Comparative Study between Locally Synthesized Activated Carbon and Commercial Activated Carbon and their Adsorption Isotherms on Methylene Blue

Abstract

Adsorption using activated carbon (AC) has been proven to be effective in the treatment of wastewater. In this study, Carica papaya seeds were utilized for activated carbon (AC) preparation using zinc chloride as the activating agent. Experiment was carried out to explore the methylene blue uptake by both the Carica papaya seeds activated carbon (CPSAC) and commercial activated carbon (CAC). The physicochemical characteristics, Iodine number and adsorption isotherms of CPSAC were also compared with those of CAC. The adsorption equilibrium was represented with Langmuir and Freundlich isotherm models. The Langmuir isotherm was found to be the best fit for both CPSAC and CAC with the coefficient correlation (R^2) values of 0.9922 and 0.9964, respectively. Going by the good fitting of the Langmuir isotherm, MB adsorption on both CPSAC and CAC can be ascribed to be of monolayer adsorption process, and is associated with the chemical functional groups inherent on carbon surface. The optimum adsorption capacities of CPSAC and CAC according to the Langmuir isotherm at approximately 25◦C were 238.78mg/g and 241.14mg/g, respectively. This implies that CPSAC demonstrated similar outstanding adsorption properties to CAC for MB.

Key words: activated carbon, adsorption, Carica papaya, Freundlich, Langmuir, isotherm, methylene blue.

Introduction

Activated carbon is known to be a porous carbonaceous material with continually expanding applications in water treatment, desalination, as well as air purification based on its unique properties (Kosheleva et al., 2019; Samsuri et al., 2014; Yousefi et al., 2019). Being a very versatile adsorbent material, it exhibits a high degree of porosity including high surface area. It is widely sought after for use because it is relatively cheap as well as exhibiting the tendency for universal adsorptive capacity for majority of impurities. This gives it the advantage over other prominent adsorbents, like silica gel and molecular sieves (Adewumi, 2009). Although it is a material used since antiquity, activated carbon (AC) is currently one of the prominent technologies deployed in several industrial and environmental purification process, where it is commonly used for the purification of water (Matheus et al., 2019).

Environmental pollution caused by toxic dyes is of today a matter of great concern. Dyes are broadly used as colouring agents in textile, printing, dyeing, food and paper-making industries. When lost during manufacturing process or discharged into the environment, studies have shown that these dyes can reduce wastewater oxygen solubility and transparency, and are often toxic, carcinogenic and mutagenic to aquatic flora and fauna, even at low concentrations (Dubey et al., 2012). Amongst the popular dyes in use in Nigeria especially in the textile industry is the methylene blue (MB). Although it is used for a variety of purposes, but it is used primarily in dyeing fabric, wood etc. (Rafatullah et al., 2010). MB is a cationic dye and a heterocyclic aromatic compound, having a molecular formula $C_{16}H_{18}N_3SCl$. Effluents containing methylene blue (MB) have been implicated to causing serious environmental impact on neighbouring receptor water bodies (Asamudo et al., 2005). It is known to cause eye burns, which may lead to irreversible eye injury of both humans and aquatic animals. It is also implicated in causing

irritation to the gastrointestinal tract and skin (Oliveira et al, 2008). For these reasons, it becomes pertinent to remove MB from wastewater effluents before discharging them into water bodies, so that its harmful impacts on receiving waters can be minimized as much as possible. In the past decades, several methods and techniques have been developed for the removal of dyes from waste water. These include physiochemical, chemical and biological methods such as coagulation and flocculation (Han et al., 2005), ozonation (Ho et al., 2005), electrochemical methods (Mireia et al., 2012), fungal decolonization (Ho, 2006) and adsorption (Gupta et al., 2003). Of the existing techniques, adsorption has been acknowledged as the most effective and economical process, with its simple operation and high efficiency in removing water pollutants/organic compounds or several types of colouring materials from wastewater (Chen et al., 2010). Although not much research has been done on the adsorption studies of Activated carbon produced from Carica papaya seeds as compared to Commercial Activated Carbon (CAC). The few works that have been carried out on the seeds of carica pappya have not given much detailed study on its characterization and adsorption on MB in particular. Hence Carica papaya seeds that are locally and readily available to us here were considered for this work, in order to carry out its characterization and study its adsorption isotherm on methylene blue comparatively to the commercial activated carbon.

