1.29
7.	Average Pore Diameter (nm)	3.16
.8	Micropore Percent	54.25
.9	Mesopore Percent	45.74

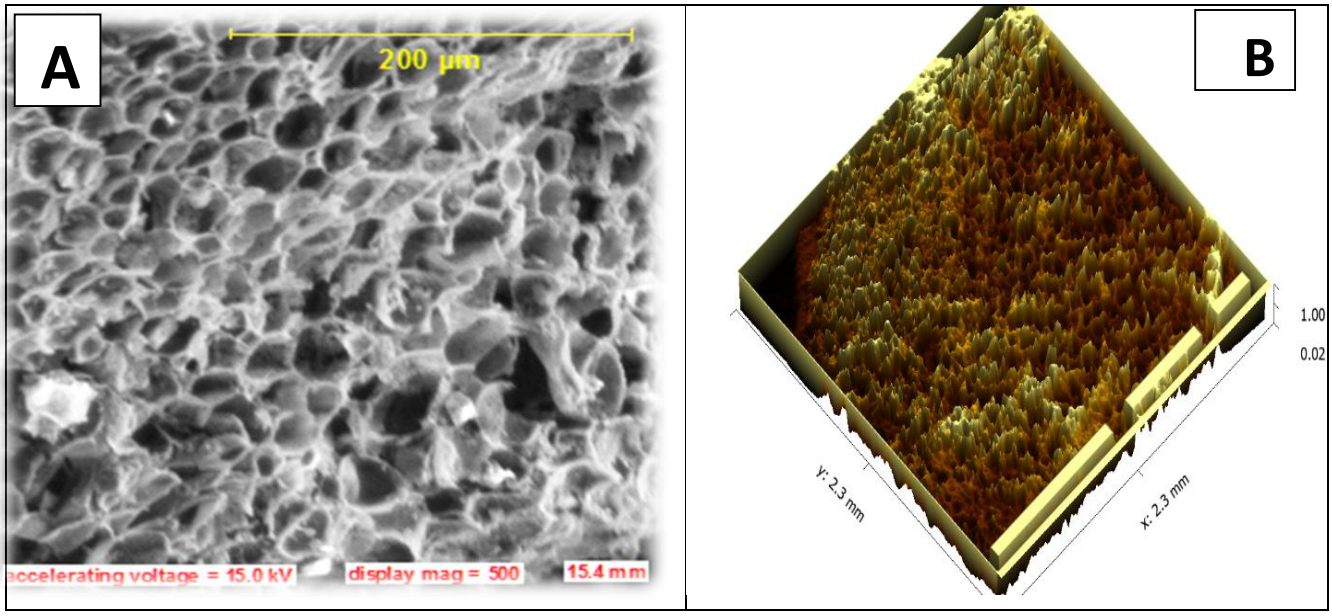

Figure 2: (A) SEM Image of DRPAC, (B) 3D Projection of Porosities of DRPAC

FTIR spectra of DRPAC (Figure 3) revealed several peaks on the surface of DRPAC. The peaks found at 1996.21 and 1852.28 cm^{-1} could be assigned to overtones or weak aromatic stretches. The peaks at 3726.11 and 3684.22 cm^{-1} can be assigned to the O-H stretching and H-bonding of alcoholic phenols, those at 2964.59 and 2913.00 cm^{-1} can be assigned to the C-H stretching of alkanes. The peaks at 1622.65

and 1599.61 cm^{-1} could be assigned to the N-H bend of alkenes, while those at 1066.00 and 1033.00 cm^{-1} can be assigned to the C-N stretching of aliphatic amines. The peaks at 667.41 and 564.37 cm^{-1} can be assigned to the C-Cl stretch of alkyl halides. Similar peaks were reported by [31] in their studies on preparation and characterization of NaOH-modified *Delonix regia* pod activated carbon as well as [33] in their work on removal of MB dye from solution using KOH and CO_2 modified periwinkle shells as adsorbents.

