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Experimental Investigation of the Treatment of Tebujor Crude Oil Polluted Water using Barbados Legume Activated Carbon by Adsorption-Filtration Method

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Manuscript History *Received:* 05/03/2022 *Revised:* 06/04/2022 *Accepted:* 15/04/2022 *Published:* 20/04/2022 **Abstract:** Crude oil is a toxic environmental pollutant which needs to be mitigated from the domestic water of the crude oil producing area of Nigeria. Crude oil polluted water was collected from Tebujor community in Delta State and Barbados legume was collected from Okada town in Edo State. Activated carbon was prepared using the Barbados legume and was used for the removal of crude oil from the crude oil polluted water. Analysis of the results show that Toth isotherm gave better fit compared to other isotherms used for the crude oil emulsion adsorption from Tebujor polluted water onto BLAC. The kinetic study shows that the adsorption agrees with the pseudo second order equation, while the thermodynamic parameters for the crude oil adsorption are as follows; change in standard enthalpy (Δ H^o) 12.9KJ/mol, change in standard entropy (Δ S^o) 61.2 $\frac{J}{mol.K}$ and change in standard Gibbs free energy

Keywords: Adsorption isotherm, Barbados legume, Crude oil, Kinetic, Thermodynamic

INTRODUCTION

Crude oil is a commodity which is very important all over the world (Kelle, 2018). One major environmental problem which continue to exist in marine waters across the world today, where Crude oil exploration take place, especially in Tebujor community, is oil spill. Water and land pollution caused by oil spill, is petroleum hydrocarbon discharged into the water or land, accidentally or operationally, whenever crude oil is produced or transported. Oil spill can impact negatively, the fishes, birds, humans and plantation (Maulion *et al.*, 2015; Werth *et al.*, 2019). Its effects also include skin irritation, eyes infection and mucus membranes, increasing vulnerability to infection and damage the gastrointestinal track and internal organs when ingested (Werth *et al.*, 2019). This repeating problem has grown to a frightening magnitude with increased level of the production and transportation of crude oil (Maulion *et al.*, 2015).

In August and September 2016, oil spills were reported in three States of the Niger-Delta region, in Delta State, Ten communities in Ijaw land along the Escravos River in Warri South West Local Government Area were affected by the crude oil spill from a facility belonging to the Nigerian National Petroleum Corporation (NNPC) (Egufe, 2016; Muhammad, et al., 2020). This spill occurred on August 17th 2016, and reporters in the area were told that the spill was traced to a crude oil trunk line from the Pipelines and Products Storage Company (PPSC), the products marketing and distribution subsidiary of the NNPC. The communities that were affected includes: Tebujor, Okpele-Ama, Ikpokpo, Oto-Gbene, Meke-Ama Communities, all in Gbaramatu Kingdom (Muhammad et al., 2020). These oil spills have had devastating negative effect on the agriculture, environments and general well-being of the local communities. It has acute and long-term effects on human health because it is covert and slow in action (Ordinioha and Brisibe, 2013; Muhammad et al., 2020). The aquatic lives and plantation are also being affected. The locals suffer skin irritation, eves and mucus membranes, susceptibility to infection and damages to their gastrointestinal track and internal organs when they take in this water. These effects are not given the deserved attention by the Government officials in Nigeria, and these effects can be major contributors to the disease burden in oil-bearing communities (Ordinioha and Brisibe, 2013).

The people of Tebujor and it environ, deserve safe portable water for their livelihood, however, the surface and ground water, which are their only sources of domestic water of this community, are been contaminated by crude oil exploration. Presently, polluted oil-water treatment is carried out by gravity separation, centrifugal separation, coalescence method, filtration, membrane separation, chemical demulsification, chemical oxidation, salting-out, coagulation, sedimentation, electrochemical method, biochemical method, oxidation pond, anaerobic contact, adsorption, the combination between these methods etc, but adsorption operation using adsorbent is mostly used to treat polluted water, because of its effectiveness and affordability. Beside, commercial activated carbon is expensive, so is the cost of regeneration. Therefore, the people in these rural areas cannot afford it, hence the persistence of lack of safe potable water in these areas. Asadu et al., (2021) worked on treatment of crude oil polluted water using stearic acid grafted mango seed shell (magnifera indica) composite. T, hey used crude oil obtained from shell facilities in Bonny Island, Rivers State, mixed with distilled water (simulated crude oil polluted water). They used selected operating conditions for the carbonization, activation and adsorption. They did not carry out design of experiment to obtain the optimum conditions at which the carbonization and activation of the grafted mango seed shell and adsorption of the crude oil was carried out. Ogbodo et al., (2021) researched on preparation and characterization of activated carbon from agricultural waste (musa-paradisiaca peels) for the remediation of crude oil contaminated water. They obtained their crude oil sample from shell facilities in Bonny, Rivers State mixed with distilled water (simulated crude oil polluted water). They selected the operating conditions at which they carried out carbonization and activation of musaparadisica peels. The operating conditions at which adsorption was also carried out was selected. Design of experiment was not carried out to obtain these operating conditions.

Research show that pride of Barbados, activated with Nitric acid (HNO_3) has been used to adsorb copper and lead from dye wastewater collected from a local dye industry, Jafaru Mairiga Street, Flayout Minna, Niger State (Idris *et al.*, 2011). They studied the kinetic of the adsorption, but the carbonization, activation and characteristics of this activated carbon and the thermodynamic behavior of the adsorption were not researched. So, there is need to explore more low cost agro-based materials and bridge these gaps to make significant difference in crude oil polluted water treatment by the rural dwellers. In this work, Barbados legume was explored for the preparation of adsorbent for the adsorption of crude oil emulsion from Tebujor polluted water.

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MATERIALS AND METHODS

2.1 Pride of Barbados

Pride of Barbados belongs to the Pea family, that is, *Fabaceae*. Pride of Barbados is also known as *Caesalpinia pulcherrima*. It has other common names, including Poinciana, Barbados Flowerfence, dwarf Poinciana, Peacock Flower, Dwarf Flamboyan, *Caesalpinia*, and Mexican Bird of Paradise. It is a small tree or an evergreen shrub in a frost free climate (Rodriguez 2006; Peggy, 2013). Pride of Barbados originated from the West Indies and tropical America. It is grow easily in alkaline to acidic soil that is well-drained. Pride of Barbados has become an established plant in tropical regions throughout the world and widely cultivated, including the Niger-Delta region of Nigeria (Norman, 2016).

2.2 Physical characteristics of Adsorbent

2.2.1 Area of Adsorbent Surface

The surface area of an adsorbent aids the rate and capacity of adsorption rate; the larger surface area, the greater number of vacant sites of the solid adsorbent the adsorbate will occupy.

$$S_{\text{area}} = \frac{V_m x A x N x 10^{-20}}{M_W} \tag{1}$$

Where S_{area} is area of adsorbent surface in $\frac{m^2}{g}$; A represent the specific surface area occupied by a molecule of adsorbent = 233 A^2 ; N represent Avogadro's number 6.02 × 10²³mol⁻¹; and M_w represent the molecular weight of the adsorbent, 696.65 $\frac{g}{mol}$ (Sekeran *et al.*, 1995).