Materials and Methods

Chemicals and equipment: Analytical grade (> 98 %) chemicals were used in this study They are; hydrochloric acid solution, sodium carbonate, sodium thiosulfate, iodine, potassium iodate, potassium iodide, , , starch (for the preparation of starch solution), zinc chloride and methylene blue (all obtained from Charlec, Nigeria ltd & Steve Nicholas, Nigeria ltd). Commercial activated carbon (obtained from Great Obidave Limited, Lagos State, Nigeria). It has the

following specifications: iodine adsorption value (mg/g) ≥900; hardness (%) ≥ 90; bulk density (kg/m^3) = 480 ± 30 ; ash content (%) = 10.0; moisture content (%) = ≤ 5. Equipment used include the following: analytical weighing balance, ultraviolet spectrophotometer, scanning electron microscope (SEM), measuring cylinder, spatula, funnel, oven, muffle furnace, beakers, conical flask with stoppers, burette, retort stand, filter papers, and pipettes.

Sample preparation

Seeds from Carica papaya were the primary raw materials used in producing the activated carbon (AC). The seeds were obtained from Polokor market, Warri, Delta State. The papaya seeds were washed with distilled water severally to take away dirt and slime. The seeds were thereafter sun dried for 3 months and also air dried for another 3 months before storage for the next step of action of achieving the AC.

Preparation of the activated carbon

Two main processes were deployed in the synthesis of the AC: the semi-carbonization and chemical activation. Starting with the semi-carbonization process, the papaya seeds were subjected to temperature of 300^{o}C for about 60 mins and later allowed to cool to room temperature in the muffle furnace. The resulting material was tagged semi-carbonized carbon (SCC). Following this, the SCC was then brought to chemical activation by agitating with aqueous solution of 200 mL zinc chloride of $ZnCl_2$:SCC (wt:wt) at 1:1, where they were thoroughly mixed together. The resulting samples were returned to the muffle furnace for activation at 500^{o}C for 2hrs before cooling. After cooling, the sample was subsequently washed with 5% HCl and, then with deionized water several times. The sample was dried in a hot air oven at 110 °C, ground, and sieved to obtain the desired particle size (<212 µm) and stored in desiccators for further use.

Solution preparation and proximate analyses

Preparations of solutions as well as proximate analyses were carried out according to prescribed standard methods of the America Society for Testing and Materials (ASTM). Proximate parameters determined were moisture content (ASTM D7582; Rengaraj et al., 2002), volatile matter (ASTM D7582), fixed carbon (ASTM D5373), ash content (ASTM D3174) and iodine number (ASTM D4607-94). Prepared solutions were; hydrochloric acid solution (5 % by weight), sodium thiosulfate (0.100 N), standard iodine solution (0.100 ± 0.001 N), potassium iodate solution (0.1000 N) and starch Solution. While the sodium thiosulphate normality was determined according to Equation (1), that of iodine solution was however determined according to Equation (2) (ASTM D4607-94, 2011).

$$N_1 = (P.R)/S \quad (1)$$

where:

N_1 = sodium thiosulfate (N); P = potassium iodate (mL); R = potassium iodate (N) and S = sodium thiosulfate (mL).

$$N_2 = (S.N_1)/I \quad (2)$$

where:
N_2 = iodine (N); S = sodium thiosulfate (mL); N_1 = sodium thiosulfate (N) and I = iodine (mL)

Note: The titration steps for both (N_1 & N_2) were done in triplicates and the normality results averaged bearing in mind that the range of values did not exceed 0.003.

Determination of iodine number

This method is hinged on a three-point isotherm (ASTM D4607-94). To determine the iodine number, an estimation of three carbon dosages are needed. The experiment usually involves interacting the samples of the activated carbon (both the commercial and locally synthesized) with 10.0 mL (5%) HCl. Here, the mixture was heated to boil for 30 sec and then allowed to cool. Following this, 100.0 mL (0.1 N) iodine solution was introduced into the mixture and

properly stirred for another 30 sec. The resulting solution was thereafter filtered, and 50.0 mL of the filtrate was titrated with sodium thiosulfate (0.1 N), where starch was used as an indicator. The amount of iodine adsorbed per gram of carbon (*X/M*) was plotted against the concentration (*C*) of iodine in the filtrate, using logarithmic axes. The iodine number is the *X/M* value when the residual concentration (*C*) is 0.02 N (0.02 mol L^{-1}). The *X/M* and *C* values were thus calculated;

a) To determine the value of X/M, the following values were first derived (ASTM D4607-94, 2011);

i. $A = N_2$ (12693.0)

where: N_2 = iodine (N)

ii. $B = (N_1)$ (126.93)

where: N_1 = sodium thiosulfate (N)

iii. DF = (I + H)/F

where: DF = dilution factor; I = iodine (mL); H = 5 % hydrochloric acid used (mL); and F = filtrate (mL).