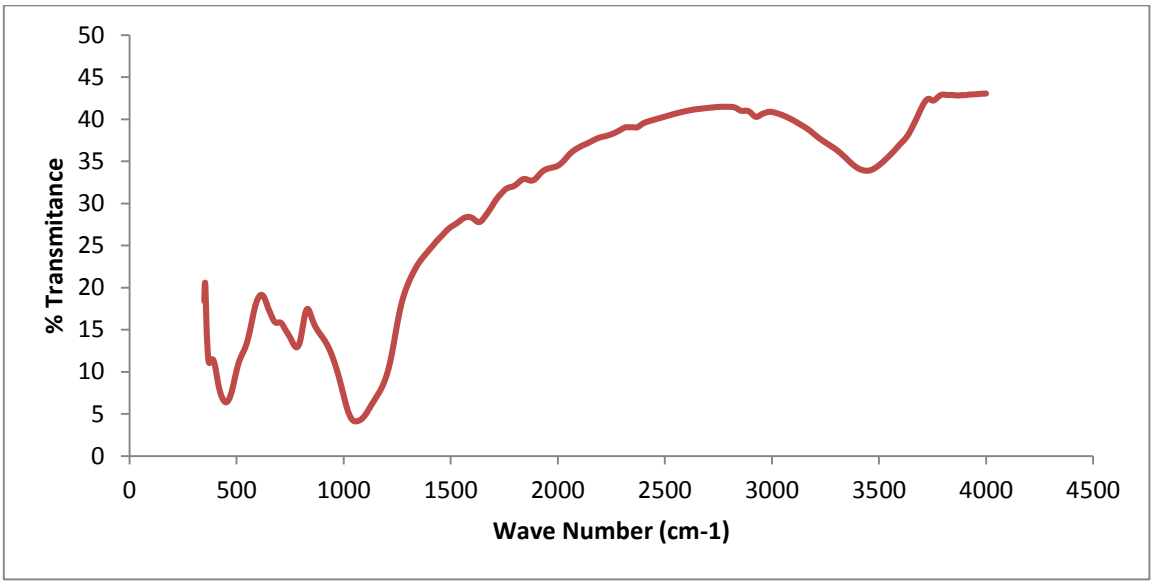

Figure 3: FTIR Spectrum of DRPAC

3.1 Effect of adsorbent dosage

Results of the effects of adsorbent dosage on MB removal efficiency and adsorption capacity are presented in Figure 4. It was observed that the least removal efficiency of 64.6 % was observed at the adsorbent dose of 0.2 g, while the adsorbent dose of 0.6 g gave the highest removal efficiency of 88.5 %. Beyond the adsorbent dose of 0.6 g, no further increase in adsorption was observed. The increase in removal efficiency with increase of adsorbent dose is however expected due to the fact that the higher the adsorbent dose in the solution, the greater the available exchangeable sites for the ions. Hence, the optimum adsorbent dose was found to be 0.6 g.

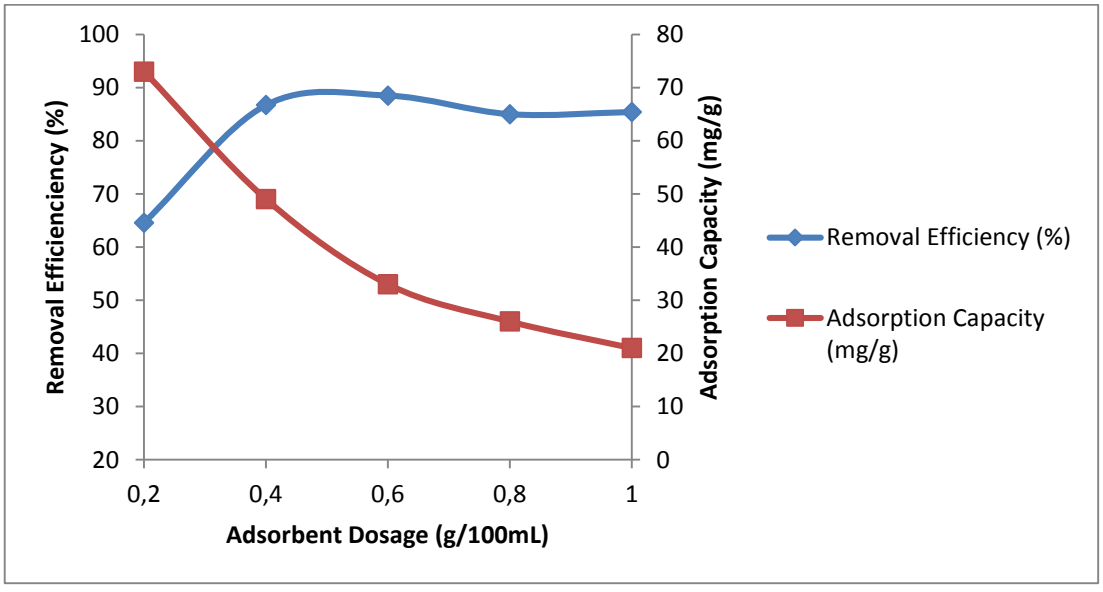

Figure 4: Effect of Adsorbent Dosage on MB Removal by DRPAC (pH = 7; T = 30 ^{0}C; Contact time = 40 min)

Conversely, the adsorption capacity of DRPAC for MB removal was observed to be decrease from 73 – 21 mg/g as the adsorbent dosage was increased from 0.2 – 1.0 g/100mL. The decrease of adsorption capacity with increasing adsorbent dose suggests heterogeneity of the adsorbent surface sites. According to the surface site heterogeneity model, the adsorbent surface is composed of sites with a wide spectrum of binding energies. At low dosage for such adsorbents, all types of sites are entirely exposed for MB adsorption and the surface get saturated faster resulting in a higher value of the adsorption capacity (q_e). At higher adsorbent dose, however, the availability of higher energy sites decreases with a large fraction of lower energy sites occupied which results in a lower adsorption capacity [34-35]. The observed trend in the current study agrees with the observations of *[36]* and *[37]* who also reported a decrease in adsorption capacity of their adsorbent for Pb (II), Cu (II), Ni and hexavalent chromium ions respectively as adsorbent dosage was increased.

3.2 Effect of pH

The pH of solution has the ability to alter the surface charge of adsorbents, thus influencing its adsorption potentials. Therefore, it is an important parameter to be studied in any adsorption experiment. For the current study, the effect of pH on the removal of MB from aqueous solution was investigated by varying the solution pH from 4 - 10. Figure 5 shows the graph of percentage of methylene blue removed against pH at constant contact time 40 minutes and carbon dosage of 0.6 g/100 mL as well as the amount of MB adsorbed per gram of DRPAC at varying solution pH values. From Figure 5, it can be seen that both removal efficiency and adsorption capacity were slightly increased as the pH of the solution increased from 4 -7. Beyond pH 7, it was noticed that both removal efficiency and adsorption capacity began to decrease. Thus pH 7 was taken to be the optimum for effective MB removal by DRPAC. This is because pH affects the solubility of the dye, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [38].