2.2.2 Bulk Density

This is the ratio of mass of the particle (M_P) to the total volume of the particle (V_{tp}). It is a property of particulate material. Bulk density can be expressed as:

(2)

(3)

(4)

$$=\frac{M_p}{V_{tp}}$$

2.2.3 Pore Volume and Porosity

Pore volume is the ratio of the increase in volume of a mixture of a known weight of sample and known volume of water when heated and dried, to the density of water. Porosity can be defined as the pore volume of a sample divided by the bulk volume. Porosity is usually expressed as:

$$\phi = \frac{v_{pore}}{v_{bulk}}$$

 ρ_b

Where V_{pore} represent the pore volume and V_{bulk} is the bulk volume (Gumus and Okpeku, 2015).

2.2.4 Ash Content

Ash content can be defined as the residue left behind when carbonaceous portion of carbon material is burnt off. This residue is mainly mixture of minerals such as iron, silica, aluminum, calcium and magnesium (Gumus and Okpeku, 2015).

Ash content $A_c = \frac{D-B}{C-B} \times 100$

Where D is the weight of given sample and crucible used after drying, B is mass of the crucible used; C is the mass of crucible and sample before drying (Debela, 2016).

2.2.5 Moisture Content

This is the quantity of water present in a material. It is used in a wide range of technical areas. Moisture content involves continues heating of the sample until the mass of the sample is constant. $X_{0} = \frac{W_{1} - W_{2}}{W_{1}} \times 100$ (5)

 W_1 = mass of sample before drying, W_2 = mass of sample after drying (Gumus and Okpeku, 2015).

2.2.6 pH Measurement

pH simply means power of hydrogen ions. It can also be defined as a measure of the hydrogen ion concentration or hydroxide ion concentration in a solution. $pH = - Log [H^+]$ (6)

(0)

pH + pOH = 14 (7) Where pH is the measure of hydrogen ion concentration and pOH is the measure of hydroxyl concentration.

2.2.7 Iodine Value of the Adsorbent

This can be defined as a measure of the milligram of iodine that is adsorbed per 1g of the carbon used. The quality of an activated carbon is determined by measuring the amount of iodine it can adsorb. It is the most important parameter that is used for determining the effectiveness of any activated carbon (Debela, 2016). The method involves adding 10ml of hydrochloric acid (5% stock to the activated carbon in question (Debela, 2016; Ekpete *et al.*, 2017). This mixture is boiled for 20mins and mixed with 100ml of known concentration of iodine solution, then stirred for 20mins. 50ml obtained from the filtration of the resultant mixture is titrated with 0.1 normality of sodium thiosulphate using an indicator of starch solution. The iodine number is expressed as:

$$\frac{X}{M} = \frac{(N_i X M_w X V_i) - \left((\frac{V_i + V_{HCl}}{V_F}) X N_{Na2S203} X M_w) X V_{Na2S203}\right)}{M_c}$$
(8)
Where $\frac{V_i + V_{HCl}}{V_F}$ = Dilution factor

 N_i = concentration of iodine solution used, V_i represent the volume of iodine solution used, V_{HCl} represent the added volume of 5% stock HCl used, V_F represent the volume of filtrate used, $N_{Na2S2O3}$ represent the sodium thiosulphate concentration, $V_{Na2S2O3}$ represent the volume of sodium thiosulphate solution consumed in the titration, M_c represent the mass of activated carbon used (Debela, 2016). If the concentration of iodine obtained does not fall within the range of 0.008 to 0.04N $(\frac{mol}{dm^3})$, the entire procedure for the determination should be carried out again using new masses of carbon (Nunes and Guerreiro, 2011).

2.2.8 Carbon Yield

Carbon yield is defined as the dried mass of char produced at the end of the heating stage in the process, to the mass of the feedstock. The percentage yield of the carbon can be evaluated by dividing the weight of the produced carbon by the weight of the raw material that is been used for carbonation (Debela, 2016; Kumar and Jena, 2016).

$$Y\% = \frac{W_f}{W} \times 100$$

(9)

Where W_o represent the dry mass before carbonization and W_f represent the mass of char after carbonization (Debela, 2016).

2.2.9 Surface Morphology

This is the important part in the microstructure of electro-less plating alloy films (Zang *et al.*, 2011). The surface morphology reveals the surface texture and surface porosity of the material. The surface morphology influences the performance of the activated carbon (Nayak *et al.*, 2017).

2.2.10 Functional Group Bond Structure

The surface chemistry of activated carbon is very important. Functional group bond structure shows the type formation of chemical bond that exist between the functional groups on the surface of the investigated material (Debela, 2016). The number of peaks indicates the number of functional groups (Olufemi and Otolorin, 2017; El-Araby *et al.*, 2017; Rafatullah *et al.*, 2012).

2.2.11 Surface composition

Carbonaceous material has various structures, ranging from amorphous to crystalline, with high degree of graphitization and crystalinity. The quantitative analysis allows researchers to calculate the structural parameters (interpolar distance and crystallite size) of carbonaceous materials directly from their X-ray diffraction patterns, which primarily determine the structure. The interpolar distance is calculated from the angles of diffraction peaks and the crystallite sizes, L_c and L_a can be obtained at half maximum of the diffraction peak using the angles and full width (Lee *et al.*, 2021).

2.3 Adsorption Isotherms Equation

Adsorption isotherm equation shows how an adsorbed molecule is distributed between the adsorbent and liquid phase when the vacant site of the adsorbent is filled up (Ogbeide *et al.*, 2019). The analysis of these model data by fitting these data to different isotherm equations is a very significant step to obtain a suitable isotherm equation that can be used for design purpose Hammed and El-Khaiary, 2008). Langmuir and Freundlich are some two parameter isotherms used commonly in Engineering, while Redlich-Peterson and Toth isotherms are some three parameter isotherms commonly used in Engineering (Ghogomu *et al.*, 2016).

2.3.1 Langmuir Isotherm of Adsorption

Langmuir isotherm is one of the models first used to represent theoretical treatment given to nonlinear adsorption operation and it suggests that adsorption will occur by monolayer adsorption without interaction between the adsorbed molecules on a homogenous surface (Yuh-Shan *et al.*, 2009). It was first developed for the adsorption of gases onto solids. This physically convincing isotherm was developed from three assumptions based theoretical consideration; Adsorption operation cannot proceed more than the monolayer coverage, all the surface sites of the adsorbent are equivalent and can make room for at most one adsorbed atom, also the ability of a molecule to be adsorb at a given site is not dependent on the occupation of a neighboring site, but when the amount of material adsorbed equals the vacant sites, there is no net change in surface coverage. Langmuir isotherm is deducted when the rate of change in concentration of the adsorbate due to adsorption is equal to the rate of change in concentration of the adsorbate due to desorption. Consequently, the Langmuir isotherm of adsorption is as expressed in equation (10)

$$q_e = \frac{a b c_e}{1 + b c_e}$$

(10)

Rearranging equation (10), linearized the equation and the values of a and b can be evaluated from the slope and intercept of the equation respectively of the plot of Ce/q_e versus C_e

$$\frac{1}{q_e} = \frac{1+b\ C_e}{a\ b\ C_e} \tag{11}$$

$$\frac{1}{q_e} = \frac{1}{a} + \frac{1}{b a} \cdot \frac{1}{c_e} \tag{12}$$

Equation (12) can also be rewritten as $\frac{ce}{q_e} = \frac{1}{ba} + \frac{ce}{a}$ (13) Where b represent Langmuir constant, 'a' represent the adsorption capacity of the monolayer (mg/g). $q_{e'}$ represent adsorption capacity or amount of solute removed when the adsorption is at equilibrium $\left(\frac{mg}{g}\right)$. C_{e} , represent the concentration of mixtures at equilibrium. As a result, a and b are adsorption parameters estimated by Langmuir model, while the squared correlation coefficient is used to predict whether the adsorption operation can be represented by Langmuir isotherm model (Yuh-Shan *et al.*, 2009). The Langmuir adsorption isotherm gives more appropriate description for chemical adsorption, but can also be adopted for some systems where the coverage is low (Onwuka *et al.*, 2018).