With these values, the value of X/M was thus calculated using Equation (3) (ASTM D4607-94, 2011):

$$X/M = [A – (DF).(B).(S)] / M \quad (3)$$

where**:** X/M = iodine absorbed per gram of carbon (mg/g); S = sodium thiosulfate (mL); and M = carbon used (g).

a. The value of C was calculated using Equation (4) (ASTM D4607-94, 2011):

$$C = (N_1 \cdot S)/F \quad (4)$$

where: C = residual filtrate (N); N_1 = sodium thiosulfate (N); and F = filtrate (mL); S = sodium thiosulfate (mL).

However, the activated carbon dosage was estimated via Equation (5) (ASTM D4607-94, 2011):

$$M = [A- (DF) (C) (126.93) (50)] / E \quad (5)$$

where: M = carbon (g); A = (N_2) (12693.0); DF = dilution factor; C = residual iodine; and E = estimated iodine number of the carbon.

Note: the three carbon dosages were calculated using three values of C (usually 0.01, 0.02, and 0.03, respectively).

Adsorption study

0.1 g of CPSAC was interacted with 50.0 mL of MB solution at different initial concentrations (150 - 350 mg L^{-1}) for 24hrs under room temperature (~25 °C). The final concentration of MB was analyzed with the help of UV/Vis spectrophotometer programmed at 645 nm. The amount of MB adsorbed from each solution was thus calculated using Equation (6) (Deepak et al, 2017):

$$q_e = (C_O - C_e)\frac{v}{m} \quad (6)$$

where:
q_e = amount of dye in mg per gram of adsorbent.
C_o (mg L^{-1}) = concentration of the methylene blue solution at starting time (t = 0).
C_e (mg L^{-1}) = concentration of the methylene blue solution at equilibrium time.
V (L)= volume of solution.
M (g)= mass of adsorbent.

Adsorption Isotherm

The adsorption isotherm usually reveals how molecules in adsorption process are distributed between the liquid phase and the solid phase under an equilibrium state. An adsorption isotherm study was carried out on two well-known isotherm models (Langmuir and Freundlich). The applicability of the isotherm equation is assessed using the correlation coefficients, R^2.

Langmuir isotherm model

The Langmuir model generally is on the assumption that adsorption takes place on the surface of homogenous adsorbent whose sites are identical and are equally available and energetically

equivalent. It is known for success in processes involving monolayer adsorption (Allen et al, 1988).

This Langmuir equation can be written as (Langmuir, 1916):

$$q_e = \frac{q_m K_L C_e}{1 + k_L C_e} \quad (7)$$

where:
C_e = equilibrium concentration of the dye solution
q_e = equilibrium adsorption capacity
q_m = maximum equilibrium adsorption capacity
K_L = energy of adsorption

However, the linear form of the Langmuir isotherm equation can be described with Equation (8) (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (8)$$

Freundlich Isotherm Model

The Freundlich isotherm assumes that the adsorption occurs on heterogeneous surfaces at sites with different energies of adsorption and with non-identical adsorption sites that are not always available. Mathematically, it is characterized by the heterogeneity factor '1/n' (Mckay et al., 1990).

The model can be described by the following form (Freundlich, 1906):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (9)$$

While the linear form of the Freundlich isotherm can be described as Equation (10) (Foo, 2012):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

where:
K_f = Freundlich constant related to sorption capacity
1/n = Freundlich constant related to the intensity of adsorption
C_e = dye concentration ate equilibrium state

Scanning Electron Microscopy Study

The surface structure of the produced adsorbent was carried out using the Jeol 840 electron scanning microscope. Here, 35 mg of CPSAC was placed on aluminium stubs, using colloidal graphite as a mounting medium. Following this, a thin layer of gold palladium was deposited unto the samples to make it conductive, and the surface study was analysed at 100 µm magnifications.

