Comparative Study of Locally Produced Activated Carbon from Carica Papaya Seeds 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. Overall, CPSAC demonstrated similar outstanding adsorption properties to CAC for MB.

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

Introduction

Activated carbon is known to be a porous carbonaceous material with continually expanding applications in water treatment, desalination, and air purification due to its unique characteristics

(Kosheleva et al., 2019; Samsuri et al., 2014; Yousefi et al., 2019). It is a very diverse adsorbent material, exhibiting a high degree of porosity and high surface area. It has wide acceptance for use because of its relative cheapness and universal adsorptive capacity for majority of impurities over other favoured adsorbents, such as 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). One of the most widely used dyes in Nigeria is methylene blue (MB), which happens to be a model cationic dye employed by industries such as textile industry for a variety of purposes and, serves primarily as a chemical agent for dyeing cotton, silk, wood etc. (Rafatullah et al., 2010). It is a heterocyclic aromatic chemical compound with 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 permanent injury to the eyes of humans as well as aquatic animals. Besides, it can also cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. Methylene blue also causes irritation to the skin when in contact with it (Oliveira et al, 2008). For these reasons, it becomes pertinent to remove methylene blue 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). Hence Carica papaya seeds that are locally and readily available were considered for this work, and to study its adsorption isotherm on methylene blue comparatively to the commercial activated carbon.

Materials and Methods

Chemicals and equipment: All the chemicals used in this study are of analytical grade (> 98 %). They included Hydrochloric acid solution, sodium thiosulfate, iodine, potassium iodide, sodium carbonate, potassium iodate, starch (for the preparation of starch solution), zinc chloride and methylene blue (all obtained from Charlec, Nigeria ltd & Steve Nicholas, Nigeria ltd). 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 species were used as the raw material to produce the activated carbon (AC). The papaya seeds were collected from a fruit shop at Polokor market, Warri, Delta State.

The papaya seeds as the precursor material were washed with distilled water several times to remove dirt and slime covering the seeds. The seeds were then sun dried for 3 months and then air dried for another 3 months before being stored for the next step in the process of preparing the AC.

Preparation of the activated carbon

Two main processes were used in preparation of the AC: the semi-carbonization and chemical activation. In the semi-carbonization process, the papaya seeds were heated to 300^{o}C for about 1hr under self-generated atmosphere and cooled to room temperature in the muffle furnace. The resulting material was labeled as semi-carbonized carbon (SCC). The SCC was then subjected to chemical activation. The SCC was agitated with aqueous solution of 200 mL of zinc chloride ($ZnCl_2$) according to the (wt:wt) of $ZnCl_2$:SCC at 1:1. The chemical activating agent ($ZnCl_2$) and pre-carbonized carbon were mixed together. The resulting samples were then placed back into the muffle furnace for activation at the optimum temperature of 500^{o}C for 2hrs before cooling. After cooling, the sample was subsequently washed with 5% HCl and, then with deionized water several times.

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).

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

where:

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

$N_2 = (S.N_1)/I$ (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. Also, additional replications were done whenever the range of values exceeded 0.003 N.

Determination of iodine number

This method is based upon a three-point isotherm according to the ASTM D4607-94 method. Determination of iodine number requires an estimation of three carbon dosages. The experiment usually involves treating the activated carbon samples (both CPSAC and CAC) with 10.0 mL of 5% HCl. This mixture was boiled for 30 sec and then cooled. Soon afterwards, 100.0 mL of 0.1 N of iodine solution was added to the mixture and stirred for another 30 sec. The resulting solution was thereafter filtered, where 50.0 mL of the filtrate was titrated with 0.1 N sodium thiosulfate, using starch as an indicator. The iodine amount adsorbed per gram of carbon (*X/M*) was plotted against the iodine concentration (*C*) 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 calculated as shown below;

a) To calculate the value of X/M, the following values were first derived;
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):

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

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): (4)

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

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):

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

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 placed in contact with 50.0 mL of a methylene blue solution at different initial concentrations (150 - 350 mg L^{-1}) for 24hrs at room temperature (approximately 25 °C). The final concentration of methylene blue was analyzed using a UV/Vis spectrophotometer at

645 nm. The amount of methylene blue adsorbed from each solution was thus calculated using Equation (6):

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

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 = volume of solution.
M = mass of adsorbent.

