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Adsorption of Chemically Prepared Cocoa Nibs Based Activated Carbon Onto Methylene Blue: Equilibrium and Kinetic Studies

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Abstract

This study was aimed to prepare cocoa nibs based activated carbon (CNAC) via chemical activation for methylene blue (MB) dye adsorption from aqueous solution. The activation process was performed at 500°C under inert condition using K_2CO_3 as activation agent. The effect of contact time and initial concentration of adsorbate on the adsorption process were examined. Langmuir isotherm model fitted well the adsorption equilibrium data with monolayer adsorption capacity of 64.98 mg/g at 30°C. The adsorption kinetic was found to follow the pseudo-second-order kinetic model.

Keywords: Activated carbon, Chemical activation, Cocoa nibs, Methylene blue.

Introduction

Water pollution has become a highlighted issue as some of the industrial effluent is directly discharged into the river and water bodies without proper treatment [1]. Dyes effluent treatments from textile industries are divided into biological, physical and chemical treatment processes. All these processes have different color removal capabilities, capital costs, and operating rates [2]. Physical treatment via adsorption process using Agrowaste based activated carbon as adsorbent is among the most efficient and cheap method for dyes removal. Several studies on agrowastes have been employed to remove the contaminants such as methylene blue (MB) dye from the water bodies [3] [4]. Agrowaste is appreciated as economical, sustainable and ecologically friendly materials. In this study, an attempt was made to utilize cocoa nibs waste into activated carbon using chemical activation process. The performance of CNAC was studied in removing MB dye from aqueous solution.

Experimental

Chemicals

All reagents and chemicals used in the research were analytical grade chemicals. For impregnation process, potassium carbonate (K_2CO_3) was used. Commercial methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$) (MB) textile dye was obtained from Sigma-Aldrich (M) Sdn Bhd.

Preparation of Stock and Test Solutions

Stock solution of MB with concentration of 500 mg/L was prepared by dissolving approximately 0.50 g of MB in 1000 mL distilled water. Test solution of MB ranging from 10 mg/L to 100 mg/L were prepared by subsequent dilution from stock solution.

Production of Pellet

The cocoa nibs waste was ground and sifted to a uniform size of 0.5 mm or smaller. The samples were shaped into pellets by compressing the mixture with a hydraulic press, in which the cocoa nibs were compacted into pellets with a specific density of 1.8 g/cm.

Preparation of Activated Carbon

The carbonization was performed by placing approximately 60 g of cocoa nibs pellet in a vertical furnace, which contained in a tubular stainless steel reactor. This step was carried outat 700°C for 1 hour under purified nitrogen (99.99%) with flowrate of 120 mL/min. Then, the furnace was allowed to cold to ambient temperature. Char yield was determined using following equation:

$$\% \text{ Yield} = \frac{w_c}{w_i} \times 100\% \quad (1)$$

where is the mass of char after carbonization process and w_i is the initial mass of cocoa nibs pellet. An amount of dried char was added with K_2CO_3 at various impregnation ratio (IR) in a 250 ml beaker. Both were mixed with deionized water to dissolve the salt. The IR was calculated as follows:

$$\text{Impregnation ratio, IR} = \frac{w_{K_2CO_3}}{w_{char}} \quad (2)$$

where $w_{K_2CO_3}$ is the dry weight of potassium carbonate pellets and w_{char} is the dry weight of cocoa nibs char. The mixture was then dehydrated in an oven at 105°C for 24 hours. The activation step was done using similar reactor as in carbonization step but at final temperature of 500°C under nitrogen flowrate of 120 mL/min for 2 hours. The sample was then cooled to room temperature and washed with hot deionized water until the pH of the washed solution reached 6.5-7.

Removal of MB by Batch Adsorption Study

The batch equilibrium experiments of the adsorption capacity studies were conducted at 30 °C in a 250 mL conical flask in a water bath shaker. The stock solution (1000 mg/L) of MB was prepared by dissolving approximately weighed 1.0 gram of the MB in 1000 mL of distilled water in a 1500 mL volumetric flask. The stock solutions were stored in dark place to prevent direct sunlight. The sample solutions were withdrawn at equilibrium to determine the residual concentration. The concentrations of the filtrates were measured using UV-Visible Spectrophotometer (Model Agilent Cary 60, USA).