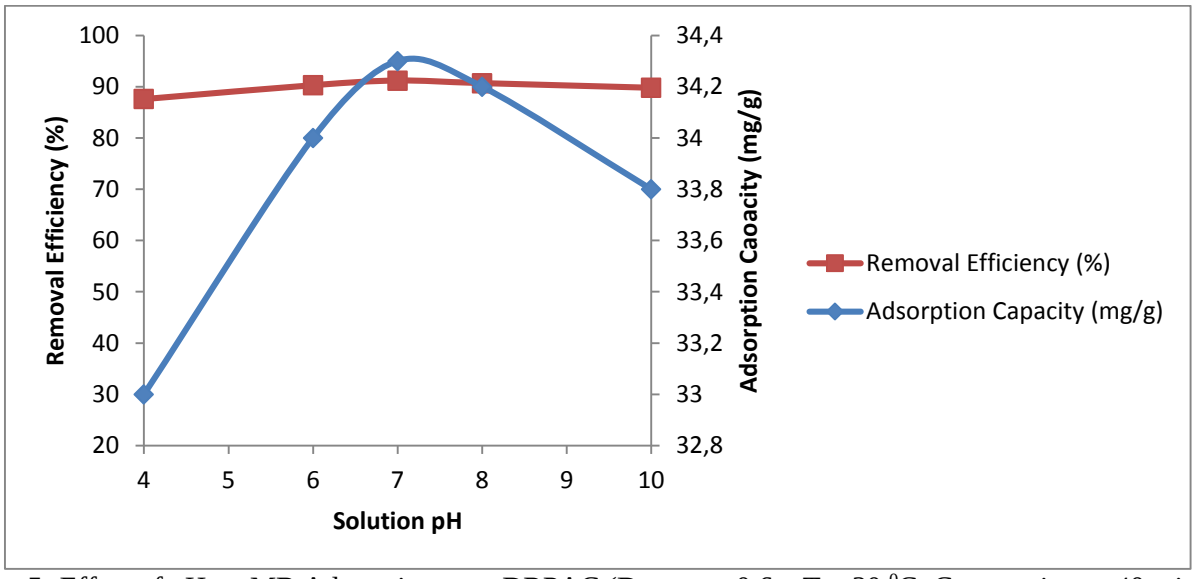

Figure 5: Effect of pH on MB Adsorption onto DRPAC (Dosage = 0.6g; T = 30 ^{0}C; Contact time = 40 minutes)

When the pH of the adsorbing medium was increased from pH 4 - 7, there was a corresponding increase in deprotonating of the adsorbent surface leading to a decrease in the H^+ ion on the surface of the adsorbent. This created more negative charges on the adsorbent surface, thus, favouring adsorption of positively charged species onto the adsorbent (DRPAC) surface. Although the pH of point of zero charge (pH_{pzc}) of DRPAC was not succinctly determined in the current study, the observed effect of pH on MB adsorption onto the studied adsorbent is a pointer to the likelihood of the pH_{pzc} of DRPAC falling in the

alkaline pH range. The optimum removal efficiency of 91.2% was observed at pH 7 with a corresponding adsorption capacity of 33.4 mg/g. Generally, it was noticed that pH had mild effect on the MB adsorption potentials of DRPAC as the removal efficiencies and adsorption capacities recorded for all pH ranges studied were found to be satisfactory. Again, the findings of this study are in agreement with those of [25], [39] who also noticed slight influence of pH of wastewater solution on pollutants' removal effectiveness and posited that adsorption was more favourable within the acidic to neutral pH range of the solutions.

3.3. Effect of Contact Time

Results of the effects of contact time are as shown in Figure 6. It was noticed that when contact time was increased from 10 – 40 minutes, the removal efficiency of methylene blue also increased from 96.9 % to 100 % and similarly, the adsorption capacity was found to increase from 36.5 – 37.7 mg/g. It can be seen that both MB removal efficiency and adsorption capacity of the adsorbent generally improved slightly with increasing contact time (Fig. 6) because the adsorption reaction was found to be spontaneous and rapid in nature. This could be attributed to the fact that at longer contact times, the adsorbate (MB) has more time to be adsorbed on the surface of the adsorbent and also diffuse into the pores, thus creating room for more adsorption sites. Just like with pH, contact time was also found to exhibit limited influence on the removal MB from aqueous solution using DRPAC. Beyond 40 minutes which is was chosen as the equilibrium time, the adsorption capacity and removal efficiency remained constant under operating conditions. This was because micro-pores of the adsorbent became filled up when contact time reached 40 minutes, so a further increase in contact time only lead to a resistance to the diffusion of aggregated dye molecules in the adsorbent, thus preventing any further adsorption reaction [21]. Hence, the optimum contact time was observed to be 40 minutes. This finding is in line with those of several authors [37], [41], [42] who also posited in their various studies that adsorbate removal efficiency and adsorption capacity increase with an increase in contact time up to a maximum point where further increase in time does not accompany any significant increase in pollutant removal efficiency or adsorption capacity.