Adsorption Isotherm

The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches 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 compared by judging the correlation coefficients, R^2.

Langmuir isotherm model

The model assumes that adsorption occurs on a homogenous adsorbent surface of identical sites that are equally available and energetically equivalent, and it is used successfully in many monolayer adsorption processes (Allen et al, 1988).

This model can be described by the following form:

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

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):

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

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:

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

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

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

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

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)

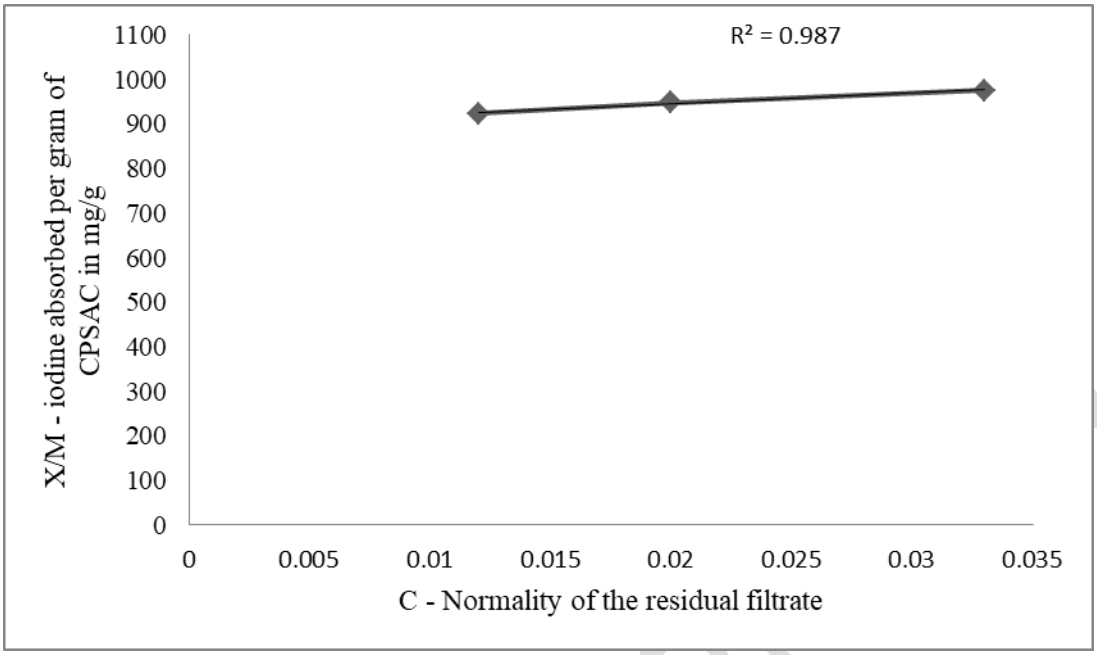

Figure 1: CPSAC iodine adsorption Isotherm

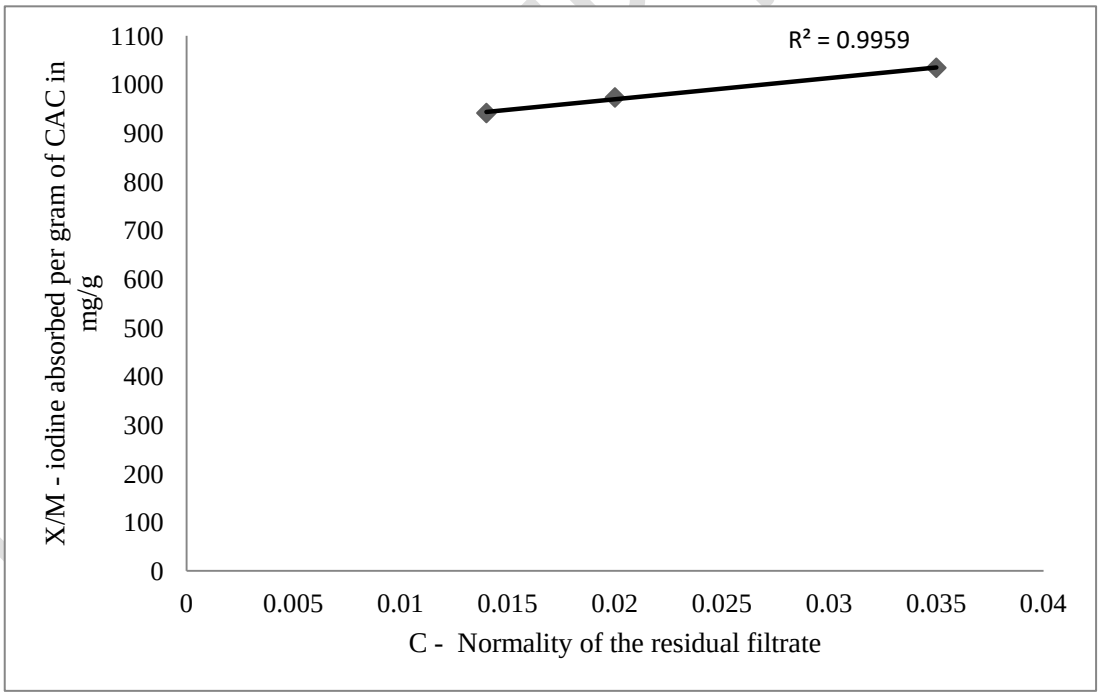

Figure 2: CAC iodine adsorption Isotherm

(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.

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.