Results and Discussion

The proximate analyses of the commercial activated carbon (CAC) and the locally produced Carica papaya seeds activated carbon (CPSAC) are shown in the Table 1. Parameters considered were the moisture content, volatile matter, ash content, and fixed carbon content. Usually the moisture content dilutes the carbon and increases the weight during treatment process (Basari et al., 2012). Thus, the lower the moisture contents in activated carbons, the better. The moisture

Table 1: Proximate comparative analysis of commercial activated carbon and Carica papaya seeds activated carbon

Component (%)	**CPSAC (%)**	**CAC (%)**
Moisture content	3.47	2.93
Volatile matter	14.89	11.84
Ash content	7.39	6.81
Fixed carbon content	74.25	81.79

Key: CPSAC = Carica papaya seeds activated carbon; CAC = Commercial activated carbon

contents for CPSAC and CAC as presented in Table 1 were as low as 3.47% and 2.93% respectively, indicating a good carbon. The low ash content values for CPSAC (7.39%) and CAC (6.81 %) also shown in Table 1 indicate that the activated carbons have low inorganic content and high fixed carbon (Kosha., et al, 2018). This is because ash content can reduce the efficiency of the activated carbon. Therefore, the lower the ash content, the better the activated carbon.

The Iodine Number

The Iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration in the residual filtrate is at a concentration of 0.02 normal (i.e. 0.02N) (Mianowski et al., 2007). The results obtained as presented in Figures 1 and 2, revealed iodine number of CPSAC and CAC at 0.02 normality to be 948 mg/g and 973 mg/g, respectively. The higher the iodine value, the higher the microporosity (Mianowski et al., 2007). The iodine number of CPSAC and CAC are quite identical (r^2 values of 0.987 and 0.996, respectively, though very slightly in favour of CAC) and they both show high micropore content.