2.3.2 Freundlich Isotherm of Adsorption

The Freundlich adsorption model often times gives more convincing model for the experimental data because it an empirical relationship (Yuh-Shan, *et al.*, 2009). It is useful in predicting the adsorption capacity of an adsorbent (Onwuka *et al.*, 2018). The Freundlich adsorption model suggests that adsorption operation occur by multilayer adsorption on a heterogeneous surface. It can be represented as follows;

$$q_e = K_f C_e^{1/n} \tag{14}$$

However, when linearized, Freundlich isotherm of adsorption can be presented in the following way;

$\log q_e = \log \left(\mathcal{C}_e \right) + \frac{1}{n} \log \mathcal{C}_e \tag{15}$

Where C_e represent concentration of the adsorbate at equilibrium q_e represent adsorption capacity of the adsorbent at equilibrium, K_f and n represents Freundlich constants, which incorporates all the factors affecting the adsorption operation. Values of K_f and n are usually evaluated from the intercept and slope of a plot of amount of solute removed q_e , against the concentration of adsorbate at equilibrium C_e . K_f parameter and n parameter affect the adsorption operation, the larger the values of K_f and n, the higher the value of the adsorption capacity at equilibrium. In addition, the size of the exponent n, gives an indication of how favorable the adsorption operation is (Yuh-Shan *et al.*, 2009).

2.3.3 Redlich-Peterson (R-P) Adsorption Model

The Redlich-Peterson adsorption model combines three adjustable parameters to form an empirical model from the properties of Langmuir and Freundlich (Meriem and Fatima, 2011; Bridelli and Crippa, 2008). The Redlich-Peterson adsorption model can be expressed as follows:

$$q_e = \frac{\kappa_R c_e}{1 + a_R (c_e)\beta}$$

$$(16)$$

$$(17)$$

 $q_e = K_R = a_R$ Where K_R represents the R-P model constant $(\frac{1}{mg})$, a_R is also a constant $(\frac{1}{mg})^{\frac{1}{\beta}}$ and β represents the exponent of the isotherm which exist between 0 and 1. The R-P model of adsorption depends on concentration of the adsorbate linearly in the numerator and has exponential function dependence as the denominator. At high concentration, R-P model approaches the Freundlich model of adsorption operation and is in accord with the Langmuir model of adsorption operation at low concentration. In addition, the R-P equation can be applied to either homogenous or heterogeneous systems due to its high flexibility (Bokanyi, 2012).

2.3.4 Tóth Isotherm of Adsorption

This isotherm assumes adsorption of adsorbate on surfaces that is heterogeneous energetically with most of the vacant sites having adsorption energy that is lower than maximum adsorption energy (Bridelli and Crippa, 2008). The following form is applicable to liquid-phase adsorption:

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$$q_{e} = \frac{b_{T}C_{e}}{\left(\frac{1}{q_{s}} + C_{e}^{t}\right)^{1/t}}$$

$$\alpha \neq 0$$

$$\left(\frac{C_{e}}{q_{e}}\right)^{t} = \left(\frac{1}{q_{s}b_{T}}\right)^{\alpha} + \left(\frac{1}{b_{T}}\right)^{t}C_{e}^{t}$$
(18)
Where $b_{T} \left(\frac{mmol}{q_{s}}\right)$ represent the total adsorption capacity, $q_{s} \left(\frac{mg}{q_{s}}\right)$ serve as the inverse of an adsorptive

Where $b_T \left(\frac{1}{g}\right)$ represent the total adsorption capacity, $q_s \left(\frac{1}{dm^3}\right)$ serve as the inverse of an adsorptive potential, t is Toth model exponent which shows the quality of the heterogeneity of the adsorbent (Bridelli and Crippa, 2008); Bokanyi, 2012].

2.4 Adsorption Kinetic

The kinetic study of adsorption operation gives information about the behavior and features of the adsorption (Debela, 2016). Adsorption occurs at a variety of rates from rapid to very slow (Sharma and Sharma, 2013). The pseudo-first order adsorption kinetic equation and pseudo-second order adsorption kinetic equation is usually tested to determine which of the models agrees with experimental value, that is, adsorption capacity of adsorbent q_e , consequently, suggesting which of the equations the adsorption operation follows.

2.4.1 Pseudo-First Order Adsorption Model

First order reaction can be represented by

 $A \rightarrow Products$

Taking C as the concentration of reactant A at any time t, the rate at which reactant A is used up can be represented as

$$\frac{-dc}{dt} = k_1 C \tag{19}$$

$$\frac{-d(a-x)}{dx} = k_1 (a - x)$$
(20)

$$\frac{dx}{dt} = k_1 (a - x)$$
(21)

Largergren postulated in 1898 the pseudo-first order adsorption kinetic and this can be expressed by the following equation (Gottipati, 2012):

(22)

$$\frac{dt}{t} = k_1 \left(q_e - q_t \right)$$

Where q_e (a) and q_t (x) represents adsorption capacities of the adsorbent at equilibrium and at time t, respectively $\left(\frac{mg}{g}\right)$, K_1 represent the rate constant of pseudo-first order adsorption equation (min^{-1}) (Adie *et al.*, 2012; Sharma & Sharma, 2013).

Taking boundary conditions at t = 0, $q_t = 0$ and at t = t, $q_t = q_{e}$, Therefore.

$$\int_{0}^{q_{dt}} \frac{dq_{t}}{(q_{e} - q_{t})} = k_{1} dt$$
(23)
$$\ln (q_{e} - q_{t}) = \ln(q_{e}) - k_{1} t \text{ or}$$

$$\log (q_{e} - q_{t}) = \log (q_{e}) - \frac{K_{1}}{2.303} t$$
(24)

The plot of the values of Log $(q_e - q_t)$ versus the values of t will give a linear relationship with the slope and an intercept from which K₁ and q_e can be obtained respectively. The relevancy of the pseudo-first order adsorption model to experimental data differs in two ways: firstly, the parameter $(q_e - q_t)$ does not represent the number of sites available and the parameter Log (q_e) , is an adjustable parameter which is usually found not to be equal to the intercept value of the of plot of Log $(q_e - q_t)$ versus t, whereas in pseudo-first order adsorption equation, Log (q_e) ought to be equal to the intercept (Adie *et al.*, 2012).

2.4.2 Pseudo-Second Order Model

The pseudo-second order model of adsorption operation for equal moles of the adsorbate and adsorbent is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{25}$$

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Where k_2 represent the pseudo-second order model rate constant of the adsorption $\left(\frac{g}{mg.min}\right)$ (Sharma and Sharma, 2013).