Effect of Initial Concentration

In order to study the effects of initial adsorbate concentration, 100 mL of adsorbate solutions with known initial concentration (10, 25, 50, 80, 100 mg/L of MB) were prepared in a series of 250 mL Erlenmeyer flasks. The amount of adsorbent that was added into each flask was fixed at 0.1 g. The flasks were placed in an isothermal water bath shaker at temperature and rotation speed of 30°C and 120 rpm, respectively until equilibrium point was reached.

Effect of Contact Time

In order to study the effects of contact time on the adsorption uptake, 100 mL of adsorbate solutions with known initial concentration (10-100 mg/L) were prepared in a series of 250 mL Erlenmeyer flasks. The amount of CNAC that was added into each flask containing MB solution was fixed at 0.1 g. The flasks were then placed in an isothermal water bath shaker of 30 °C with rotation speed of 120 rpm for 360 minutes. The percent removal of adsorbate was calculated as follows:

$$\% \text{ Removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (3)$$

Where C_e is the concentration of adsorbate at equilibrium and C_i is the initial concentration of adsorbate. The MB uptake at equilibrium is calculated as follows:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (4)$$

where m is the mass of the adsorbent and V is the volume of the adsorbate.

Adsorption Isotherm

Adsorption isotherm study was carried out by fitting the equilibrium data to three isotherm model which are the Langmuir and Freundlich isotherm models, respectively represented by Equations (5),(6) and (7). The applicability and suitability of the isotherm equation to the equilibrium data was compared by judging the values of the correlation coefficients, R^2. The Langmuir model is atypical model used to measure the amount of adsorbate on an adsorbent at equilibrium. The relation is expressed by following equation [5]:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (5)$$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_m is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites(mg/g), K_L is the Langmuir constant related to the energy of adsorption(L/mg)

The Freundlich adsorption isotherm or Freundlich equations are a relation between the concentrations of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The relationship is stated as follows [6]:

$$q_e = k_f c_e^{\frac{1}{n}} \quad (6)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

In this equation, q_e (mg/g) is amount of adsorbed material in adsorbent surface k in arrangement are adsorption capacity and adsorption intensification.

Kinetic Model

The kinetics of adsorption describes the rate of adsorbate uptake on activated carbon prepared and it controls the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process. Therefore, models for liquid-phase adsorption such as pseudo-first-order and pseudo-second-order were used to analyze the adsorption kinetic data. The pseudo-first-order kinetic model equation of Largergren [7] is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time (mg/g), k_1 is the rate constant of pseudo-first order sorption (1/h). The pseudo-second-order equation is expressed as [8]:

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{t}{q_e} t \quad (9)$$

Where k_2 is the rate constant of pseudo-second-order sorption (g/h.mg).

Results and Discussion

Effect of contact time and MB initial concentration on adsorption equilibrium

Figure 2 and Table 1 show the effect of various initial concentrations on adsorption of MB by CNAC. An equilibrium time of 100 min was needed for MB dye solution with initial concentrations of 10-25 mg/l to reach equilibrium. However, for initial concentrations of 50-100 mg/l, longer equilibrium times of 22-24 hours were required for the system to reach equilibrium. Initially, adsorbate molecules have to first encounter the boundary layer effect. Then it has to diffuse from boundary layer film onto adsorbent surface and finally, it has to diffuse into the porous structure of the adsorbent [10]. The ratio of the initial number of dye molecules to the available surface area was low at lower initial concentration compared to higher initial concentration. Therefore, MB solution with higher initial concentration would take relatively longer contact time to attain equilibrium due to the higher amount of MB molecules.