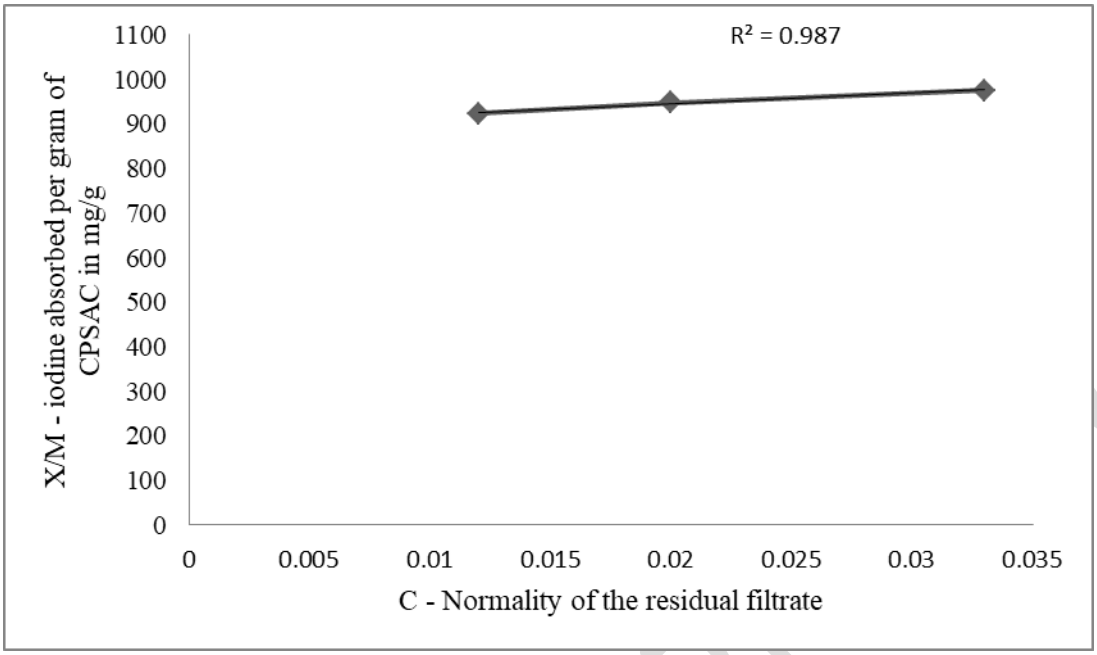

Figure 1: CPSAC iodine adsorption Isotherm

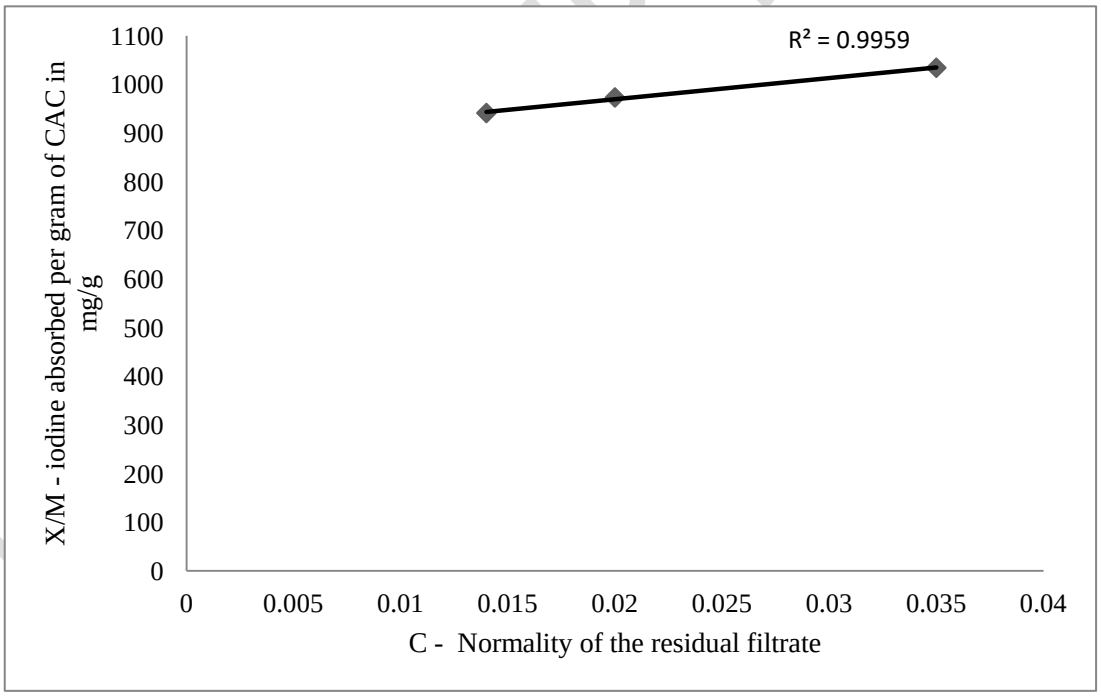

Figure 2: CAC iodine adsorption Isotherm

Adsorption Isotherm Studies

The results presented in Figures 3, 4.5, and 6, showed higher values of correlation coefficient of Langmuir adsorption isotherm of MB on both CAC and CPSAC over the Freundlich isotherm. This indicates the applicability of Langmuir isotherm which assumes a monolayer coverage and uniform activity distribution on the sorbent surface. The data presented in table 2 showed the related parameters for the adsorption of MB on CPSAC and CAC. From the correlation coefficients reported in Table 2, the Langmuir model of CPAC and CAC (R^2 = 0.9922 and R^2 = 0.9964, respectively) gave a much better fit than the Freundlich model of CPAC and CAC (R^2 = 0.8444 an R^2 = 0.8342) for adsorption of MB onto the different activated carbons, which suggests that the adsorption of MB would take place on identical and energetically-equivalent homogeneous sites of the activated carbons. The results also demonstrated no interaction and transmigration of dyes into the plane of the neighboring surface (Foo, 2012). It was observed that the adsorption capacity of the adsorbent, CPSAC and CAC are almost identical (i.e 238.78mg/g and 241.14mg/g, respectively) which signifies that the adsorption capacity of CPSAC is significant and comparable to the commercial activated carbon (CAC) for the removal of methylene blue.