Considering boundary conditions for the system; at t = 0, q_t = 0, at t = t, q_t = q_t $\int_{0}^{q_{t}} \frac{dq_{t}}{(q_{e} - q_{t})^{2}} = k_{2} \int_{0}^{t} dt$ $\frac{1}{q_{e} - q_{t}} = \frac{1}{q_{e}} + k_{2} t$ (26)(27) $q_e - q_t \quad q_e$

Rearranging equation (27) gives a linear form as below

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(28)

Plotting $\left(\frac{t}{q_e}\right)$ against t in equation (28) will produce a linear expression from which q_e and k_2 can be evaluated using the slope and the intercept data of the graph, respectively. (29)

$$q_t = \frac{(C_0 - C_t)V}{X}$$

dt

Where C_0 , C_t , x and V represents the initial concentration $(\frac{mg}{l})$, concentration $(\frac{mg}{l})$, mass (mg) and solution volume respectively (Adie et al., 2012).

2.4.3 The nth Order of the Adsorption $\frac{dq_t}{dt} =$

$$k_n (q_e - q_t)^n \tag{30}$$

Where n is referred to as the power (order) of the adsorption, k_n represent rate constant of the nth order of the adsorption,

$$\frac{dq_t}{(q_s - q_t)^n} = k_n dt \tag{31}$$

$$\int_{0}^{q_{t}} \frac{dq_{t}}{(q_{e} - q_{t})} = k_{n} \int_{0}^{t} dt$$
(32)

$$\frac{\left[\frac{(q_e-q_t)^{-(n-1)}}{(n-1)}\right]_0^{q_t} = k_n t$$

$$\frac{(q_e-q_t)^{-(n-1)}}{n-1} - \frac{q_e^{-(n-1)}}{n-1} = k_n t$$
(33)
(34)

2.6 Thermodynamic Study of the Adsorption

The basic parameters of thermodynamic to be determined for the adsorption are Change in standard enthalpy of the adsorption (ΔH°), Change in standard Gibb's free energy of the adsorption (ΔG°) and change in standard entropy of the adsorption (ΔS°). Determination of these parameters is essential as it provides good judgment to predict favorability of the adsorption operation from the thermodynamic stand point, the accessibility of the sudden nature of the system, to ascertain whether the adsorption is physical or chemical and exothermic or endothermic in nature. Adsorption operation is generally considered to be physical when $\Delta H^{o} < 84 \frac{KJ}{mol}$ and as chemical when ΔH^{o} lies between 84 and 420 $\frac{KJ}{mol}$ (Ozcan *et al.*, 2006; Zang *et al.*, 2011). These parameters of thermodynamic of the adsorption operation will be evaluated from the data obtained from the experiment at various temperatures using the following Gibbs free energy equations $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ (35)Where T is the temperature of the system Also, Gibbs free energy isotherm equation

$$\Delta G^{o} = -RTInK_{d}$$
(36)
Where $K_{d} = \frac{q_{e}}{c_{e}}$
(37)

Where $K_d = \frac{1}{Ce}$ Evaluating equations (35) and (36) gives $InK_{d} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT}$ (38)

 K_d represent the adsorption distribution coefficient, q_e represent the amount of crude oil (mg) adsorbed onto the adsorbent per liter (l) at equilibrium, C_e represent the concentration of the crude oil at equilibrium $\left(\frac{mg}{l}\right)$ in the solution, T represent absolute temperature, R represent gas constant. ΔG^o , ΔH^{o} , and ΔS^{o} are standard change in Gibbs free energy, standard change in enthalpy and standard

change in entropy respectively. These values are evaluated from the slope and intercept of plot of ln K_d against $\frac{1}{\tau}$ (Emrah *et al.*, 2008).

2.7 Design of Experiment for Carbonization of Barbados Legume

The Barbados legumes were picked from Okada town environment, Edo State, Nigeria. They were washed several times thoroughly with tap water, to ensure that every water-soluble material attached to them was removed, and thereafter they were dried under the sun for several hours. Five levels factorial design using Design Expert 11, 13 runs was generated by the statistical package software, for a temperature between 400 – 500°C and a time of 2 – 4 hour, with temperature and time as the independent variables. A constant mass of 70.0g was weighed with a top loading balance (K500BH) before it was fed into a Furnace (Nabertherm GmbH) at the corresponding temperature and time obtained from the design of experiment. At the end of the 13 runs, with the temperature, time and mass of the runs, using the Design Experiment software, the optimal temperature and time for the carbonization were obtained as 498°C and 233min. 1834.4g of the Barbados legume was fed into the furnace set at 498°C, in bit of 120, 120, 200, 160, 160, 200, 200, 200, 200, 74.4g and were withdrawn after 233min for each of the runs, kept in a desiccator where it was allowed to cool down. The char were withdrawn from the desiccator and crushed with a mortar and pestle. The crushed Barbados legume Carbon (BLC) were then sieved with a standard sieve of less than 800µ size and kept in an air tight container. A total mass of 346.67g was obtained.

2.8 Design of Experiment for Chemical Activation of Carbonized Barbados Legume

5.0 gram of the Carbonized Barbados legume was weighed in a Crucible and 15ml of 0.15M HCl solution (impregnation ratio of 1:3), was added and thoroughly mixed to form slurry. The slurry was loaded into the furnace set at 900 \pm 5°C and was withdrawn after 180min. The crucibles were kept in a desiccator were it cooled down till it attain room temperature. The sample was thoroughly washed severally using distilled water and when the pH of the used water was 7.0 \pm 0.5, the sample was allowed to drain out water and it was loaded into an oven set at 110 \pm 5°C. After 120 min, the sample was withdrawn and kept in a desiccator were it cool down till it attains room temperature. The entire procedure was repeated for other variable conditions of the experimental design data, using constant mass of 5.0g and their corresponding iodine number was obtained.

2.8.1 Iodine Number Determination of the Barbados Legume Activated Carbon

1.0g of the Barbados Legume Activated Carbon (BLAC) was put a 250ml conical flask and 10ml of 5% HCl was added and stirred with a magnetic stirrer (CD142). 100ml of standard iodine solution $(0.013\frac{mol}{dm^3})$ was added to the mixture. It was shaken for a period of 20min at 300rpm with a magnetic stirrer (CD142). The resulting mixture was filtered with a Whatmann filter paper. 50ml volume of the filtrate was measured and titrated against $0.1 \frac{mol}{dm^3}$ sodium thiosulphate solution with starch solution as indicator (Ekpete et al, 2017). Then, the iodine number of the BLAC was calculated using equation (8). The entire procedure was also repeated for all the variable conditions of the experimental design data and their corresponding iodine number was calculated. The iodine number data calculated and the corresponding values of the independent variables after the 20 runs were inputted into the design expert software to generate the optimal conditions at which the activation of the Barbados Legume will be carried out. The optimum temperature was obtained as 857°C, optimum time was obtained as 230min and the optimum concentration of the acid was obtained as 0.130mol/dm³. After obtaining the optimal conditions, 112.8g, 70.6g and 168.3g of the carbonized Barbados legume was weighed using analytical weighing balance (AX423/E) and mixed with 338.4ml, 212ml and 205ml of 0.175 mol/dm³ HCl respectively (impregnation ratio of 1:3), to form paste [14]. This was fed into the furnace (Nabertherm GmbH) set at 857±5°C. After 230min, it was withdrawn from the muffle furnace and the sample was kept in a desiccator to cool down till it attains room temperature.

