Adsorption of Methylene Blue onto Activated Carbon Impregnated With KOH Using Cocoa Shell

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Abstract— A low cost carbonaceous adsorbent prepared from Agricultural waste by impregnation with KOH was tested for its efficiency in removing methylene blue (MB) solution. The process parameter investigated include: particle size, carbon dosage, initial concentration, pH and temperature. Freundlich, Temkin and Langmuir Isotherm model were applied to equilibrium data. The study indicated that the highest MB adsorption was absorbed by particle size of 800µm; the carbon dosage increase with 0.05g. The percentage removal of MB solution increase with increase in initial concentration, contact time, temperature, and pH. Adsorption models with Freundlich and Langmuir Isotherms were found to be applicable. Thermodynamic analysis shows negative values of ΔG^o(-312.649) indicating adsorption was favourable and spontaneous, positive values of ΔH^o (30.318) indicating endothermic physical adsorption and positive value of ΔS (96. 941) indicating increased disorder and randomness at solid to liquid interface of MB with adsorbent of cocoa shell activated carbon

Index Terms— cocoa shell, adsorption, activated carbon, methylene blue

I. INTRODUCTION

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The ever-increasing demand for making life easy and comfortable has lead to an increase industrialization, which in turn has boosted the utilization of chemical as raw materials. The use of these chemicals has contributed immensely in major sectors such as industry, agriculture etc. that have contributed to the improvement in standard of living among populates of the world.

The discharge of the by-product as well as the waste product has causes environmental pollution of the air, land, and water sources, however the contaminated discharge are toxic and hazardous to the environment and the eco-system at large. Most of these chemicals are natural occurring substance like colouring organic compounds (methylene blue), heavy metals, gases and soluble organic compounds etc. a large fraction of waste in the environment is in the form of highly diluted ground water and surface-water.

The presence of these colouring contaminants (methylene Blue) in water inhibits photosynthesis which in turn affects the green aquatic ecosystem. It has been reported worldwide that dyes are associated with skin, lungs and respiratory disorder. Dye and pigments are used in many industries such

as textile and pulp mills to colour their products. Most dyed have been reported to be hazardous, they contain appreciable concentration of materials with high biological oxygen demand (BOD) and suspended solids. (Mckay et al 1999)

.These coloured compounds impede light penetration in the biological treatment plant.

Adsorption has been described as an effective separation process for treating industrial and domestic effluents. It is widely used as effective method of separation in order to eliminate or lower the concentration of a wide range of dissolved pollutants, organic or inorganic onto effluent The material been absorbed is known as adsorbate and the adsorption involves the accumulation of molecules from a solvent onto the exterior and interior surface of an adsorbent. This surface phenomenon is a manifestation of complicated interaction among the three components involved, i.e. the adsorbent, adsorbate, and solvent.

Activated carbon has been widely employed as adsorbent in decontamination process due to its high adsorption capacity, fast adsorption kinetic, case of regeneration, extended surface area, and micro pores structure and special surface reactivity. The use of activated carbon as sorption for the treatment of industrial waste water is a recent practice that has been used to purity water from electroplating waste, and the removal of methylene Blue from waste water. No matter the use of this method in waste water purification, activated carbon adsorption remains a cost effective treatment process. This has spurred researches for low-cost activated carbon from a variety of carbonaceous material.

Characterization of the adsorbent, preparation of MB from aqueous solution for batch adsorption, equilibrium and thermodynamic studies of the adsorption operation.

The decomposition of carbonaceous matter during pyrolysis is very complicated and depends also on the three modes of heat transfer. Some numerical model, were proposed in literatures to predict the decomposition rate and final yield of char and volatile matter. One-step global model predicting the devolatilization state of pyrolysis process, it was assumed that the carbonaceous sample is decomposed in one step to produce the volatile substance and solution, to de-volatilize characteristics of various biomasses (wheat straw, coconut shell rice husk and cotton stalk) during flash pyrolysis on a plasma heated laminar untrained flow reactor with average heating rate of 104^0C/s. Their experiments were conducted at temperature between 477 and 627^0C and the particle residue time varies from about 0.115 to 0.2405s. They also employed the one-step global modal to stimulate the flash pyrolytic process and predict the yield of volatile products during the pyrolysis. Although the single-step global model is the simplest kinetic model for density; the prolysis process of biomass, but for some system the kinetic characteristics of pyrolysis is too complex which the one step is not capable to employ.

Therefore, more flexible and accurate model is needed for some pyrolysis systems.

Also a shrinkage model for the pyrolysis of a large wood particles was developed by (Bellais and other, 2003). The shrinkage was considered in three different ways, uniform shrinkage, spherical shell and shrinking cylindrical. All shrinkage model showed good agreement with the experimental result for mass loss varies with time at a high temperature range (higher than 600°C) but failed to stimulate correctly at low temperatures. The degredation kinetics of wood pyrolysis in the temperature range of 300-400°C at an atmospheric pressure was investigated by (Thurner and Mann, 1981). They used the three parallel model to describe thermal decomposition of such wood pyrolysis. Thus kinetic model assumes that the wood was pyrolyzed into gas, tar and char according to three parallel reactions. They found that the three-parallel reactions product distribution of gas, tar and char that agreed considerably well with the experimental data. Pyrolysis model with three primary reactions (parallel reactions) and one secondary reaction (tar decomposing into gas and char) was developed by (Chan et al, 1985). The products of the secondary tar reaction are assumed to consist of light gases (carbon monoxide ethane, ethylene) and aromatic tars.