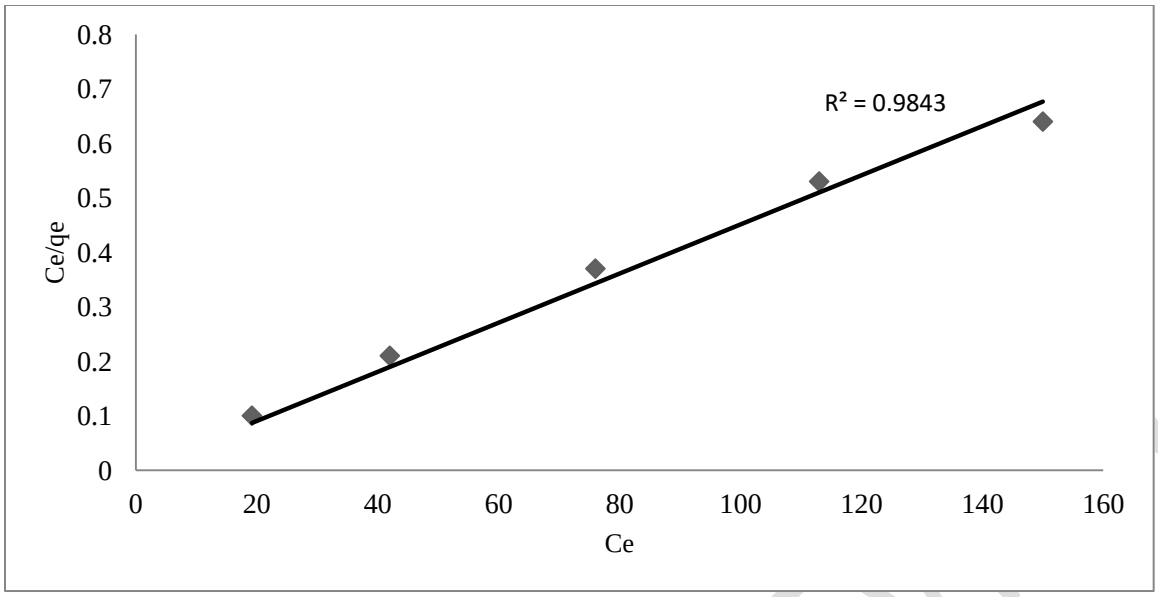

Figure 3: Langmuir adsorption isotherm of MB on CPSAC

Slope 0.004188
Intercept 0.034806

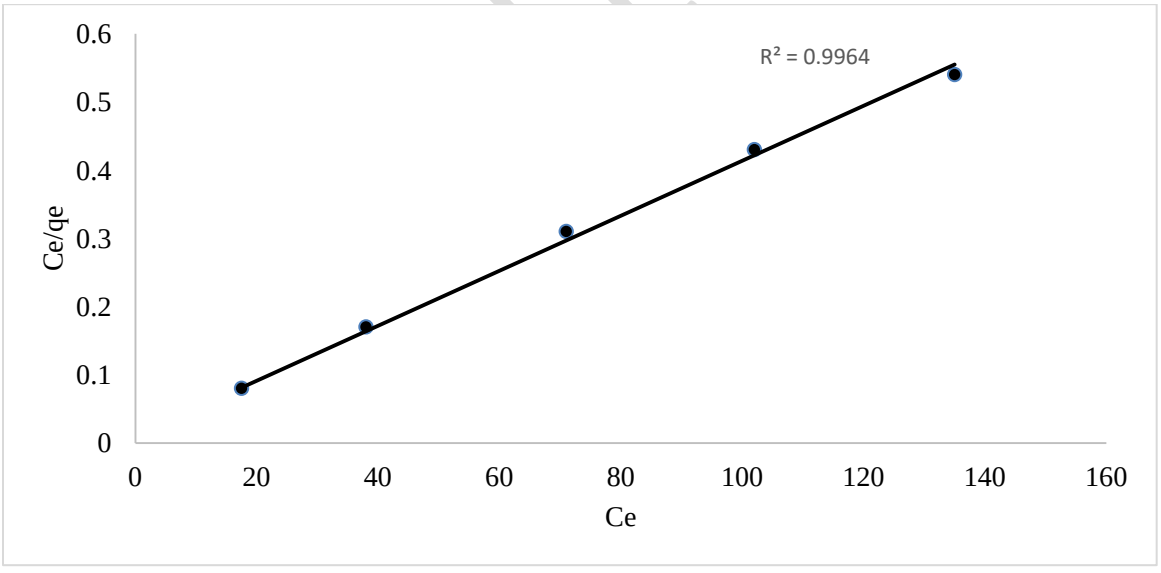

Figure 4: Langmuir adsorption isotherm of MB on CAC

slope 0.004147
Intercept 0.019858

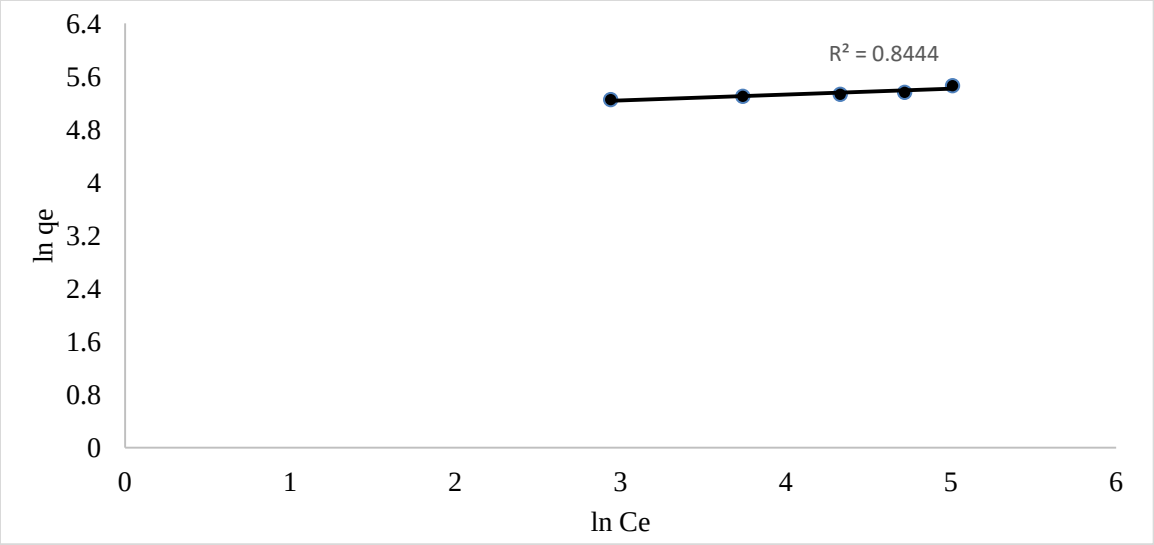

Figure 5: Freundlich adsorption isotherm of MB on CPSAC

Intercept 4.978106
Slope 0.087246

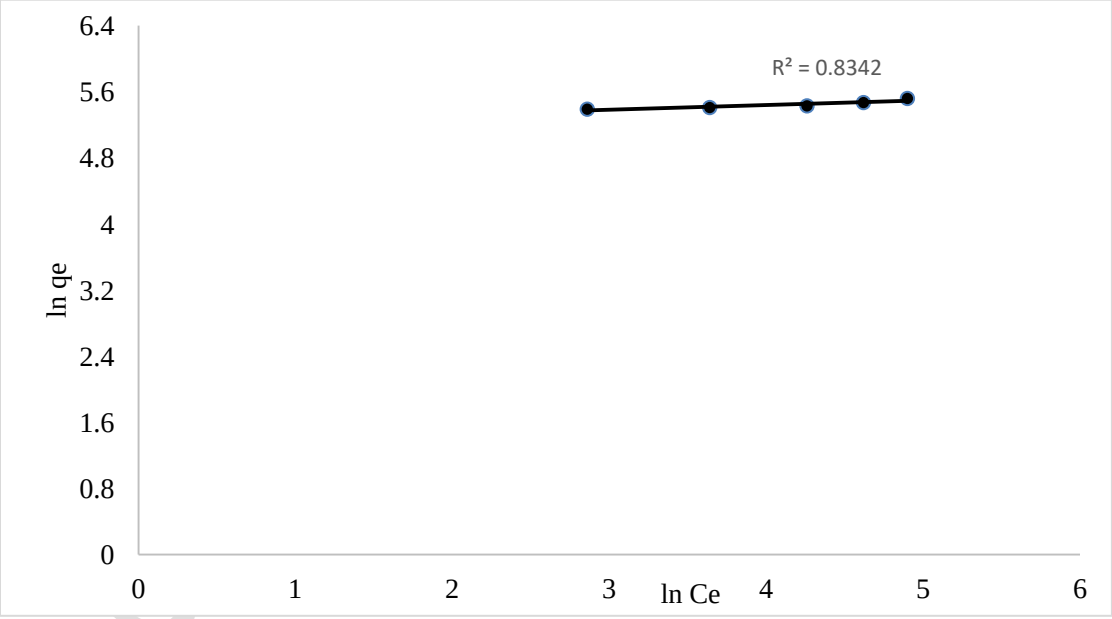

Figure 6: Freundlich adsorption isotherm of MB on CAC

Intercept 5.21
Slope 0.0578

Table 2: Related parameters for the adsorption of MB on CPSAC and CAC

	Product	
Langmuir adsorption isotherm constants	CPSAC	CAC
q_m	238.78	241.14
K_L	0.12	0.21
R^2	0.9922	0.9964
Freundlich adsorption isotherm constants		
K_f	145.20	183.09
1/n	0.09	0.06
R^2	0.8444	0.8342

Scanning Electron Microscopy Study

The result of the Scanning Electron Microscope (SEM) study of the locally produced activated carbon from the seeds of carica papaya before and after adsorption is shown in Figure 7. The scanned (image a) showed a porous carbonaceous solid having irregular pore sizes, which were able to accommodate the molecules of the MB on contact. However, after contact and adsorption, image b showed less of the activated carbon, because of the reduced number of white appearing solid surfaces, an indication of physisorption of MB on the locally produced carbon.