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It was thereafter washed severally, with distilled water and sieved using standard sieve while the pH of the filtrate was continuously measured with a pH meter (PH-2601) until the pH was 7.0 ± 0.5 . The wet Barbados legume activated carbon was then fed in batches into the oven (MINO/75/F/DIG) set at $110\pm5^{\circ}$ C. After 120 min it was withdrawn and kept in a desiccator to cool down and attain room temperature (Gumus, and Okpeku, 2015).

2.9 Barbados Legume Activated Carbon Characterization

2.9.1 Surface Area Determination of the BLAC using Brunauer Emmett Teller (BET) Analysis

2.9.1.1 Preparation of Samples

4 liter of liquid nitrogen (-118°C) was lined and the cold trap Dewar was filled with the liquid nitrogen to three quarter (3/4). The cold trap Dewar was mounted to Autosorb-1. The Helium (He) and nitrogen (N₂) gas cylinder valves were opened and ball valves located after the pressure regulators were confirmed to be set at 10psi. 9mm cell with fill glass rod for sample was chosen. The empty sample cell with fill glass rod was weighed 3 consecutive times and the average value was recorded. The fill glass rod was removed and the BLAC was inserted using a funnel until half full volume of the cell. The fill glass rod was replaced. The sample cell with the fill glass rod and sample was weighed again 3 consecutive times and the average value recorded. The sample mass was evaluated by subtracting initial mass from the mass before degassing. The temperature was set at 200°C. The heat was turned on and the sample was allowed to degas for 90min. immediately after degassing, the analysis automatically commenced. The (BET) surface area is presented in table 1.

2.9.2 Scanning Electronic Microscope (SEM) Analysis of BLAC

Barbados legume activated carbon (BLAC) sample was placed on the stub of the aluminum holder, using a double sticky carbon tape. The sample was located with carbon, and ground electrically. Also, silver point was used to electrically ground the sample. The sample was dried in a laboratory oven (MINO/75/F/DIG) for 3 hour at 60°C. The valves of the nitrogen gas tanks were opened; the vent button was located at the display panel of the microscope (JSM-7600F) table was pressed. High vacuum was achieved after 40 minute (<5 x 10⁻⁵Pa), the filament light turns on and the key was switched to 'on' position, the monitor turns 'on'. The acceleration voltage was 15KV and the spot size was large and 1. The astigmatism, filament emission, aperture alignment and beam alignment were checked. The least magnification (10x) was located, the TV scan mode was selected and BLAC sample was found using trackball. The z-position was found on the screen were the image is in focus and this was written down. The coarse focus was turned off. Operation was switched over to slow scan mode and magnification was increased to 8000x. The image was previewed, contrast and brightness were adjusted. The image set up window was closed and acquire image icon was clicked to record the image. The image of BLAC is represented as plate 1.

2.9.3 Fourier Transform Infra-red (FTIR) Analysis of BLAC

The computer was turned on and the notebook signed into. The power of the instrument was put on and initialization was allowed to succeed. The sample holder was cleaned with acetone and care was taken to ensure the acetone did not splash on the instrument. The sample name Barbados legume activated carbon (BLAC), scan range (650-4500 cm⁻¹), and scan number were inputted. 1.6g of BLAC sample was kept in the sample holder and the "monitor" button, "instrument Setup and scan" dialog was clicked, and the pressure arm lowered, through the "monitor" dialog, to monitor the total pressure applied to the BLAC. The spectrum is presented in Fig. 1.

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2.9.4 X-Ray Diffractometer Analysis of BLAC

The Barbados legume activated carbon (BLAC) sample was taken using aluminum alloy grid (35 x 50mm) in a flat glass plate and covered with a paper. The sample was closely packed by gently pressing them with the hand with gloves on. The sample was analyzed using the X-ray diffractometer (Rigaku D/Max-111C). The scanning rate was set at 2°/min in the 2 to 50° range, to produce diffractions at room temperature while the Cu K alpha radiation was set at 40KV and 20mA. The relative intensity and the d-value which are the diffraction data obtained from the analysis was compared with standard data of mineral pelletized data file, International center for diffraction data (ICDD) which contains standard data of more than 3000 minerals. Similar diffraction data means the same minerals to standard minerals which exist in the BLAC. The spectrum is presented in Fig. 2.

2.9.5 Determination of pH of the Activated Carbon

2.0g of the Barbados legume activated carbon (BLAC) was weighed and put in a 250ml conical flask. 100ml of distilled water was measured and heated to boil in a round bottom flask using a heating mantle. The boiling water was transferred into the conical flask containing the activated carbon. The mixture was allowed to boil further for 5 minute on the heating mantle, then it was withdrawn and placed on a magnetic stirrer (CD162) where it was agitated for 20 minutes at 300rpm and allowed to cool to room temperature. The cooled mixture was filtered with a Whatmann filter paper and the pH of the filtrate was measured with a pH meter (PH-2601). The result is presented in Table-1.

2.9.6 Determination of Pore Volume and Porosity of the Barbados Legume Activated Carbon

2.0 gram of the Barbados legume activated carbon (BLAC) was weighed and transferred to a 10ml measuring cylinder. The volume of the 2.0g BLAC in the measuring cylinder was obtained as 6.1ml. The sample was kept in a beaker and 10ml of distilled water was added to it and boiled for 5 minutes with a heating mantle to displace air from the BLAC. The content was withdrawn from the heating mantle and allowed to dry lightly at room temperature before it was weighed. The increase in mass of the BLAC was divided by the density of water to obtain the pore volume of the BLAC, while the porosity was evaluated by dividing the pore volume of the BLAC by the total volume of the BLAC used. The results can be seen in Table-1.

2.9.7 Determination of the Ash Content of the Activated Carbon

A clean dry crucible was weighed and 4.0g of Barbados legume activated carbon (BLAC) was also weighed and placed in the crucible. This was transferred to a furnace set at 957°C. After 230min, the sample was withdrawn and kept in a desiccator were it cool down to room temperature. It was reweighed to obtain the new mass of the sample. The ash content of the Barbados legume activated carbon was obtained using equation 4. The result is presented in Table-1.

2.9.8 Determination of Moisture Content of the Barbados Legume Activated Carbon

Thermal method of drying was used to determine the moisture content of the activated carbon. 2.0g of BLAC was weighed accurately and placed in a clean, dried crucible with known weight. This was transferred to an oven set at 105°C. After 60min, it was withdrawn and weighed, and subsequently after 30min interval, the mass was weighed and a constant mass was obtained after 120min. The result is presented in table 1. The moisture content was evaluated using equation 5 and the result is presented in Table-1.

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2.9.9 Iodine Number Determination of the Activated Carbon

1.0g of the Barbados legume activated carbon (BLAC) was placed in a 250ml conical flask and 10ml of 5% HCl was added and stirred for about 2 min with a magnetic stirrer. 100ml of 0.009mol/dm³ iodine solution (mixture of 2.7g of iodine and 4.1g of Potassium iodide solution titrated against 0.1mol/dm³ Sodium thiosulphate) was added to the mixture and stirred using a magnetic stirrer (CD142) for about 20min at 300rpm. The resulting mixture was filtered with a Whatmann filter paper. 50ml of the filtrate was titrated against 0.1mol/dm³ sodium thiosulphate using 3 drops of starch solution as indicator (Ekpete *et al.*, 2017). 0.4ml of sodium thiosulphate was consumed in the titration. The iodine number was calculated using equation 8. The result is presented in Table-1.