The pyrolysis of palm shell using a one step global model and the two-step consecutive model was investigated by (Guo and Lua, 2001). The one step global model showed faster pyrolysis conversion than the actual experimental values, especially at high temperature region. While the two-step consecutive model agreed reasonably will with the experimental data.

The batch sorption removal of Pb^{2+} from aqueous solution using treated oil palm fruit fiber was studied. They found that equilibrium data for Pb^{2+} adsorption fitted well to the Langmuir equation more than Freundlich equation. The adoption of cadmium and lead on the modified oil palm shell was investigated (Othman et al 1994). The capacity of the activated carbon obtained from the different parts of oil palm and modified pal shell activated carbon to remove phenol from wastewater has also been studied by (Abubaker 1999, Salim et al 2002).

The economics of this process depends largely on the cost of adsorbent material. Therefore low cost absorbent are the centre of investigations low cost adsorbent could be produce from many raw material such as Agricultural and Industrial waste material. On the use of low cost absorbent in removal of dye materials. Investigation shows that adsorption of methylene blue into activated carbon prepared from periwinkle shells. (Bello et al 2008). Cocoa shell is an agricultural waste obtained from every cocoa producing region of the world, in Nigeria it produced in large quantity with the west region of the country. Since it is a carbonaceous in nature is a good raw material for the production of activated carbon. Using cocoa shell as the raw material for the production of activated carbon will minimized waste disposal and thereby encourage recycling. The choice of agricultural waste product for the production is based on reducing cost of production of activated carbon, environmental pollution through indiscriminate disposal of the waste material. Therefore the aim of this work was to characterize cocoa shell activated carbon (CSAC), determine the effect of some operating parameters. Potassium hydroxide (KOH) is usually used to activate coal. It has been reported that Zinc chloride produces activated carbon with high surface area than that produced by using phosphorus acid (Thomas and Thomas 1997).

Activated carbon usually increases the cost of the treatment process. Its economical setback has been stimulated by the interest of researcher to utilize cheaper raw materials for the production of activated carbon (Rengarag, et al, 2002).

II. MATERIAL AND METHODS

A. Sample collection and method

The cocoa shell was collected from a local farm at Ede, Ede Local Government Area of Osun State Nigeria. The shell were cut to a sizable length, washed with de-ionised water to removed debris, the cut and washed shells were sun dried for 3 days before subjecting it for further drying at a temperature of about 105°C in an electric oven for 2 hours to removed moisture.

B. Chemical Activation Carbonization

The activated carbon was produced from the oven dried cocoa shell by chemical activation; the dried shells were treated with 1000ml of 1M solution of sodium hydroxide (KOH_{aq}) and expose for about 6 hours for impregnation, and finally subjected to oven drying for 2 hours at a temperature of 105°C. The impregnated shell was charge into a batch reactor for pyrolysis. It was pyrolyzed at a temperature of about 400-500°C in the absence of air for 3 hours. The charred produced was allow to cool at ambient temperature, then it was grinded to different sizes with mortar with pistol. A set of sieves were used to sieve crushed activated carbon to unifom sizes. Preparation of dye solution: Stock solution of methylene blue solution the standard solution of MB was prepared at different concentration by dissolving 1g of methylene blue ($C_{16}H_{18}N_3SCl$) into 1000ml of deionized water. The same procedure was carried for 100gm/l into 1000ml, 80gm/l into 1000ml, 60gm/l into 1000ml, 40mg/l into 1000ml, and 20mg/l into 1000ml of deionized water.

C. Determination of the Physiochemical activated carbon cocoa shell

1 Moisture content analysis
Procedure
A Petri-dish was washed and dried in the oven
- Exactly 2g of the sample was weighed into Petri dish
- The weight of the Petri dish and sample was noted before drying
- The petridish and sample were put in the oven for another 30 minutes and the weight was noted

The drying procedure was continued until a constant weight was obtained.The difference in mass constitutes the amount of moisture content of the adsorbent (Langmuir, 2003) is given by:

$$\text{moisture content} = \frac{w_1 - w_2}{weight\ of\ sample} \ x100 ....1$$

Where w_1 –weight of petridish and sample before drying w_2 weight of petridish and sample after drying Ash content.
2 Ash content
Principle: The ash of foodstuffs is the inorganic residue remaining after the organic matter has been burnt away. It

should be noted, however, that the ash obtained is not necessarily of the composition as there may be some from volatilization.

Procedures
- Empty platinum crucible was washed, dried and the weight was noted.
- Exactly 2g of wet sample was weighed into the platinum crucible and placed in a muffle furnace at 500^0c for 3 hours.