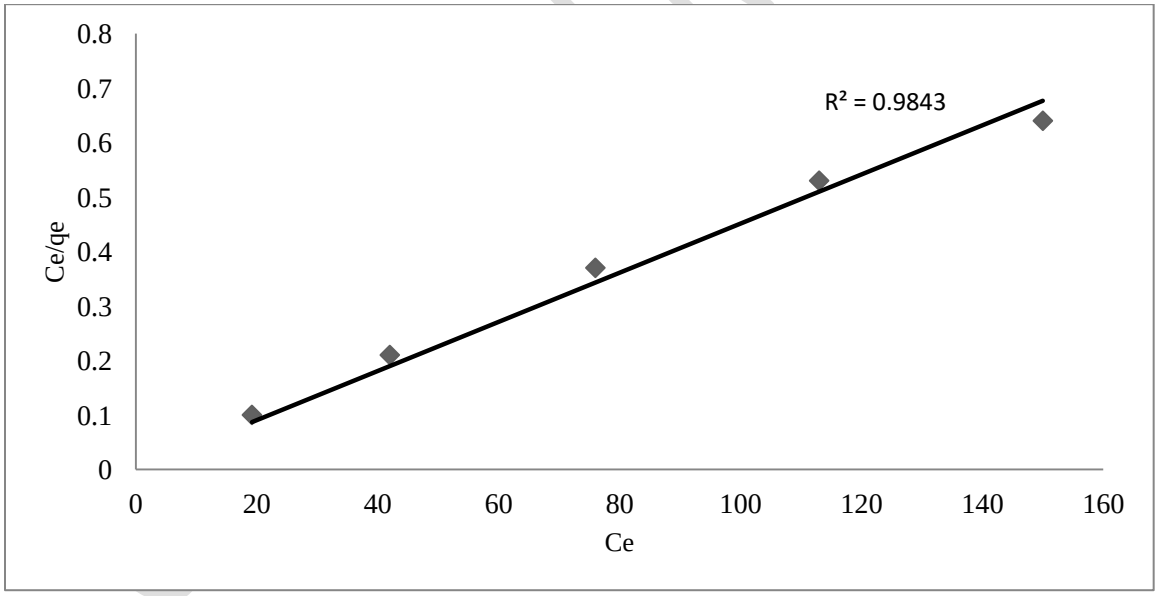

Figure 3: Langmuir adsorption isotherm of MB on CPSAC

Slope 0.004188
Intercept 0.034806

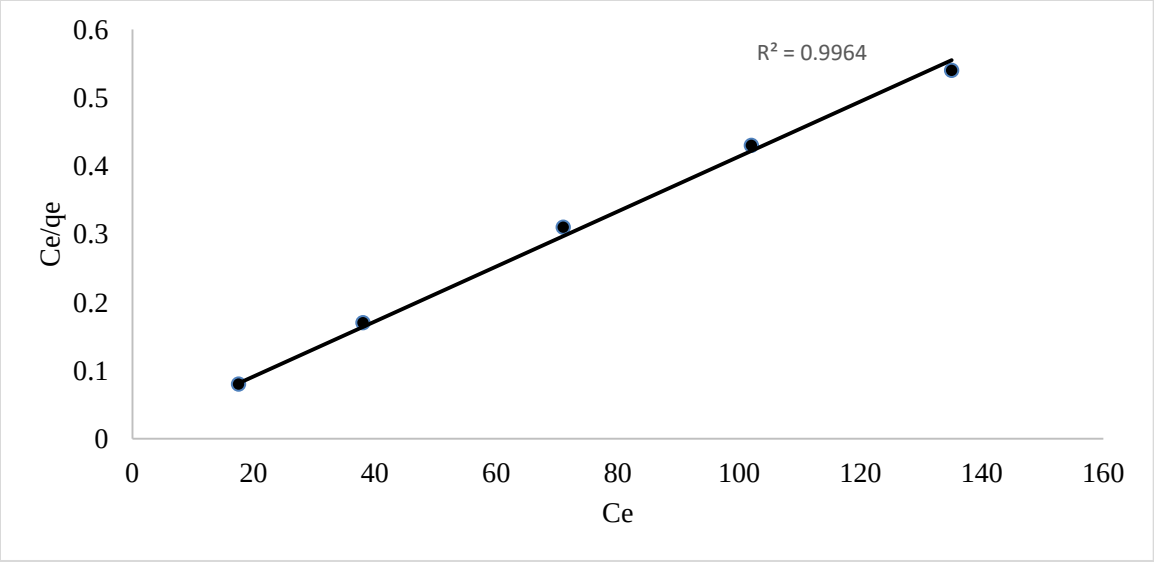

Figure 4: Langmuir adsorption isotherm of MB on CAC

slope 0.004147
Intercept 0.019858

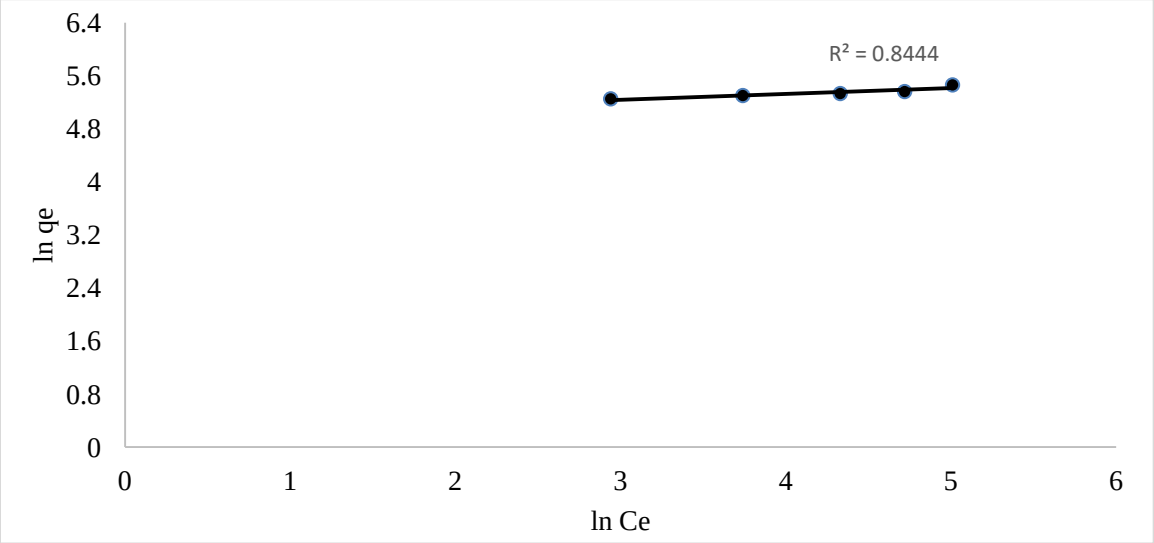

Figure 5: Freundlich adsorption isotherm of MB on CPSAC