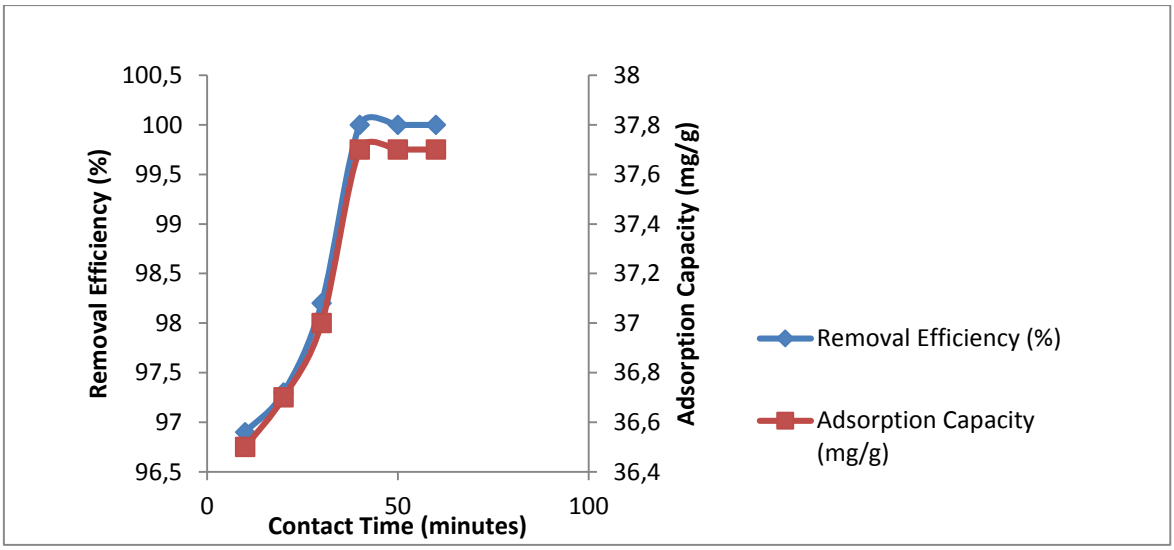

Figure 6: Effects of Contact time on MB Adsorption onto DRPAC (Adsorbent dose = 0.6 g; pH = 7; T = 30 ^{0}C)

3.4 Effect of Temperature

The effects of temperature on MB adsorption on DRPAC are shown in Figure 7. It was observed from Figure 7 that the amount of methylene blue removed by DRPAC increased as the temperature increased. Similarly it was found that methylene blue removal efficiency of DRPAC increased from 93.8 % to 96.5

% when temperature was increased from 20 °C to 30 °C and remained fairly constant as temperature was increased to 60 °C, This is because increase in temperature increases the movement of the solute [24].

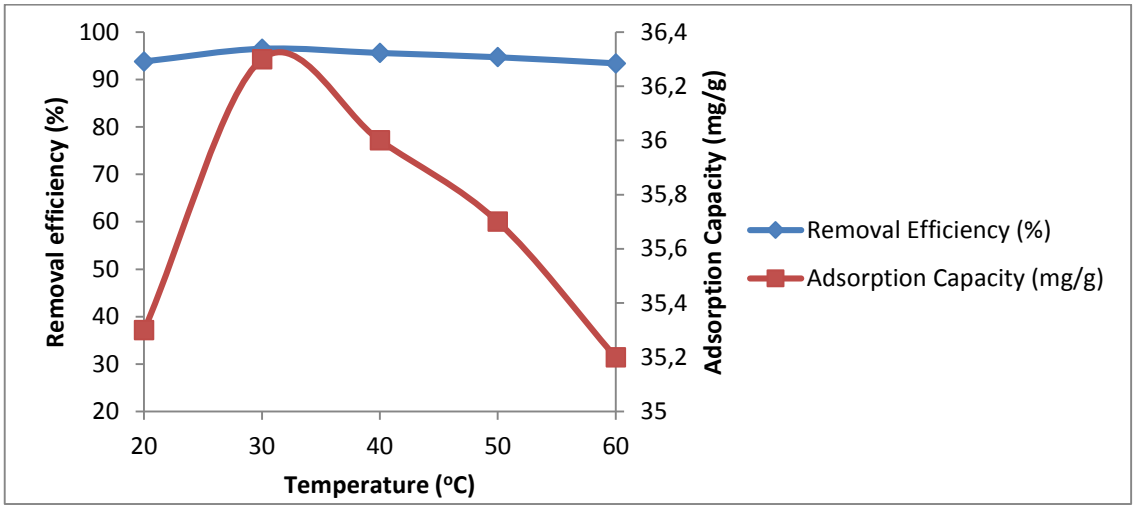

Figure 7: Effect of Temperature on MB Adsorption onto DRPAC (Contact time = 40 min; pH = 7; Adsorbent dose = 0.6 g)

This trend is not well understood but may be related to the excitation energy of the MB molecules in solution as temperature increased drastically and can also be linked to a possible desorption of MB back into solution at elevated temperatures. Hence, the optimum temperature was found to be 30 °C. A similar trend was observed for the adsorption capacity as it increased from 35.3 – 36.3 mg/g, when temperature was raised from 20 – 30 °C, further increase in temperature beyond 30 °C, resulted in a decrease in the adsorption capacity (Figure 5). Therefore, 30 °C was taken as optimum for efficient MB removal by the studied adsorbent. This trend could be linked to the non-exothermic nature of the MB adsorption reaction on the surface of DRPAC, which made the reaction to be non-enthalpy driven [9], thus making temperature to be slightly influential to the adsorption process just as it was with solution pH. A similar result was obtained by [40] in their study of MB adsorption onto $ZnCl_2$ modified tea seed shells. The slightly positive effect of temperature on fluoride removal efficiency and adsorption capacity from aqueous solution is an indication that active sites present on the surface of the adsorbents increase and expand with increase in temperature and thus improves adsorption performance [41]. A similar observation was reported for adsorption of hexavalent chromium from aqueous solution by *Leucaena leucocephala* seed pod activated carbon [37].