The sample was cooled in desiccators after burning and weighed.

Calculations

Ashe content

$$\frac{w_3 - w_1}{w_2 - w_1} x \frac{100}{1} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2$$

Where:

W_1- weight of empty platinum crucible

W_2- weight of platinum crucible and sample before burning

W_3-weight of platinum and ash.

3 Specific surface area

Saer's method was used for the determination of the surface area (Shawakah and Al-Qodah, 2009). A sample containing 0.5g of CSCA was acidified with 0.1M HCl to pH 3-3.5, the volume wasmade up to $50cm^3$ with de- ionized water after addition of 10.0g of NaCl. The titration was carried out with standard 0.1M of NaOH. Th volume V required to raise the pH from 4.0-9.0 was noted and the surface area was calculated from the expression.

$$S \ (m^2/g) = 32V - 25 \dots\dots\dots\dots\dots\dots\dots 3$$

4 Determination of bulk density

The determination of Bulk density the bulk density of cocoa shell was determine using Archimedes' principle by weighting a $10cm^3$ measuring cylinder before and after filling with the sample. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, and weighed. The weight of the sample packed in the measuring cylinder was determined from the different in weight of the filled and empty measuring cylinder. The volume of water in container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation

$$\text{Bulk density} = \frac{W_2 - W_1}{V} \quad \dots\dots\dots\dots\dots\dots\dots\dots 4$$

W_1=weight of empty measuring cylinder W_2 = weight of cylinder filled with sample V=volume of cylinder.

III. EXPERIMENTAL CONDITIONS

A. Effect of adsorbent dosage

About 0.1g of 212μm of Cocoa Shell Activation Carbon (CSAC) as weighed, introduced into 250ml beaker; 20ml of (MB) solution was measured and poured into beaker containing 0.1g of CSAC

Cocoa Shell Activation Carbon (CSAC) it was then observed for 20 minutes and filtered with filter paper. Some quantity of the filtrate was poured into curvet and tested for adsorbance using spectrophotometer and reading was recorded. The same

procedures were also repeated for 0.15, 0.2 01.25, 0.3 0.4, and 0.5g to determine the adsorbent dosage.

B. Effect of initial concentrations

Initial Concentration: In order to determine the effect of concentration on adsorption, experiment was conducted with different initial concentration ranges from 20mg/L to 100mg/L for adsorption. Using 0.1g of CSAC into 20ml of MB solution, at a pH of 6.2, and at contact time of 20 minutes.

C. Effect of contact time

The effect of duration of contact between and adsorbent and the adsorbate on the removal of the MB solution was determined by keeping the particle size, initial concentration and adsorbent dosage constant, using 0.1g CSAC into 20ml on the same concentration of MB and observed for 15, 30 45, 60, 90, 120 and 150minutes respectively under the same condition

D. Effect of temperature:

The effect of temperature; In order to determine the effect of temperature on adsorption, experiment were conducted with different temperature rage (308^oK, 313^oK, 323^oK, and 333^oK), using 0.1g of CSAC unto 20ml of 40mg/L of MB.

E. Effect of pH

The effect of pH was carried out by adjusting the pH rage from 1.5 – 12 by adding 0.5M. sulphuric acid or 0.5M of sodium hydroxide.

F. Effect of adsorbent particle size

The effect of particle size on adsorption of MB was determined by changing the particle size from 150μm to 800μm with initial concentration of 40mg/L and adsorbent dosage of 0.1g for 20minutes.

IV. EQUILIBRIUM STUDY

Adsorption Isotherms or equilibrium data are the fundamental requirement for the design of adsorption system. There are many isotherms use in adsorption process, but the most frequently used are the Langmuir, Freundlich and Tempkin Isotherm for describing, the non-linear equilibrium. Langmuir, Freundlich and Tempkin adsorption Isotherm models were applied to the system in order to ascertain the nature of adsorption of the activated carbon. The adsorption experiments were conducted at room temperature. The Isotherm model is given by the relation of:

Langmuir Isotherm is expressed as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_c} \ \frac{1}{C_e} \dots\dots\dots\dots 5$$

Where K_c is the constant related to the overall solute adsorptivity (l/g)

Freundlich Isotherm is expressed as:

$$ln \ q_e = ln K_f + \frac{1}{n} \ ln C_e \text{------------------------------}6$$

Where K_f is the constant related to overall adsorption capacity (mg/g), $1/n$ is a constant related to the surface heterogeneity.