Intercept 4.978106
Slope 0.087246

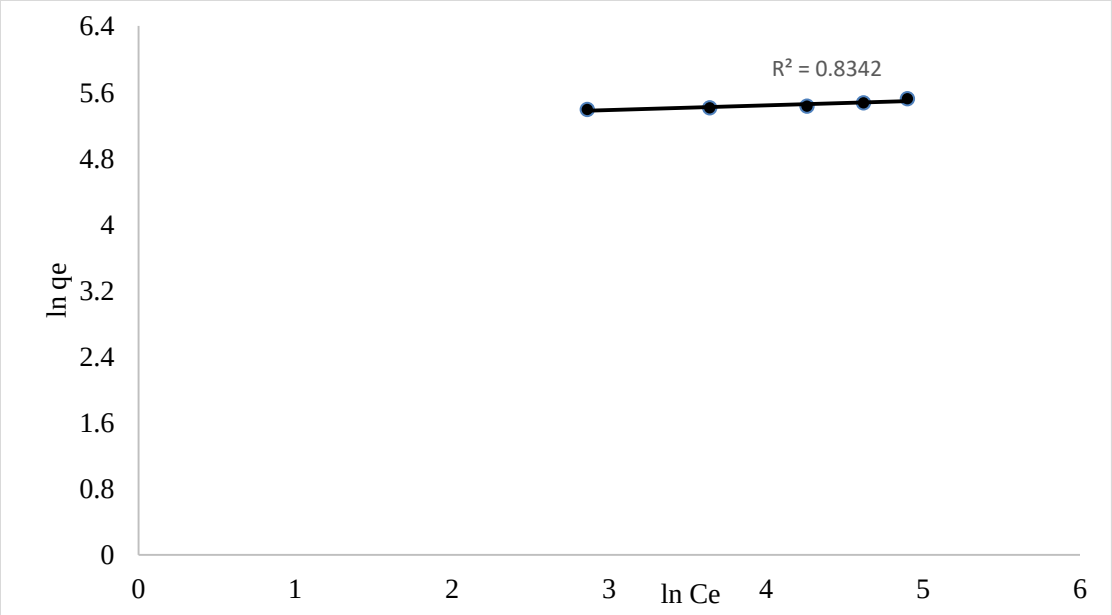

Figure 6: Freundlich adsorption isotherm of MB on CAC

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

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 was found to best fit the

experimental data over the whole concentration range as indicated from the higher values of the correlation coefficients. The closeness of the correlation coefficient to unity was an indication of a perfect fit. Overall, similar to CAC, the CPSAC demonstrated outstanding adsorption properties to MB. Thus, CPSAC is very promising for use in wastewater treatment to mitigate dye pollution.

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