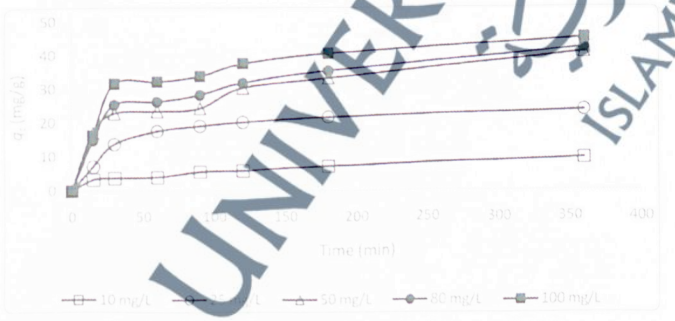

Fig. 2: Effects of contact time of MB onto CNAC

Table 1. MB percent removal by CNAC with IR 3:1

Initial Concentration (mg/L)	Concentration Left (mg/L)	Concentration Adsorbed (mg/L)	Percent Removal (%)	Concentration adsorbed at equilibrium, q_e (mg/g)
10	0.00	10.00	100.0	5.00
25	5.04	19.96	79.8	9.98
50	11.57	38.43	76.9	19.22
80	25.16	54.84	68.6	27.42
100	33.39	66.61	66.6	33.31

Effect of IR on adsorption equilibrium

Fig. 1 shows the influence of IR on CNAC in removing MB. Sample impregnated with 2:1 ratio has the lowest capability to adsorb the adsorbate where the value is 27.8 mg/g.

Fig. 1: Effect of IR on MB uptake

The adsorption capacity of CNAC was decreased with increased in IR from 1:1 to 2:1 before increased at IR of 3:1. CNAC with 3:1 ratio managed to adsorb 30.9 mg/g of MB at equilibrium. Higher IR was favorable for enhancing the MB adsorption as more pores are developed on the sample surface [9].

Adsorption Isotherm

The most appropriate correlation for the equilibrium curve needs to be established in order to understand the adsorption system. Therefore, the equilibrium adsorption data were analyzed using the Langmuir and Freundlich isotherms as shown in Figure 3 whereas Table 2 summarizes all the constants from both isoterm models.

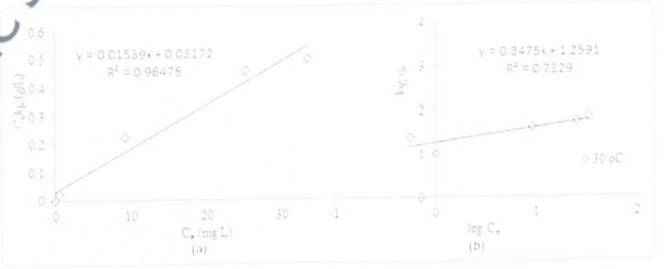

Fig. 3: Linear plots of (a) Langmuir and (b) Freundlich adsorption models

Table 2.Parameters of Langmuir and Freundlich adsorption isotherm for MB.

	Equation	R^2	q_m	K_L	K_f	n
Langmuir	y = 0.0154x + 0.0317	0.965	64.98mg/g	0.152	/	/
Freundlich	y = 0.3475x + 1.2591	0.733	/	/	3.52	2.88

Langmuir model gave the highest R^2 values which were greater than 0.96. Conformation of the experimental data into the Langmuir isotherm equation proved that the surface of CNAC for MB adsorption was made up of homogeneous adsorption patches with monolayer coverage of MB onto CNAC [9]. The monolayer saturation capacity of CNAC was found to 64.98 mg/g at 30 °C.

Adsorption Kinetics

All the experimental and calculated q_e values obtained from the pseudo-first-order and pseudo-second-order kinetic model for adsorption of MB at 30 °C are tabulated in Table 3. Comparing the R^2 values, pseudo-second-order model showed a significant agreement with adsorption mechanisms, which indicated the chemisorption with the heterogeneous active sites occurred on the surface of CNAC [11].

Table 3: Parameter values of the kinetic studies of the adsorption of MB onto CNAC.

	Pseudo-first-order			Pseudo-second-order		
MB concentration	q_e, cal (mg/g)	R^2	K_1	q_e, cal (mg/g)	R^2	K_2
10 mg/L	8.47	0.9721	0.3284	8.45	0.9278	0.1553
25 mg/L	18.46	0.9447	0.6468	25.97	0.9946	0.069
50 mg/L	29.59	0.9343	0.4191	36.63	0.9663	0.0626
80 mg/L	42.60	0.8889	0.231	39.53	0.9876	0.0577
100 mg/L	50.99	0.777	0.1965	45.25	0.9908	0.0575

Conclusion

CNAC was found to be suitable for the removal of MB from aqueous solution. Adsorption of MB was found to increase with increase in contact time and initial dye concentration. The Langmuir isotherm model was well described by the equilibrium data with maximum adsorption capacity of 64.98 mg/g. The pseudo-second-order kinetic model fits well with the kinetic data.