Temkin Isothem is expressed as:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ ln\ C_e$$ -----------------------------------7

V. THERMODYNAMIC MODEL

The thermodynamic study of adsorption process is necessary to determined whether the reaction is spontaneous or not. The Gibbs free energy change ΔG^o is an indication of the spontaneity of a chemical reaction, and therefore is an important criteria for spontaneity. Both energy and entropy factors must be considered in order to determined the Gibbs free energy of the process. Reaction occurs spontaneously at a given temperature if ΔG^o is negative value. The free energy of an adsorption, considering the adsorption equilibrium Ka. Therefore the thermodynamic parameters namely, free energy, enthalpy, and entropy changes of adsorption were estimated by using van Hoff's equation stated as follows

$$\ln k_c = -\frac{\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$ 8

Where ΔG^o is the free energy of adsorption (J mol^{-1}), ΔH^o is change in enthalpy (Jmol^{-1}), and ΔS^o is change in entropy (J mol^{-1}), and ΔS^o is change in entropy (J mol^{-1} K^{-1}).

$$\ln k_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$ 9

where $Kc = Fe/(1-Fe)$ and

$$F_e = \frac{C_o - C_e}{C_o}$$ 10

Adsorbed at equilibrium while T is temperature in degree Kelvin and R is the gas constant (8.314J/mol K). From the slops the intercept of van Hoff plot, the value of ΔG^o and ΔS^o ware estimated.

The Gibbs free energy change ΔG^o was calculate using Equation 5

$$\Delta G^o = - RT \ln K_e$$ 11

VI. RESULTS AND DISCUSSION

A. *CHARACTERIZATION OF COCOA SHELL*

FTIR spectra of the sample analyzed for the sample is shown in Figure 1 and Table .1 Infra-red spectra which serves as a characteristic medium for identification of compounds and its functional group, was thus found in the analyzed (CSAC sample) . Thus the spectra lines gives rise to nine important compounds. The analyzed CSAC was found that the small weak band at 1094.05291cm^{-1} was assigned to O-H bend of alkanes compounds. The peak value at 1452.82661 cm^{-1}, 1581.57184 cm^{-1}, 2371.79356 cm^{-1}, 2935.59073 cm^{-1}, 3333.47165 cm^{-1}, and 3784.09752 cm^{-1} gave rise to characteristic medium band of the C-H symmetric and anti-symmetric stretch of the methylene compound., secondary and tertiary amine compounds. The peak around 3784.09752 cm^{-1} corresponded to OH hydroxyl stretching of the aromatic phenolic compounds.

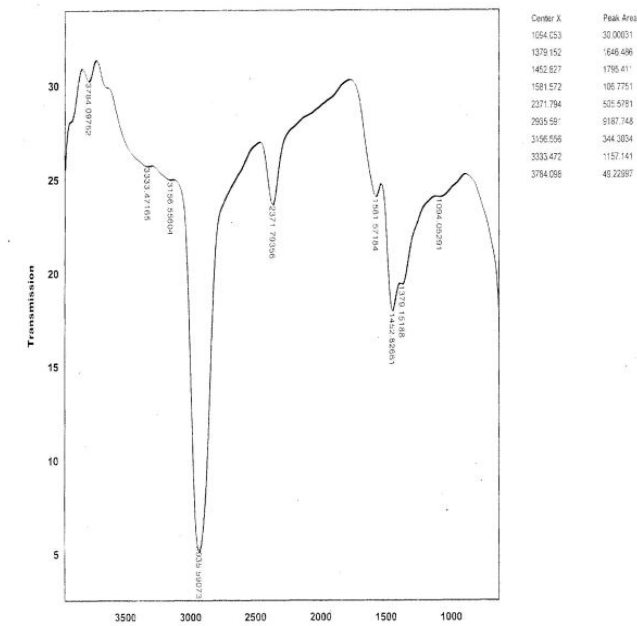**Fig TIR Fig .1: FTIR spectra of CSAC spectra of CSAC**
Fig .1: FTIR spectra of CSAC

Table.1: FTIR Spectra Interpretation of CSAC

S/N	Frequency cm^{-1}	Functional Group	Compounds
1	1094.05291	O-H Bend	Alkenes
2	1379.1588	C – H bend	Alkanes
3	1452.82661	C-H bend	alkanes
4	1581.57184	C-C stretch (in ring)	Aromatic
5	2371.79356	C≡C stretch	Alkynes
6	2935.59073	C-H stretch	Alkanes
7	3156.55604	O-H stretch	Carboxylic acids
8	3333.47165	O- H stretch	Alcohols phenols
9	3784.09752	O- H hydroxyl	Stretching aromatic phenol

B. *A physico – chemical characterization*

Physico-chemical characterization of activated carbon from CSAC are shown in Table 2, the value of the moisture content, is same with that of the range gotten by (Nwabame and Igbokwe 2012).

Ash reduces the overall activity of activated carbon and it reduces the efficiency of reactivation. The presence of ash has been shown to impede surface development. (Valix,et al 2004), from the analysis of CSCA the ash content was low. Also activated carbon with high ash content usually has a low specific surface area (Pendyal et al 1999).

The most important property of activated carbon is its adsorptive capacity, which depends largely on the specific surface area; the higher the specific surface area the higher the adsorptive capacity. The moisture content, shows a relative low value, this depicts that the CSAC was properly prepared, dried and handled. It should be worth noting that when CSAC is exposed to air is capable of adsorbing moisture from atmosphere. This normally could lead to high moisture content (Verla et al 2012).