2.9.10 Bulk Density of the Activated Carbon

2.0g of Barbados legume activated carbon (BLAC) was weighed and placed in a 10ml measuring cylinder. The volume of the BLAC in the measuring cylinder was obtained as 6.1ml. The bulk density of the BLAC was determined by substituting the mass and volume obtained of the BLAC into equation 2. The result is presented in Table-1.

2.10 Design of the Crude Oil Adsorption Experiment

Full factorial design of adsorption experiment was applied, five levels was used with four independent factors (time (min), temperature ($^{\circ}$ C), concentration (mol/dm³) and dosage (g)) as the main effects and adsorption capacity (mg/g) as the response variable.

2.10.1 Determination of Initial Concentration of Crude Oil in the Sample

The visible spectrophotometer (6700 vis.) was used to scan the blank solution; 540nm was obtained as the maximum operating wavelength (λ_{max}). The visible spectrophotometer was set at 540nm and the cuvette was filled with the stock sample (Tebujor crude oil polluted water) and loaded into the machine. The concentration of the Tebujor stock sample was obtained as 263mg/l.

2.11 Experimental runs for the Crude oil Adsorption

25ml of the sample from Tebujor Creek with various concentrations (100, 120, 140, 160 and 180mg/l) were measured and corresponding dosage of Barbados legume activated carbon (BLAC) was weighed and transferred to a 250ml beaker. The waterbath (DK-420) was set at corresponding temperature according to the design of experiment carried out. The mixture was transferred to the waterbath (DK-420). After corresponding contact time, the samples were withdrawn from the water bath and filtered. 5ml of the filtrate was transferred to the cuvette and loaded into the visible spectrophotometer (6700 vis.) set at 540nm. The concentrations of the samples were measured and recorded. The optimal conditions were obtained as 176.0mg/l, 39min, 1.03g, 45°C and 2.732mg/g.

2.12 Determination of the pH of the Sample at Optimum Conditions

25ml of 176.0mg/l of sample from Tebujor Creek was measured into 250ml conical flask. 1.03g of Barbados legume activated carbon was added to the adsorbate in the conical flask. The waterbath was set at 45°C and allowed to stabilize for 10 minute. The sample was fed into the waterbath and after 39 minute the sample was withdrawn and filtered, the filtrate was placed on a pH meter (PH-2601) and the pH of the sample was measured.

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2.13 Batch Adsorption Experiment of Crude Oil from the Sample

2.13.1 Effect of Adsorbate Concentration on the Batch Adsorption Operation

Batch adsorption operation was carried out by agitating 1.03g of Barbados legume activated carbon (BLAC) with 25ml of the crude oil sample from Tebujor, having the following concentrations 100, 120, 140, 160 and 180mg/l in a water bath set at 45°C. The samples were withdrawn from the waterbath after 39 minute. They were filtered using Whatmann filter paper. Crude oil concentration in the filtrate was determined using a visible spectrophotometer (6700 vis.) by monitoring the concentration at 540nm.

2.13.2 Effect of Contact Time on Crude Oil Batch Adsorption

Adsorption experiment was carried out by agitating five (5) samples containing 1.03g of activated carbon from Barbados legume with 25ml of 176mg/l concentrations of the Tebujor crude oil polluted water at 45°C, in a temperature controlled waterbath. The samples were withdrawn after 20, 25, 30, 35 and 40 minute respectively and filtered with Whatmann filter paper. Crude oil concentrations in filtrates were measured spectrophotometrically by monitoring the concentration at 540nm, using a visible spectrophotometer (6700 vis.).

2.13.3 Effect of BLAC Dosages on Crude Oil Batch Adsorption

The adsorption experiment was carried out by agitating 1.0, 1.5, 2.0 2.5, and 3.0g of the activated carbon from Barbados legume with five samples of 25ml each of the crude oil sample from Tebujor at constant concentration of 176mg/l at 45°C in a temperature controlled waterbath. The samples were withdrawn from the waterbath after 39minute and filtered using Whatmann filter paper. Crude oil concentrations in filtrates were measured visible spectrophotometer (6700 vis.) by monitoring the concentrations at 540nm.

2.13.4 Effect of Temperature on Crude Oil Batch Adsorption with BLAC

Adsorption experiment was also carried out by agitating 1.03g of Barbados legume activated carbon (BLAC) with five samples of 25ml of 176mg/l concentration of the crude oil polluted water from Tebujor Creek at 30, 35, 40, 45 and 50°C in a temperature controlled waterbath. One sample was fed into the waterbath at each of the temperatures. The sample was withdrawn after 39 minute at each of the temperatures. The mixture was filtered using Whatmann filter paper. Crude oil concentrations in the filtrates were measured spectrophotometrically by monitoring the absorbance at 540nm using a visible spectrophotometer (6700 Vis.).

RESULTS AND DISCUSSION

The characteristics of the Barbados legume activated carbon (BLAC) determined in the experiment are surface area, pore size, bulk density, pH, porosity, moisture content, iodine number, pore volume and ash content. The results are reported in Table-1. The Brunauer-Emmett-Teller (BET) surface area of the BLAC was obtained as 1067.66m²/g by the nitrogen adsorption method. This trend agrees with the report of Maulion *et al.*, (2015), on corncob activated carbon though the value is a little less than what they obtained in their research. The bulk density of the BLAC was obtained as 0.40g/cm³, which agrees with the report of Olufemi and Otuoze, 2018 on coconut shell activated carbon but higher than the value reported by Maulion *et al.*, (2015) on corncob activated carbon. The pH of the BLAC was obtained as 7.27, a trend which agrees with the report of Olufemi and Otolorin (2017) on corncob shell activated carbon. The extent of adsorption using BLAC was further evaluated by measuring moisture content (36.5%), ash content (4.93%), pore volume (0.63m³/g), porosity (20.86%), BET pore size (38.52A), Barrett-Joiner-Halenda (BJH) pore size (48.55) and iodine value (105.86mg/g).

Characteristic	Value
pH	7.27
Moisture content (%)	36.50
Porosity (%)	20.86
Ash content (%)	4.93
Pore volume (m^3/g)	0.63
Iodine value (mg/g)	105.86
Bulk Density (g/cm ³)	0.40
BET Surface area (m^2/g)	1067.26
BJH Surface area (m^2/g)	665.26
BET PS (A)	38.52
BJH PS (A)	48.53

Table-1 Characteristics of the Barbados legume activated carbon



Fig. 1 scanning electronic microscope (SEM) image of BLAC



Fig. 2 Fourier transform infrared (FTIR) spectrum for Barbados legume (BLAC)

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Fig. 3 XRD spectrum for Barbados legume (BLAC)

Fig.1 shows the scanning electronic microscope (SEM) microgram of Barbados legume activated carbon (BLAC). It is obvious from figure 1 that BLAC has reasonable layers of pores with reliable possibility for adsorbates to be adsorbed into these pores. Fig. 2 shows the Fourier transform infrared spectroscopy (FTIR) spectrum analysis of the Barbados legume activated carbon (BLAC). The spectrum shows variation of adsorption peak intensities which corresponds to the existence of different functional groups detected in the adsorbent. The spectrum peak at 3445.00cm⁻¹ represents – OH stretching vibration of phenol group of cellulose and lignin. This trend agrees with the reports of Rafatullah et al., (2012) and El-Araby et al., (2019). The peak at 2927.76cm⁻¹, represent -CH₂ stretching of aliphatic compound. This trend agrees with the report of Rafatullah et al., (2012). The band 2375.83 cm⁻¹ is from carbon dioxide (CO₂) in air, which agrees with the report of El-Araby *et al.*, 2019. The band 1877.00cm-1 is C=O, 1631.73 correspond to non-ionic carboxyl group -COOH-, (-COOH, -COOCH₃) may be assigned to carboxylic acid or ester. The functional groups OH and CO shown by the FTIR could be responsible for the removal of Crude oil from the solution by adsorbent. The XRD pattern of the BLAC is presented in fig. 3. The two wide peaks that appeared at 15° and 38° in the crystalline pattern of the BLAC are typical of XRD pattern of alpha cellulose. The peaks with importantly reduced intensity were observed in the pattern of the BLAC which indicate that the BLAC is amorphous in structure.