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RESEARCH ARTICLE

Removal of methylene blue from aqueous solution using cocoa (Theobroma cacao) nib-based activated carbon treated with hydrochloric acid

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Abstract

Chemical activation process was applied to prepare a cocoa nib-based activated carbon using potassium carbonate (K_2CO_3). The performance of the activated carbon in removing Methylene Blue from aqueous solution was investigated by batch adsorption studies. The adsorptive properties were studied in terms of initial concentration (C_0: 100-300 mg/L) and contact time effects. The experimental isotherm data fitted well the Langmuir and Temkin models. The adsorption kinetic followed the pseudo-second-order model and Boyd model explained the mechanism of adsorption. The results indicate that the chemically produced activated cocoa nib carbon has significant potential to be used as an adsorbent material for adsorption of Methylene Blue from aqueous solution.

Keywords: Cocoa nib-based activated carbon, Methylene Blue, Langmuir model, Temkin model, Boyd model

INTRODUCTION

The cellulosic originated precursors have been continually explored and tested as adsorbents. This is due to the fact that they possess significant values: abundant in nature, cheap, renewable and comparable with the conventional and commercial adsorbents (Lim and Aris, 2013). Agricultural wastes or by-products are an alternative source to be exploited in order to overcome issues on expensive precursor, regeneration and the effect of regeneration on adsorption capacity (Oladoja *et al.*, 2008). Study on low cost and non-conventional adsorbent could offer significant opportunity for environmental sustainability and at the same time, recommend promising benefits to commercially transform the waste into promising prospects (Ahmad *et al.*, 2012).

Some of the precursors used in the production of cellulosic-based or agricultural waste-based activated carbons in the recent past are cocoa shells (Ahmad *et al.*, 2012; Mylsamy and Theivarasu, 2012), cocoa pod (Pua *et al.*, 2013; Bello and Ahmad, 2011), peanut shells (Wu *et al.*, 2013), rice straw (Ratnangkoon *et al.*, 2016), papaya seeds (Collin and Lee, 2008), olive stones (Larous and Meniai, 2016), coconut husk (Tan *et al.*, 2008), coconut mesocarp (Ferreira *et al.*, 2015), beet pulp (Dursun *et al.*, 2005) and avocado kernel seed (Rodrigues *et al.*, 2011). All of these carbons were successfully applied for the removal of contaminants from aqueous solution.

Contaminants such as dyes normally accumulate and remain in the environment for a substantial period due to their resistance to chemical and photo degradation. They have the potential to inhibit sunlight penetration and consequently jeopardise the living of aquatic organisms (Ahmad *et al.*, 2012). Such dyes are Methylene Blue, Basic Red 29 and Basic Yellow 28 which classify as cationic dyes. Therefore, physical and or chemical management methods have to be used to remove the dyes from the water system. The use of activated carbon (AC) is one of the effective solutions (Lim and Aris, 2013).

Cocoa nibs (CN) have not been received serious consideration as sorbent, as it is the main precursor in production of chocolate and other cocoa products. However, there are significantly high amounts of waste during the manufacturing processes. The valuable cocoa precursors are discarded after fermentation process due to some deformities and infections. The cocoa nibs are also discarded during winnowing process when the breaking process of the beans result in small fragmented cocoa nibs, which will be blown away during the process. The aim of this work is to convert cocoa nibs into activated carbon, in order to make better use of this agricultural waste. Therefore, the focus of this research was to evaluate the adsorption potential of the cocoa nib-based activated carbon (CNAC) in removing Methylene Blue (MB) from aqueous solutions.

EXPERIMENTAL

Materials

Potassium carbonate (K_2CO_3, Systerm, 99.5 %) was used as the chemical activating agent, and hydrochloric acid (HCl, Merck, 30 %) and sodium hydroxide (NaOH, Essex, 99 %) were used in pH balancing process. Commercial MB ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$) textile dye was obtained from Sigma–Aldrich (M) Sdn Bhd, Malaysia. De-ionized water was used to prepare all reagents and solutions.