Table.2: **Physical Properties of Activated Cocoa Shell**

Properties	CSCA
moisture Content	28 **%**
Bulk density	0.366g/cm^3
Particle size	212 - 800μm
Ash content	2%
Specific surface area	775m^2/g

C. Physio-chemical properties of cocoa shell activited carbon (CSAC)

1) Heavy metal component of the CSAC

Heavy metals are natural components of the earth. They cannot be destroyed. These metals enter into our bodies through different ways, via; food, drinking water, fruits and air, as trace elements some heavy metals (e.g potassium, magnesium zinc, calcium) are essential to maintain metabolism of human bodies. However at higher concentration these metals are toxic to the body system. The concentration of heavy metal in human bodies could be as a result of intake of contaminated water, food, exposure to emission source etc. The result of heavy metal analysis is shown in Table 4.3 from the analysis, it is seen that high poisonous metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and copper are relatively low compared to the essential metals such as sodium (Na), potassium (K), calcium (Ca) and Magnesium (Mg). After ashing the percentage of these metals were seems to increase with an exception of cadium (Cd) which has 0%. Calcium is oxidized easily, this reduce the availability of oxidizing agent (Udoetok, 2012). The high concentration of calcium in the CSAC and the presence of other metals like potassium, sodium, zinc and magnesium makes it suitable for the condition reaction, where reduction is paramount (Udoetok 2012).

Also since the toxic metal detected form the activated carbon from cocoa shell is of negligent percentage, CSAC can be used to remove high concentrated poisonous heavy metals from waste water.

Table. 3: Metal Analysis of CSAC before Ashing

Sample Parameters	CSAC	Percentage
Nickel (mg/100g)	0.005	0.0039
Iron (mg/100g)	2.80	2.2134
Copper (mg/100g)	1.30	1.0277
Zinc(mg/100g)	3.00	2.3715
Lead(mg/100g)	0.002	0.0016
Chromium (mg/100g)	0.001	0.0008
Cadmium (mg/100g)	0.00	0.0000
Magnesium (mg/100g)	2.33	1.8419
Calcium (mg/100g)	110	86.9565
Potassium (mg/100mg)	3.95	3.1225
Sodium (mg/100mg)	3.17	2.5059

2) Effect of initial concentration.

The percentage of adsorption of MB has been studied at various concentration levels of MB given the percentage of MB removed at varying concentration. It has been observed as in figure 4.2 that at higher concentration, the percentage of adsorption is high because of the availability of

move active site on the surface of the adsorbent. As the initial concentration of MB increase, the rate adsorption increases, as MB concentration decreases more surface sites are converted, hence lower concentration of MB. The capacity of the adsorbent gets reduced due to non-availability of the surface sites. Therefore, a rise in the percentage of adsorption of MB was observed at higher concentration and low percentage of adsorption at lower concentration.
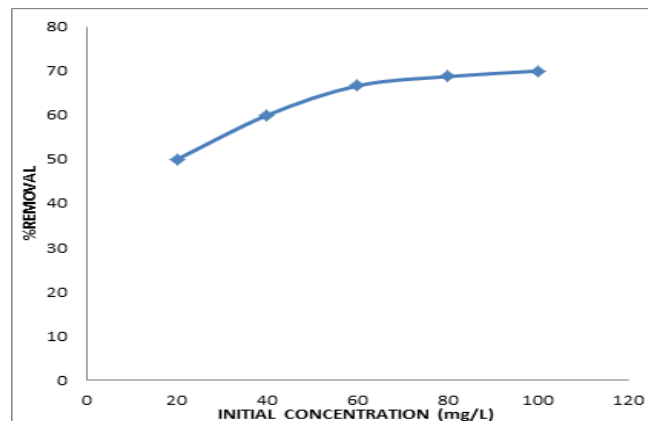

Figure 2 Effect of concentration of MB adsorbed

3) Effect of contact time

The amount of adsorbate adsorbed by an adsorbent at particular time is an important factor governing the efficiency of adsorption. The percentage adsorption of MB increases from 10 minutes to 120 minutes. Beyond this stage there was no further increase in amount of MB adsorbed by the adsorbent, this mean that at least a minimum 0f 120 minutes is required by the adsorbent material to adsorbed the maximum amount of MB as shown in Figure.3 .The relationship between the percentages of MB adsorbed by the adsorbent against the contact time. Therefore it is observed that adsorption increases in the beginning and attained an equilibrium state at 120munutes. Therefore 120 minutes is taken as the optimum period of contact required for the maximum removal of MB by cocoa shell activated carbon. The increase may be due to the increased surface area and the number of active sites.
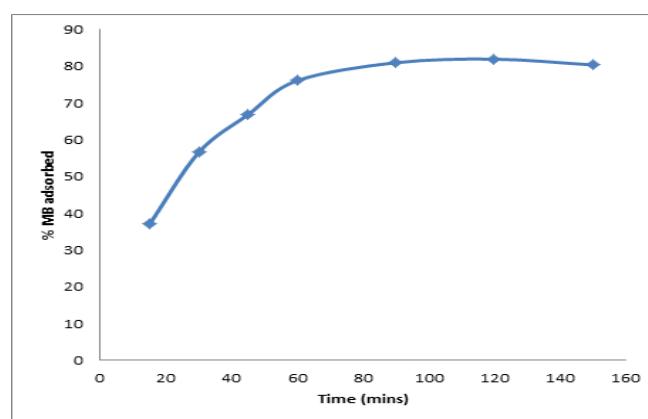