Fig. 4 Langmuir isotherm of BLAC on crude oil adsorption



Fig. 5 Freundlich isotherm of BLAC on crude oil adsorption



Fig. 6 Redlich-Peterson Isotherm of BLAC on crude oil adsorption



Fig. 7 Tóth Adsorption isotherm of BLAC on crude oil adsorption



Fig. 8 Pseudo-second order adsorption of crude oil on BLAC



Fig. 9 Effect of temperature on the crude oil with BLAC

	2 - Parameter			
Langmuir	Q _b	В	Adj R ²	
-	11.51	0.86	-0.2768	
Freundlich	n	k _f	Adj R ²	
	1.11	10.05	0.1677	
	3 Parameter			
Redlich-Peterson	a _R	K _R	β	Adj R ²
	13.49	1733.4	0.1888	-0.3020
Toth	q _s	b _T	t	Adj R ²
	-95.06	-45.81	0.5882	0.3816

Table-2 Adsorption isotherm of Tebujor crude oil sample

The results of the data fitting and analysis of the adsorption isotherms recorded in Table-2, shows that Toth isotherm gives better fit for the adsorption operation of crude oil onto BLAC from Tebujor crude oil polluted water with adjusted correlation coefficient of 0.3816 when compared to other isotherms used.

Table-3 Pseudo second order model Rate constant and adsorption capacity data

Temperature (°C)	$k_2(\frac{g}{mg.min})$	$\mathbf{q_e}\left(\frac{\mathbf{mg}}{\mathbf{g}}\right)$	R ²
45	0.0470	4.6464	0.8197

The pseudo first order model (equation 24) prediction was undefined when applied to the experimental data of the crude oil adsorbed from Tebujor polluted water onto Barbados legume activated carbon, therefore, the model of pseudo-second order kinetic was tested on the same experimental data. Figure 8 shows the plot of the adsorption of crude oil from Tebujor Crude oil polluted water. The parameters of pseudo-second order obtained from the plot and presented in table 3 confirms the relevant nature of pseudo-second order model to the adsorption operation. This trend agrees with Olufemi and Otolurin, (2017); Kelle, (2018). The optimal contact time of crude adsorption from Tebujor polluted water onto Barbados legume activated carbon (BLAC) was obtained as 39 minute. This trend agrees with the report of Kelle, 2018. The optimal adsorption capacity was obtained as $4.646 \frac{mg}{g}$ and the rate constant as $0.047 \frac{g}{mg.min}$.

Table-4 Thermodynamic parameters of adsorbent in Tebujor polluted water

$\Delta \mathbf{G}^{\mathrm{o}}\left(\frac{\mathrm{KJ}}{\mathrm{mol}}\right)$	ΔH° (KJ mo)	$\Delta S^{\circ} \left(\frac{J}{mol.K}\right)$	
6.28	12.9	61.2	

The plot of $\ln K_d$ versus $\frac{1}{T}$ for crude oil removal onto Barbados legume activated carbon is shown in Figure 9. The value of Δ H^o and the value Δ S^o of adsorption was evaluated by fitting the experimental data into Eq. (38) as shown in Figures 10. The change in standard enthalpy (Δ H^o) for the crude oil emulsion adsorption from Tebujor polluted water onto Barbados legume activated carbon (BLAC) is positive and less than 84KJ/mol (Table 4), indicating the adsorption operation is physical and endothermic in nature. The standard change in Gibbs free energy (Δ G^o) values for the adsorption operation of crude oil from Tebujor pollution water onto BLAC shows how sudden the adsorption occur and the separation work of the adsorption operation. The value of Δ S^o for the crude oil adsorption onto the adsorbent, show increased disorder at the solid–solution interface.

CONTRIBUTION TO KNOWLEDGE

The characteristics of activated carbon prepared from Barbados legume were determined and the efficiency, kinetic and thermodynamic data of the removal of Crude oil from Crude oil polluted water using this adsorbent were obtained. These data are available for further research.

CONCLUSION

In this experimental investigation of the removal of crude oil emulsion from Tebujor crude oil polluted water onto Barbados legume activated carbon, the percentage yield from carbonization of Barbados legume shows that the conversion of the waste of Barbados legume to meaningful use will not be a waste of resources. The quality or characteristics of the activated carbon obtained from Barbados legume show that this activated carbon can effectively serve as reliable substitute to commercial activated carbon.

The adsorption of crude oil from polluted water from Tebujor onto activated carbon prepared from Barbados legume was examined at variable concentration, contact time, adsorbent dosage, and temperature, after first obtaining their optimal adsorption conditions. The findings show that adsorption process increases with temperature, adsorbent dosage and contact time until their corresponding optimum condition was reached. The Toth adsorption model show better fit for the adsorption operation of crude oil from Tebujor crude oil polluted water onto Barbados legume activated carbon, compared to other isotherms used in the result analysis. The value of ΔH° obtained shows the adsorption of crude oil from Tebujor polluted water onto Barbados legume activated carbon to be endothermic process and the value falls within the range of physical adsorption. The positive data of ΔS indicates the existence of some structural changes at the solid-liquid interface which also favors adsorption stability and ion exchange. The positive data of ΔG° indicates that adsorption operation was slow. These results from the characterization, activation, adsorption; kinetic and thermodynamic studies reveal that activated carbon from Barbados legume has the potential to adsorb crude oil from crude oil polluted water and as low cost agro-based material that has no known economic value and is readily available, this activated carbon can serve as good and reliable alternative for commercial activated carbon.

CONFLICT OF INTEREST

The authors declare that they have no competing interests to influence the work reported in this paper