Preparation of deash activated carbon from cocoa nibs

CN used for the preparation of activated carbon was obtained from Cocoa Innovative and Technology Centre, Cocoa Board Malaysia, Nilai, Negeri Sembilan, Malaysia. CN was washed with water to remove dirt and later dried at 105 °C for 24 hours to remove the moisture. 60 g of the dried CN was ground into small particles and sieved to the desired particle size of 0.5 mm. The particles were then loaded into a stainless steel vertical tubular reactor (l: 130 cm, d: 38 mm of 310 grade stainless steel) placed in a tubular furnace (Model Carbolite VST 12/110/900). Carbonization was carried out at 700 °C with heating rate of 10 °C/min under purified nitrogen flow at a rate of 150 cm^3/min for one hour.

In the second step, approximately 10.0 gram of char was impregnated with 10.0 gram of K_2CO_3 before activated under the same condition to a final temperature of 800 °C for one hour. The activated carbon produced, referred to as CNAC, was then cooled down under nitrogen flow until it reached a room temperature. The impregnation step was repeated with a combination of 10.0 gram char – 20.0 gram K_2CO_3 and 10.0 gram char – 30.0 gram K_2CO_3 to achieve the desired ratios (1:1, 1:2 and 1:3).Then the CNAC was washed with hot deionized water for a few rounds and followed with 0.1 M hydrochloric acid and 0.1 M NaOH until the pH of washing solution reached approximately 6.5 – 7.0. The washing procedure was applied in order to remove the remaining K_2CO_3 (Adinata *et al.*, 2007) and, HCl and NaOH were used to adjust the pH.

Subsequently, the produced activated carbon was added into 250 mL beaker which contained 1 M of HCl, as a leach agent to remove minerals and ash from the carbon (Ahmad *et al.*, 2013). A continuous controlled heat was supplied to the mixture by using a magnetic stirrer with heating ceramic plate (IKA® C-MAG HS7, Germany). The temperature controller was used to maintain a constant temperature (50 °C) for one hour. A thermometer was placed in the beaker to monitor the temperature in real-time. After finished, the de-ash activated carbon was washed with hot deionized water and the pH was adjusted to 6.5 – 7.0 with HCl (0.1 M) and NaOH (0.1 M). Fig. 1 summaries the process in a schemic diagram.

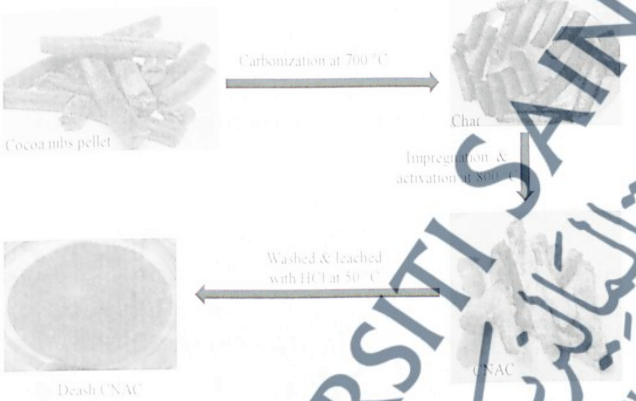

Fig. 1 Schematic diagram for preparation of deash cocoa nib-based activated carbon (de-ash CNAC)

Surface area and porosity analysis of CNAC

The prepared samples (activated carbon) were characterized by N_2 gas adsorption using a Micromeritics ASAP 2010 surface area and porosity analyzer to measure its surface area and porosity. Prior analysis, the sample was degassed at 300 °C until evacuation was completed at 950 mmHg.

Surface functional groups analysis

Surface functional groups were determined using FTIR spectra which were recorded between 4000 and 400 cm^{-1} using an Agilent 630 FTIR spectrometer, US. Diamond ATR accessory was attached to the unit to perform a fast and simple collection of infra red (I R) spectrum. The analysis was performed automatically by MicroLab PC software attached to the system and data handling was assisted by ResPro.

Morphological analysis

Scanning electron microscope (SEM) was used to study the surface morphology of the precursors, chars and the activated carbon prepared including the pore structure, surface structure and pore arrangement. The analysis on surface morphology of the precursor, char and the produced activated carbon was performed using SEM (Model FEI Quanta 450, US).