Figure 3 Effect of contact time on MB adsorbed using CSAC

4) Effect of particle size

Effect of particle size (μm) was plotted against the percentage of MB adsorbed. There is a clear indication, showing a gradual increase on MB adsorption from 150μm to 800μm. as shown in figure 4. The particle size of 150μm has

percentage of MB adsorbed as (68.98%) while 800μm has the highest percentage of MB adsorbed (72%). In this case it was found that the rate of adsorption progresses rapidly with larger adsorbent particle. Therefore, the best particle size suitable for adsorption study of MB on activated carbon is 800μm. Since adsorption is a surface phenomenon, it is evident that the greater the surface area per unit mass of the adsorbent, the greater is its capacity for adsorption.
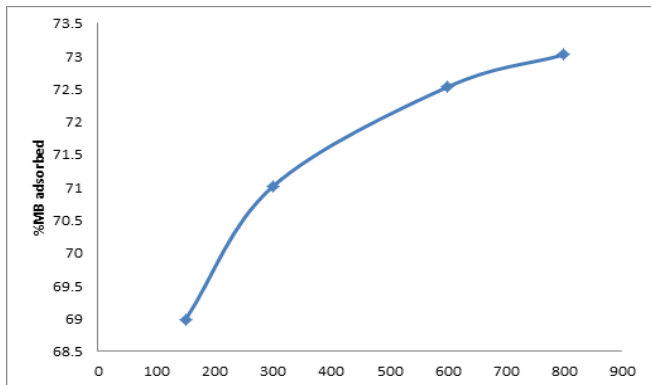

Figure. 4: Effect of particle size on MB adsorbed using CSAC

5) Effect of adsorbent dosage

The effect of dose of adsorbent on the percentage removal of MB is shown in figure 5. The percentage removal of MB increased with increase in dose of adsorbent, this due to increase in availability of surface active sites resulting from the increase from the increased in dose of the adsorbent.(Kannan and Sundarain 2001). Effect of adsorbent dosage was plotted against percentage of MB adsorbed, the result shows that 0.25g has the highest adsorbent dosage as (89.9%) and the lowest is 0.1g as (32.5%) therefore the best adsorbent dosage is 0.25g which gave the highest adsorption rate. This is due to increased carbon surface area as availability for more adsorption.
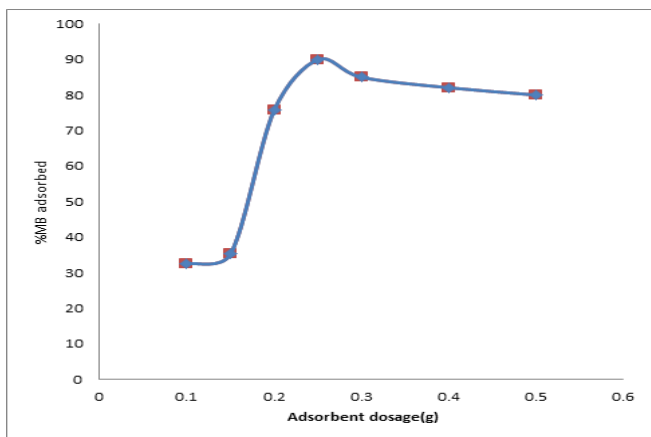

Figure. 5: Effect of carbon dosage on MB adsorbed using CSAC.

6) Effect of temperature

Temperature has strong effect on adsorption process. Thermodynamic parameters such as heat of adsorption and activation energy, play a crucial role in determining the adsorption trend. Adsorption of MB at four different temperatures of (308°k, 313°k, 323°k, and 333°k) onto cocoa shell activated carbon was investigated with 40mg/L initial MB concentration: It was observed that as temperature increase from 308 to 333°k, the dye adsorption

also increases. As the temperature increases the rate of diffusion of the adsorbate molecules across external boundary layer and internal pores of adsorbent particle increases. As show in Figure 6 changing the temperature will change the equilibrium capacity of the adsorbate.
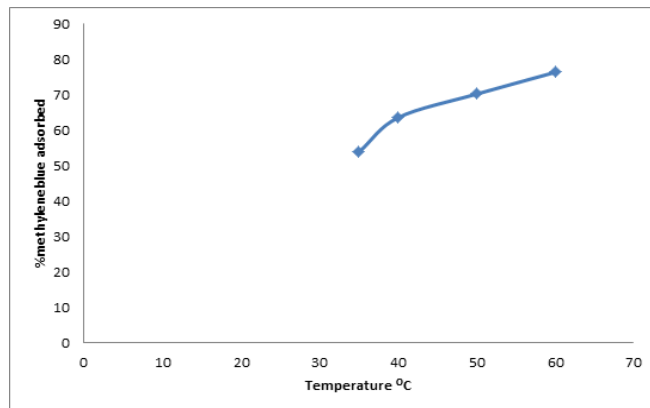