3.5 Equilibrium Isotherm Modeling

The adsorption data was fitted to the Freundlich and Langmuir equilibrium isotherm models (Figures 8 and 9) respectively. It was observed that the adsorption of methylene blue onto the synthesized adsorbent was well described by the two models with R^2 values of 0.9102 and 0.7114 respectively. This is an indication that methylene blue adsorption on Delinox regia pod activated carbon is more of a physisorption than a chemisorption process but could also involve both processes. This suggest that the process involved in MB adsorption on DRPAC may be better described with more complex isotherms such as the Temkin, Redlich-Peterson and Sipps isotherm models [9]. The parameters of the Langmuir and Freundlich models are as presented in Table 3. From Table 3, it was observed that the Langmuir constant (k_L) related to free energy of adsorption was found to be 0.0094 L/mg, indicating the highly endothermic nature of the process. The Langmuir monolayer adsorption capacity of methylene blue onto DRPAC was found to be 175.4 mg/g, suggesting that methylene blue was well adsorbed on the adsorbent when monolayer adsorption theory is considered.

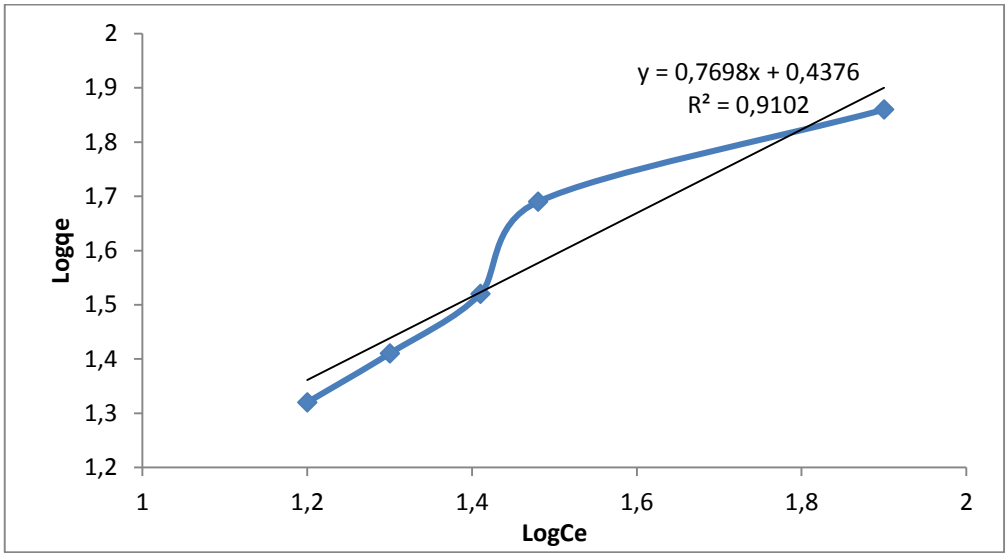

Figure 8: Freundlich Isotherm Plot of Methylene Blue Adsorption on DRPAC

Furthermore, the separation factor obtained (R_L = 0.32) for methylene blue adsorption on DRPAC indicate that the adsorption process was favourable ($0 < R_L < 1$). This further supports the earlier suggestion that methylene blue adsorption on DRPAC is not just a monolayer type of adsorption and thus cannot be completely described by the Langmuir isotherm alone as also evidenced in the moderate R^2 value of 0.7114. Conversely, the adsorption capacity of DRPSAC for methylene blue which is denoted as k_f in the Freundlich model was found to be 2.739 mg/g, with an R^2 value of 0.9102. This suggest that methylene blue adsorption on DRPAC is better described by the Freundlich isotherm as compared to the Langmuir isotherm, thus indicating that the adsorbent comprised of heterogeneous surface and as such physisorption was more dominant in the adsorption process. Furthermore, according to the Freundlich isotherm, the intensity of the adsorption process indicated by the value 1/n was found to be 0.7698, which further shows that the process was favourable. The finding of the current study compares well with others reported in literature [37], [6] but contrast with the work of [9] who found out that MB bio-sorption onto a low-cost *Citrus sinensis* bagasse was more of a chemisorption process than a physisorption process as the adsorption data was better fitted to the Langmuir model as compared to the Freundlich model.