REFERENCES

- Adie, D.B., Okuofu, C.A. & Osakwe, C. (2012). Isothermal and batch adsorption studies of the use of Borassus Aethiopium and Cocos Nucifera for wastewater treatment. *America international Journal of contemporary research*, 2(7): 119 – 130.
- Asadu, C.O., Elijah O.C., Ogbodo N.O., Anthony E.C., Onyejiuwa C.T., Onoh, M.E. Ike, I. S., Onoghwarite O.E. & Chukwuebuka, A.S. (2021). Treatment of crude oil polluted water using stearic acid grafted mango seed shell (magnifera indca) composite. *Journal of Current Research In Greenand Sustainable Chemistry*, 4: 1-15.
- Bokanyi, L. (2012). Some applications of Tóth-isotherm in mineral processing. XXVI International Mineral Processing Congress (IMPC) Proceedings: 24 28, New Delhi, India.
- Bridelli, M.G. & Crippa, P.R. (2008). Theoretical analysis of the adsorption of metal ions to the surface of melanin particles. *Adsorption*, 14: 101–109
- Debela, T.T. (2016). *Removal of lead from waste water using corn cob activated carbon as an adsorbent, A Master's Degree Thesis,* Addis Ababa, Ethiopia, Addis Ababa University.
- Egufe, Y. (2016). Gbaramatu oil spill: communities battle polluter, regulators over threat to lives. Vanguard news.
- Ekpete, O.A., A. C. Marcus, A.C. & Osi, V. (2017). Preparation and Characterization of Activated Carbon Obtained from Plantain (*Musa paradisiaca*) Fruit Stem. *Hindawi Journal of Chemistry:* 1 – 6.
- El-Araby, H.A., Ibrahim, A.M.M.A., Mangood, A.H. & Abdel-Rahman, A.A.H. (2017). Sesame husk as adsorbent for copper (II) ions removal from aqueous solution. *Journal of Geoscience and Environment Protection* 05(07): 109-152
- Emrah, B, Mahmut, O & Ayhan, I.S (2008). Adsorption of malachite green onto Bentonite:equilibrium and kinetic studies and process design. Microporous and Mesoporous materials: 234-246.
- Ghogomu, J.N., Muluh, S.N., Ajifack, D.L., Alongamo, A.A.B. & Noufame, D.T. (2016). Adsorption of Lead (II) from aqueous solution using activated carbon prepared from raffia palm (Raphia Hookeri fruit Epicarp. *Journal of applied chemistry*, 9(7): 74 85.
- Gottipati, R. (2012). Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase. Ph.D. Thesis, Odisha, Indian, National Institute of Technology Rourkela.
- Gumus, R. H., & Okpeku, I., (2015). Production of Activated Carbon and Characterization from Snail Shell Waste (*Helix pomatia*). Advances in Chemical Engineering and Sci, 5: 51-61.
- Hameed, B.H., & El-Khaiary, M.I. (2008). Malachite green adsorption by Rattan Sawdust: Isotherm, kinetic and mechanism modeling. *Journal of Hazardous Materials*, 159: 574–579.

- Idris, S., Iyaka, Y.A., Ndamitso, M.M., Mohammed, E.B.& Umar, M.T. (2011). Evaluation of kinetic models of copper and lead uptake from dye wastewater by activated pride of Barbados shell. *American Journal of chemistry*, *1*(2): 47 51.
- Kelle, H.I. (2018). Comparative analysis of removal of crude oil and some refined petroleum products from the environment using rice husk: adsorption isotherm and kinetic studies. *Nigerian Journal of basic and Applied Science*, 26(1): 1 – 13.
- Kumar, A. & Jena, H.M. (2016). Preparation and characterization of high surface area activation carbon from foxnut (Euryale Ferox) shell by chemical activation with H₃PO₄. *Elsevier Journal of Result in Physics, (6)*: 651-658.
- Lee, S.-M.; Lee, S.-H.; Roh, J.-S. (2021). Analysis of Activation Process of Carbon Black Based on Structural Parameters Obtained by XRD Analysis. Crystals, 11: 153.
- Maulion, R.V., Abacan, S.A., Allorde, G. G., Cherrielyne, M. & Umali, S. (2015). Oil spill adsorption capacity of activated carbon tablets from corncobs in simulated oil-water mixture. *Asia Pacific Journal of Multidisciplinary Research*, 3 (5): 146-151.
- Meriem, B. & Fatima, A. (2011). Adsorption of Congo red onto activated carbons having different surface properties: Studies of kinetics and adsorption equilibrium. Desalination and water treatment, 37: 122-129.
- Muhammad, S.A., Magaji, M.B. & Idris, M.A. (2020). Assessment of physicochemical parameters in crude oil contaminated water samples of three communities of Ikpokpo, Itanba and Okpele-Ama of Gbaramatu kingdom along the Escravos Rivers in Warri South west local government area of Delta State, Nigeria. *International Journal of Environment and Pollution Research*, 8(1): 57 – 76.
- Nayak, R., Padhye, R. & Arnold, L. (2017). Melt-electro spinning of nano fibers. Science Direct Journal
- Norman, W. (2016). Tribune News Service, Chicago, USA.
- Nunes, C.A. & Guerreiro, M.C. (2011). Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers. *Quimica Para um Mundo Melhor*, 34(3): 472 476.
- Ogbeide, O.M., Ezeh, E.C. & Okpara, O.O. (2019). Isotherms, kinetics and equilibrium studies of adsorption of lead (II) from aqueous solution using polymer-modified coconut shell activated carbon (MCSAC). *Journal of environmental science, toxicology and food technology,* 13(8): 28-43.
- Ogbodo, N.O., Asadu, C.O., Ezema, C.A., Onoh, M.I., Elijah, O.C., Ike, I.S. & Onoghwarite, O.E.(2021). Preparation and characterization of activated carbon from agricultural waste (Musa-paradisiaca peels) for the remediation of crude oil contaminated water. *Journal of Hazardous materials Advances*, 2: 1-11.
- Olufemi, B.A. & Otolorin, F. (2017). Comparative adsorption of crude oil using mango (mangnifera indica) shell and mango shell activated carbon. Environmental engineering research: 1-20.
- Onwuka, J.C., Agbaji, E.B., Ajibola, V.O., Okibe, F.G. (2018). Treatment of Crude oil-contaminated water with chemically modified natural fibre. *Applied water science*. 8(86): 1-10
- Ordinioha, B. & Brisibe, S. (2013). The human health implication of crude oil spills in the Niger Delta, Nigeria: An interpretation of published studies. *Nigerian Medical Journal*, 54(1): 10-16.
- Özcan, A., Öncü, E.M., Özcan, A.S. (2006). *Kinetics, isotherm and thermodynamic studies of adsorption of acid blue* 193 *from aqueous solutions onto natural sepiolite, Colloids and Surfaces A:* Physicochemical and Engineering Aspects, 277: 90-97.
- Peggy, C. (2013). Pride of Barbados. In the Garden.
- Rafatullah, M., Sulaiman, O., Hashim, R. & Ahmad, A. (2012). Removal of cadmium (II) from aqueous solutions by adsorption using meranti wood. *Wood Science Technology*, 46: 221–241.
- Rodriguez, D. (2006). Pride of Barbados"-A Great Heat Loving Plant and Future Texas SuperStar. Texas Agrilife Extension, Texas, USA.
- Sekaran, G., Shanmugasundaram, K.A., Mariappan, M. & Raghavan, K.V. (1995). Adsorption of Dyes by Buffing Dust of Leather. *Journal of Chemical Technology*. 2: 311.
- Sharma, K.K. & Sharma, L.K. (2013). A textbook of physical chemistry. 443 460. VIKAS Publishing House PVT ltd, India.
- Werth, A.J., Blakeney, S.M. & Cothren, A.I. (2019). *Oil adsorption does not structurally or functionally alter whale baleen*. 1 11. The Royal Society Publishing.
- Yuh-Shan, H., Malarvizhi, R., & Sulochana, N. (2009). Equilibrium isotherm studies of methylene blue adsorption onto activated carbon prepared from Delonix Regia pods. *Journal of environmental protection science, 3:* 111-116.
- Zhang, Z., Moghaddam, L., O'Hara, I.M.O., & Doherty, W.O.S. (2011). Congo red adsorption by ball-milled sugarcane bagasse. *Chemical Engineering Journal*, 178: 122–128.