Figure. 6: Effect of temperature on MB adsorption using CSAC

7) EFFECT OF pH

PH is an important factor in predicting the adsorption of dye onto adsorbent, the adsorption of MB with 60mg/L concentration onto cocoa shell activated carbon was studies by varying the pH from 1.5 to 12, the amount of dye adsorbed at equilibrium (q_e) increase as the pH increase. As shown in Figure 4.7. It is observed that the amount of MB adsorbed with increase in pH (Crini et al 2007). The pH of the solution places an important role on absorption process. The effect of the solution pH on MB removal was investigated using different initial pH in the range of 1.5-12 with the addition of 0.2g adsorbent at ambient temperature. The data obtained as in Figure.7. Dye removal efficiency increases with increased in pH. The pH effect the chemistry of the solution and the association of the functional group on the active side of the adsorbent.
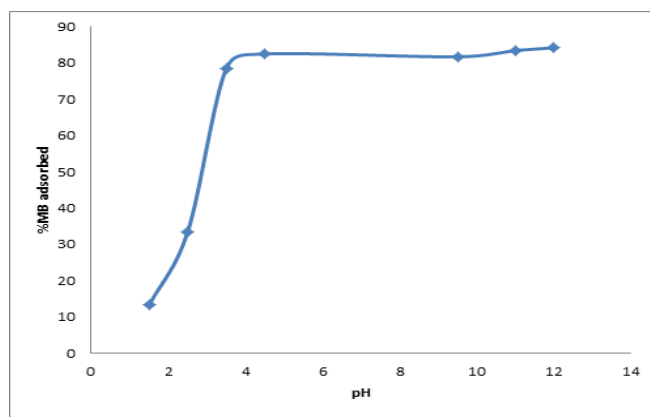

Figure. 7: Effect of pH on adsorption of MB using CSAC

8) Equilibrium adsorption models
i Freundlich

Adsorption isotherm for MB solution using cocoa shell activated carbon.

Batch adsorption isothermal data, fitted into the linear form of the Freundlich isotherm as shown in Figure 8 (Inq_e against InC_e). The adsorption capacity K and the adsorption intensity 1/n are directly obtained from the slope and the intercepts of linear plot respectively. The plot of lnq_e

against C_e for various initial concentration increases, this indicates the applicability of Freundlich adsorption Isotherm. The increase change on the surface enhance from between carbon surface and MB solution, which increases adsorption of MB. Freundlich model show that force of adsorption by activated carbon adsorbent are chemisorptions.
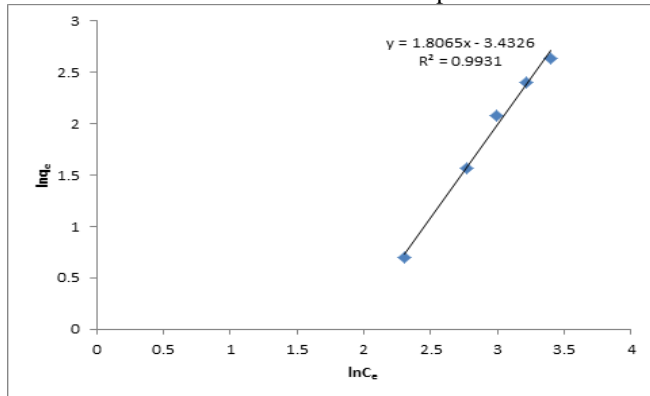

Figure. 8: Freundlich adsorption isorthem for MB Solution using CSAC

ii Langmuir adsorption isotherm for MB solution using CSAC

The value of "C_e" equilibrium concentration of MB

$$\frac{1}{qe}$$

and $\frac{1}{qe}$ the ratio of equilibrium concentration to the amount of MB adsorbed are utilized for the determination the Isothermal. As shown in Figure 9.

A plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ should give a q_e straight line of

slope $\frac{1}{q_m}$ on the $\frac{1}{q_e}$ axis. The linear plot of $\frac{1}{q_e}$ verus

$\frac{1}{C_e}$ it indicate the applicability of Langmuir adsorption

Isotherm and the adsorption process occur/through monolayer coverage the Langmuir plot showing increase in the rate of adsorption at higher concentration as shown in Figure 8. This enhanced adsorption nature of the adsorbent at higher concentration is due to the swelling in the internal pores of the adsorbent to trap in more MB on its surface. The value of q_m and k_c were determined.
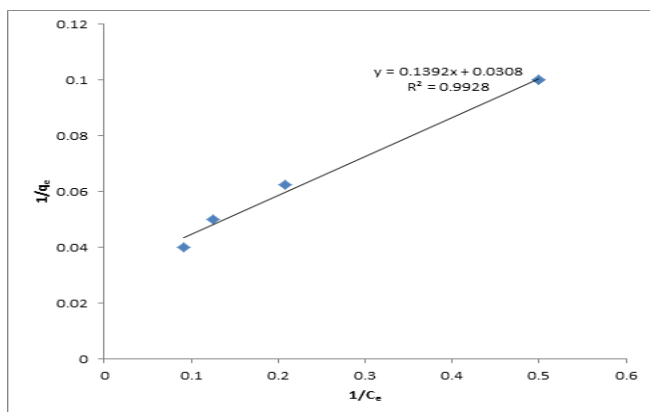