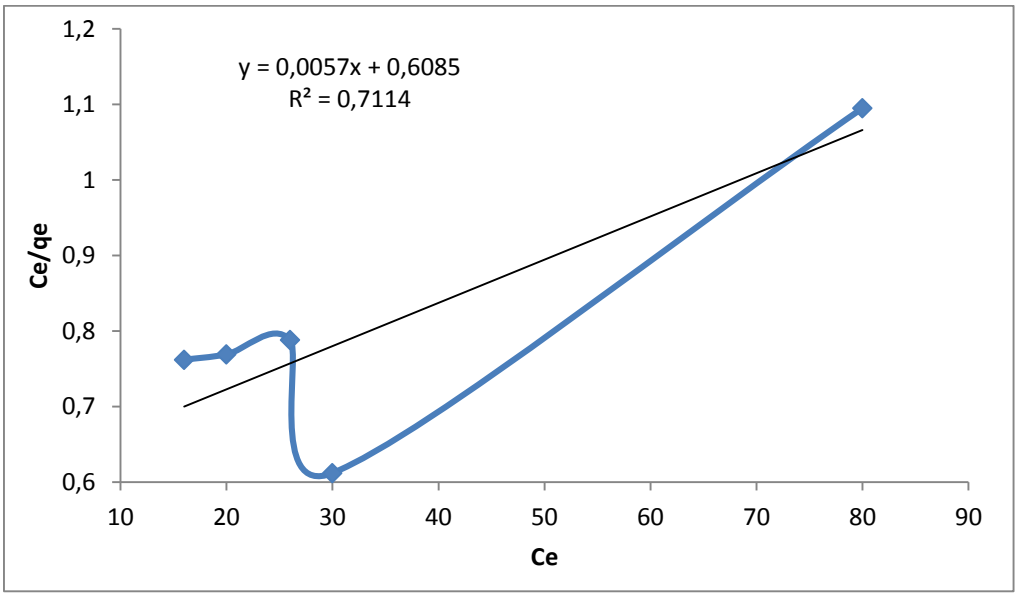

Figure 9: Langmuir Isotherm Plot for Methylene Blue Adsorption on DRPAC

Table 3: Isotherm parameters of Methylene Blue Adsorption on DRPAC

S/No	Isotherm Model	Model Parameter	Value
.1.	Freundlich	1/n	0.7689
		n	1.30
		k_f (mg/g)	1.457
		R^2	0.9102
2.	Langmuir	q_m (mg/g)	175.4
		k_L (L/mg)	0.0094
		R_L	0.32
		R^2	0.7114

3.6. Adsorption Kinetics

Results of methylene blue adsorption kinetic on DRPAC are presented in Figures 10 and 11 respectively for pseudo first order (PFO) and pseudo second order (PSO) kinetic models. From Figures 10 and 11, it was observed that the adsorption kinetic was well described by both the PFO (R^2 = 0.969) and PSO (R^2 = 0.999) models. This is another indication that both physisorption and chemisorption are deeply involved in the adsorption of MB onto DRPAC. [2], [6] also reported a better fit of the PSO model as compared to the PFO and Elovich models in their study on MB adsorption onto a low-cost adsorbent. The kinetic model parameters necessary for design of full scale adsorption systems were calculated for both the PFO and PSO and the results are as presented in Table 4. From Table 4, it can be seen that the equilibrium adsorption capacity was found to be 1.60 and 38.17 mg/g respectively for PFO and PSO kinetic models, similarly the kinetic constants (k_{ad} and k_2) were obtained as 0.0115 min^{-1} and 0.042 ($gmg^{-1}min^{-1}$) for PFO and PSO kinetic models respectively.

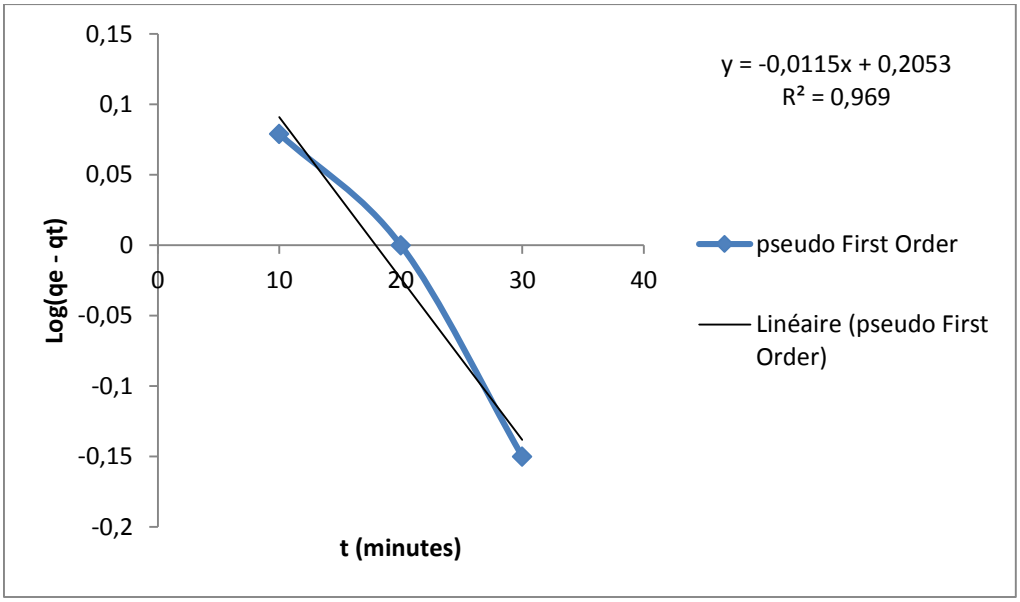

Figure 10: Pseudo First Order Kinetic Plot for Methylene Blue Adsorption on DRPAC

The higher values of the equilibrium capacity, which is close to the experimental value as well as the kinetic constants in the PSO model as compared to that of the PFO indicates that methylene blue adsorption on DRPAC is better described by the PSO kinetic model, which supports the insinuation that the process is rather a complex one than just chemisorption or physisorption as earlier evidenced in the isotherm study. There is need to evaluate the process with other kinetic models such as the intra-particle

diffusion model and the pore diffusion models in order to identify the actual mechanisms and rate limiting steps involved. These findings are in tandem with those of [32] who studied fluoride adsorption from groundwater by aluminium oxide coated pumice in the Northern region of Ghana as well as those of [23] who studied Erythrosine B dye removal by salt activated Raffia *hookeri* seeds.