a = Adsorbent surface before adsorption b = Adsorbent surface after adsorption

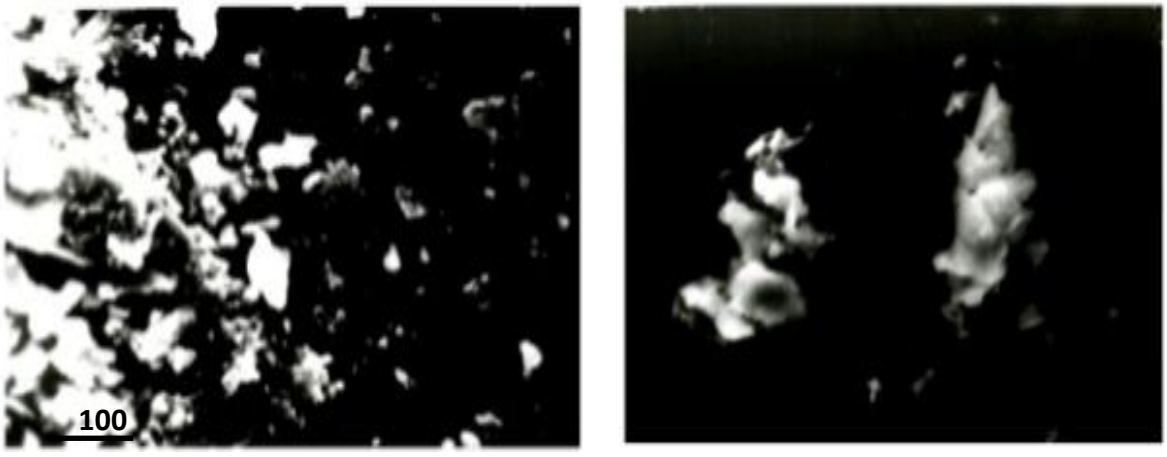

Figure 7: SEM images showing the morphology of the locally produced CPSAC before (a) and after adsorption, (b) (Idibie et al., 2021)

Other Non-Conventional Adsorbents and Their Different Adsorption Capacities

Table 3 is a list of various nonconventional low-cost adsorbents on methylene blue adsorption. Data from literature including from this work as presented in the table showed that the produced activated carbon (CPSAC) has a very large adsorption capacity compared to literature which could be due to material and process of activation.

Table 3: Comparison of Adsorption Capacities of Different Adsorbents for the Removal of MB

Activated Carbon source	q_m (mg/g)	Reference
Carica papaya seeds	238.78	This work
Commercial activated carbon	241.14	This work
Walnut shells	3.53	Aygün et al, 2003
Orange peel	5.87	Kavitha et al, 2007
Orange peel	20.50	Annadurai et al., 2002
Steam activated bituminous coal	580.00	Emad et al., 2006
Silk cotton hull	2.40	Kadirvelu et al, *2003*
Coconut tree sawdust	4.70	Kadirvelu et al, *2003*
Sago waste	4.51	Kadirvelu et al, *2003*
Banana pith	4.67	Kadirvelu et al, *2003*
Maize cob	5.00	Kadirvelu et al, *2003*
marine seaweed	5.23	Cengiz et al, 2008
Sawdust	4.89	Pekkuz et al., 2008
hazelnut shell	41.30	Ferrero, 2008
Coconut shell	277.90	Kannan et al, 2001
Groundnut shell	164.90	Kannan et al, 2001
Rattan sawdust	294.12	Hameed et al, 2007
Palm Fibre	277.78	Tan et al, 2007
Bamboo dust	143.20	Kannan et al, 2001
Date pits	123.10	Banat et al, 2003

Conclusion

Adsorption using locally produced activated carbon from Carica papaya seeds (CPSAC) has been proven to be effective in the treatment of wastewater contaminated with methylene blue.

The characterization of both the CPSAC and commercial activated carbon (CAC) showed excellent physical and chemical properties that were comparatively similar. Of the two isotherm models applied; Langmuir and Freundlich, the Langmuir isotherm gave a superior fit for the experimental data over the Freundlich for the whole concentration range considered. This was confirmed from the higher values of the correlation coefficients. The closeness of the correlation coefficient to unity was an indication of a perfect fit. The adsorption capacity of CPSAC and CAC was observed to be almost identical (i.e 238.78mg/g and 241.14mg/g, respectively).

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