Figure 9: Langmuir adsorption isotherm for MB solution using cocoa shell activated carbon

iii   Temkin adsorption isotherm for MB solution

Temkin isotherm considered the effect of some indirect adsorbate interaction on adsorption isotherms and suggested that because of interaction the heat of adsorption of all the molecules in the layer would decrease linearly. As shown in Figure. 10
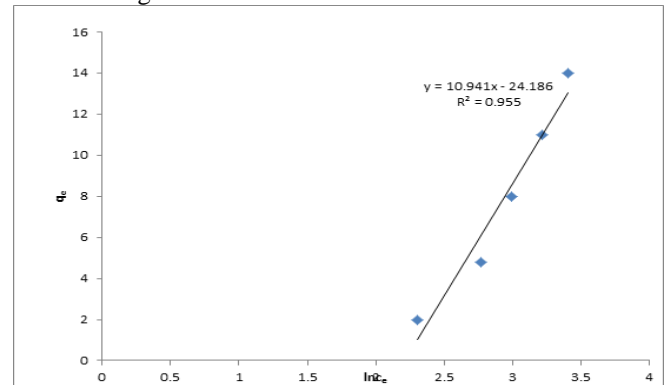

Figure 10 Temkin adsorbtion isotherm for MB solution using CSCA

9) Thermodynamic analysis

The thermodynamic consideration of an adsorption process is necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change Δ^oG, is an indication of the spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factor must be considered in order to determine the Gibbs free energy of process.

The values of the thermodynamic parameters are given in Table 4 The negative value of Δ^oG indicates the adsorption is favourable and spontaneous. Δ^oG values increases with increase in temperature and decrease with increase in initial concentration of MB. The low positive value of ΔH indicates physisorption and endothermic nature of adsorption. (Arivoli et al, 2007,). The positive value of ΔS indicates increase in disorder and randomness at the solid solution interface of MB with the adsorbent. The adsorbed water molecules which were displaced by adsorbate molecules, gain more translational energy them is lost by the adsorbate molecules, thus allowing prevalence of randomness in to the system. The increase of adsorption capacity of the adsorbent at higher temperature was due to enlargement of pore size activation of the adsorbent surface (Vedivelan et al 2005).

Table. 4: Thermodynamic Parameters

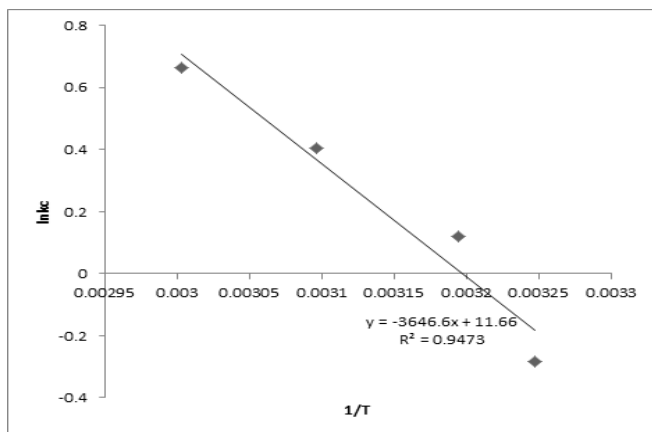| Conc.of dye (mg/L)	Δ^oH (KJ/mol)	ΔS^o (J/mol K)	T (^oK)	ΔG^o (KJ/mol)
40	30.318	96.941	308	721.7396
40			313	-312.649
40			323	-1088.84
40			333	-1836.37

Figure. 12: Thermodynamic Parameters

VII. CONCLUSION

The low cost activated carbon from Nigeria agricultural waste cocoa shell is found to have applicable capacity to adsorbed MB. The MB removal was found to occur through the process of adsorption which is basically a surface phenomenon. The activated carbon required a contact time of about 120 minute for optimum adsorption of MB. The adsorption process was found to depend on the particle size, the carbon dosage, initial concentration, the PH of the solution and temperature of the adsorbate.

Both Freundlich, Langmuir, and Temkin Isotherm have been used to describe and illustrate adsorption process showing a monolayer formation over the surface of the activated carbon. The thermodynamic parameter, ΔG^o, could be calculated from $\Delta G^o = - RTlnKc$. The values of Δ^oH and Δ^oS could also be obtained from the slope and intercept of the relationship between lnk_c and the reaction temperature. The negative value of ΔG^o is an indication of spontaneous nature of adsorption with a high temperature of MB dye on to cocoa shell activated carbon. The value of Δ^oH was positive which indicated that reaction was an endothermic. The positive value of Δ^oS shows that increasing in degree of randomness at the solid to liquid, interface during the adsorption of MB onto cocoa shell activated carbon.

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