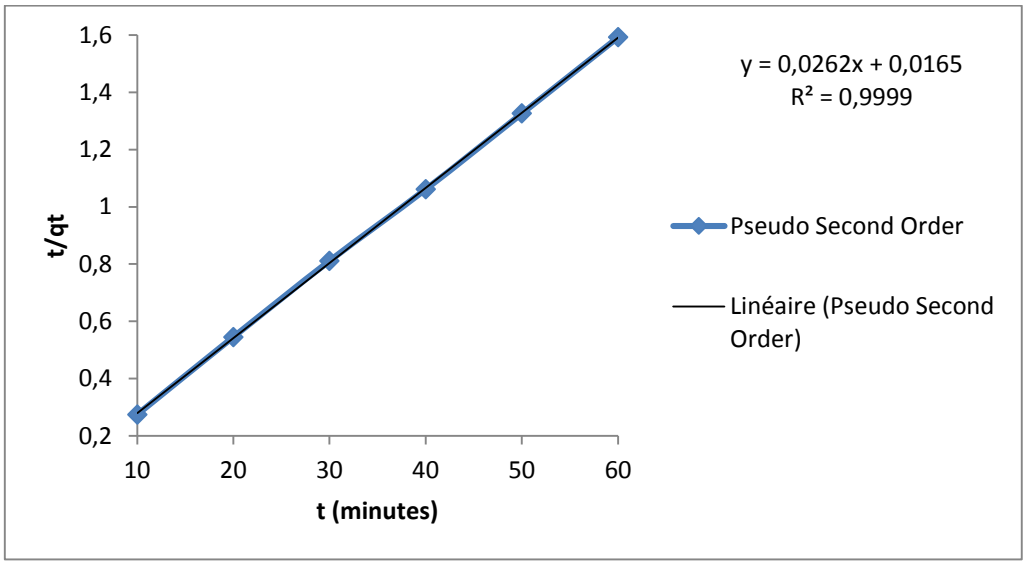

Figure 11: Pseudo second order Kinetic plot for Methylene Blue Adsorption on DRPAC

Table 4: Kinetic parameters of Methylene Blue Adsorption on DRPAC

S/No	Kinetic Model	Model Parameter	Value
1	Pseudo First Order	$K_{ad}(min^{-1})$	0.0115
		q_e (mg/g)	1.60
		R^2	0.969
2.	Pseudo Second Order	K_2 ($gmg^{-1}min^{-1}$)	0.042
		q_e (mg/g)	38.17
		R^2	0.999

3.7 Thermodynamic studies

The effects of temperature on the adsorption of MB onto DRPAC was studied and the thermodynamic parameters that explain the feasibility, spontaneity and nature of the adsorbate-adsorbent interactions (ΔG°, ΔS° and ΔH°) were estimated mathematically using the Van't Hoff's equation [7, 9] and results are as presented in Table 5. From Table 5, it can be inferred that the negative values of the Gibbs free energy (ΔG°) in kJ/mol at the various temperatures is an indication that MB adsorption on DRPAC is a spontaneous process. On the other hand, the positive values of enthalpy (ΔH°) and entropy (ΔS°) shows that the process is endothermic and feasible (entropy driven) [43] and as such cannot be said to be enthalpy driven or temperature dependent. The feasibility of the process also indicates that there was increase in randomness at the solid-liquid interface during the adsorption of MB onto DRPAC. The randomness at the solid-liquid interface could be linked with the higher translational entropy acquired by the displaced water molecules as compared to that lost as a result of dye uptake [7], [35]. The estimated value of ΔH° (13.39 kJ/mol) indicates that a more physical adsorption process occurs rather than a purely physical or chemical process, because the heats of chemisorption generally fall in a range of 80–200 kJ/mol and for physisorption are >40 kJ/mol [35]. In contrast, the adsorption of MB on low-cost *Citrus sinensis* bagasse was found to occur non-spontaneously and to be exothermic in nature [9]. The findings of the current study however agree with those of [7] who observed a similar thermodynamic

trend for Rhodamine B dye adsorption on *Raffia hookeri* epicarp-derived bio-sorbent and also that of [26] who reported that MB adsorption on *Delonix regia* pod activated carbon was endothermic, spontaneous and feasible.

Table 5: Thermodynamic Parameters of MB Adsorption on DRPAC

Adsorbent	ΔH°	ΔS°	ΔG° (kJ/mol)				
	(kJ/mol)	(J/mol/K)	293 K	303 K	313 K	323 K	333 K
DRPAC	13.39	54.49	-2.24	-3.80	-3.33	-2.93	-2.35

3.8 Regeneration studies and comparison of adsorbent performance

Regeneration studies were conducted on the MB loaded DRPAC using NaOH at a concentration of 20% in batch mode. MB adsorption-desorption was repeated for five consecutive cycles. Firstly, 100mL of 226 mg/L was mixed with 0.6 g of adsorbent and stirred at 99 rpm at room temperature (32.5 °C) for 40 minutes. Thereafter, the DRPAC was washed severally with deionized water to remove the excess MB on the adsorbent. Next, the DRPAC was treated with 100 mL of 20% NaOH solution contained in a separate flask and agitated at room temperature at a speed of 99 rpm for 20 minutes. Then the solution was filtered on a Whatman filter paper No 42 and the filtrate was analyzed for MB concentration as reported earlier in this study. The results are as presented in Figure 12.

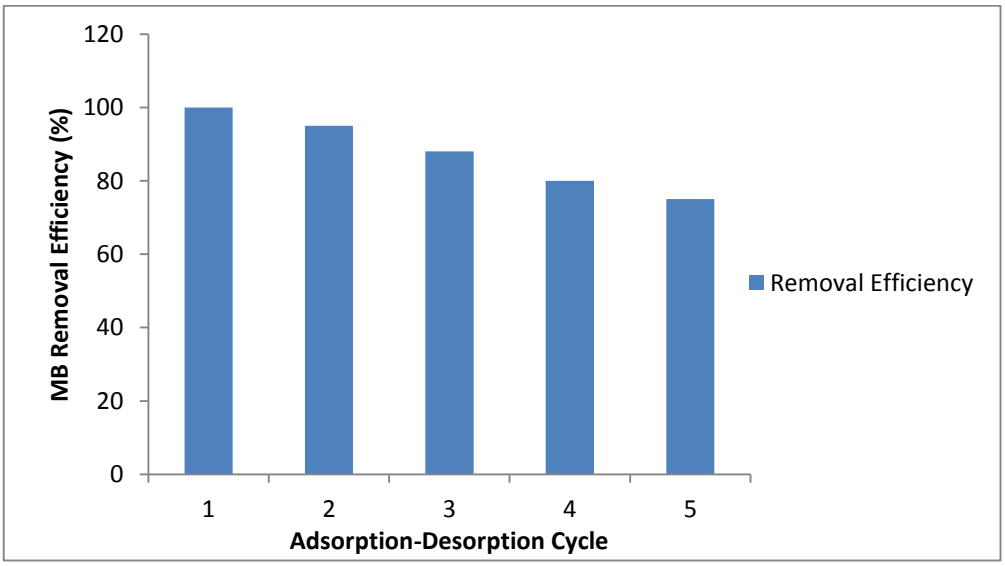

Figure 12: DRPAC regeneration and Usability

From Figure 12, it was observed that the MB adsorption ability of the adsorbent decreased with increase in adsorption-desorption cycles, probably as a result of a slight loss in adsorbent amount due to attrition as well as a reduction in the porosity of the adsorbent after several uses. Generally, the MB adsorption of DRPAC decreased from 100 -75 % as the regeneration cycles increased from 1 – 5. The findings of this study agree with those of [44] who also reported a decrease in MB adsorption potential of rice straw-based activated carbon regenerated with 0.1 M H_2SO_4 up to four cycles. The comparisons of the current work with other similar studies are as presented in Table 6. It was observed that the Langmuir maximum capacity of the studied adsorbents was mostly a function of the initial MB concentration, suggesting that q_m generally increased as initial MB concentration increased. Based on the foregoing, the current work therefore compares favorably with other studies reported in literature (Table 6).

Table 6: Comparing MB adsorption potentials for Various Adsorbents

S/No	Precursor	Activating Agent	Initial MB Concentration (mg/L)	Max. Langmuir Adsorption Capacity (q_m) (mg/g)	Reference
1	Bone Meal	Nil	100	22.72	[45]
2	Delonix regia pods	H_2SO_4	80	23.3	[27]
3	Sewage Sludge	$CaSO_4$	400	131.8	[46]
4	Almond shell/Zr_3O Composites	KOH	200	208.33	[47]
5	Rice straw	H_2SO_4	60	62.5	[44]
6	Tea waste	Nil	100	113.14	[48]
7	Coconut husk	$ZnCl_2$	900	500	[49]
8	Delonix regia pod	NaOH	1000	874.68	[28]
9	Acacia Modesta	HNO_3/HCl	NG	NG	[50]
10	Periwinkle shells	KOH/CO_2	500	500	[33]
11	Delonix regia pod	$ZnCl_2$	200	364.4	[26]
12	Raphia fibre	Nil	300	34.70	[51]
13	Cucumeropsis mannii NAUDIN	Nil	100	47	[52]
14	Citrullus lanata Rind	$ZnCl_2$	400	>200	[53]
15	Tea seed shells	Nil	400	324.7	[40]
16	Delonix Regia Pod	$ZnCl_2$	226	175.4	This study

4. Conclusion and Recommendations

In the current study, it is concluded that pH, contact time and temperature had mild effects on MB adsorption onto DRPAC, while adsorbent dosage was found to significantly affect the process. The optimum conditions of adsorption were found to be: adsorbent dose of 0.6 g, pH of 7, and temperature of 30 ^oC and contact time of 40 minutes. At optimum conditions, MB removal efficiencies were found to be 88.5%, 91.2%, 96.5% and 100% respectively for the parameters studied. Equilibrium isotherm modeling indicated that the adsorption of MB onto DRPAC was well described by both the Freundlich and the Langmuir models with Freundlich model having a better fit (R^2 = 0.9102), thus suggesting that physisorption was the main adsorption pathway. On the other hand the pseudo second order model fitted excellently to describe the adsorption rate/mechanism as compared to the pseudo first order kinetic model with R^2 values of 0.999 and 0.969 respectively. Thermodynamic estimates showed that MB adsorption on DRPAC was endothermic, feasible and spontaneous. Regeneration of the adsorbent showed that it can be reused up to the fifth cycle with considerable adsorption-desorption potentials in all cycles. A comparison of the performance of DRPAC for MB adsorption with other published work was favourable and indicated that the maximum adsorption capacities of the adsorbent depended on the initial MB concentration. The study showed that, DRPAC is an effective low - cost adsorbent for the removal of MB from aqueous solution.

It is recommended that the efficacy of DRPAC in the removal of other pollutants (metals, anions or colours etc) in wastewater should be studied. Investigations should be carried out to determine if the efficiency of DRPAC in removing MB from aqueous solution will give the same result if the pods are activated before carbonation (single step activation). Investigations should also be made on the efficiency of methylene blue removal using Delonix Regia through column method. Methylene blue adsorption onto DRPAC in presence of competing cations and anions should be tested in both simulated and actual wastewater. Finally other adsorption equilibrium and kinetic models such as the Temkin, intra-particle diffusion, pore diffusion and Evolich models should be tested on the adsorption data in order to give more insights on the mechanisms of adsorption involved.

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