Batch equilibrium studies

Batch equilibrium studies were carried out by adding a fixed amount of AC (0.60 g) each into each 250 mL Erlenmeyer flasks containing 100 mL of different concentrations (50–400 mg/L) of dye solution. The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 30 °C until equilibrium was reached. Subsequently, the adsorbent was removed from the solution by filtration. The percentage removal of MB was calculated using (1) and the amount of adsorption at time (t), q_t (mg/g) was calculated using (2).

$$\%\ Removal\ of\ MB = \frac{C_i - C_f}{C_i} \quad (1)$$

$$q_t = \frac{C_0 - C_t}{W} x\ V \quad (2)$$

where C_i is the initial liquid-phase concentration of dye (mg/L), C_e is the equilibrium liquid-phase concentration of dye (mg/L), C_0 is the initial liquid-phase concentration of dye (mg/L), C_t is the liquid-phase concentration of dye at any time, t (mg/L), V is the volume of the solution (L), and W is the mass of dry adsorbent used (mg).

The final concentrations of the dye were measured using a double beam UV–Vis spectrophotometer (Model Cary 60 UV-Vis, Agilent, US) at the λ_{max} value (668 nm).

Batch kinetics studies

Similarly, the kinetics experimental procedures were identical to those of batch equilibrium studies. The aqueous samples with the adsorbent were agitated until equilibrium reached. The concentrations at different time intervals were taken and were measured similarly. MB removal at equilibrium, q_e (mg/g), was calculated using (2).

RESULTS AND DISCUSSION

Characteristics of activated carbon

Brunauer-Emmett-Teller (BET) surface area, mesopore surface area, total pore volume, mesopore volume and pore size of CNAC and de-ash CNAC are described in Table 1.

Table 1 shows the comparison between the CNAC and the acid (1 M HCl) treated CNAC. The ash content in CNAC was recorded at 11.77 % of the whole weight, and the de-ash CNAC was left with 3.77 %. The pore diameter was increased in de-ash CNAC compared with untreated CNAC which was from 4.93 to 5.52 nm (12 % increment). Other properties were also increased such as BET (47 %), mesopore surface area (64 %), total pore volume (65 %) and mesopore volume (40 %). Therefore, de-ash CNAC contained higher BET surface area and total pore volume compared with CNAC (1,932 m^2/g and 2.67, respectively) due to increasing of pore size.

The differences between both BET surface areas and total pore volumes were due to the acid leaching process. Similar observation was reported by Ahmad *et al.*, (2013) where they suggested that acid treatment develops new structure that highly mesoporous. Acid treatment resulted in development of new structure that is highly mesoporous through elimination of carbonates and formation of amorphous silica (Ahmad *et al.*, 2013).

The changes in porosity were due to the dissolution of cations from the AC, which degraded the highly microporous structure to low microporous. The cation dissolution could lead to pore walls destruction which can create new pores and can reduce the density of the treated AC (Ahmad *et al.*, 2013).

Fig. 2 (a) and (b) show the SEM micrographs of both the untreated CNAC and acid treated CNAC (de-ash) samples, respectively. In both

(a) and (b), it can be observed that pores were developed on both surfaces. There were several pores formed on the CNAC surface but the surface of the de-ash CNAC contained more pores. This variation is believed due to that fact that the organic compounds were driven off after combustion however the silica remains were still available in the char structure. The treatment of hydrochloric acid ensures that silica was removed and more pores were obtained. The SEM results showed that the surface activated carbon which was treated with acid contains more well-developed pores where can provide a good surface for MB to be trapped and adsorbed (Hanum *et al.*, 2017).

Table 1 Surface characteristics, proximate contents, and elemental analyses of char, CNAC and de-ash CNAC.

Properties	CNAC	De-ash CNAC
BET surface area ($m^2 g^{-1}$)	1,313.88	1,932.36
Mesopore surface area ($m^2 g^{-1}$)	400.34	659.60
Total pore volume ($cm^3 g^{-1}$)	1.62	2.67
Mesopore volume (%)	30.47	42.68
Pore diameter (nm)	4.93	5.52
Ash content (%)	14.77	3.77

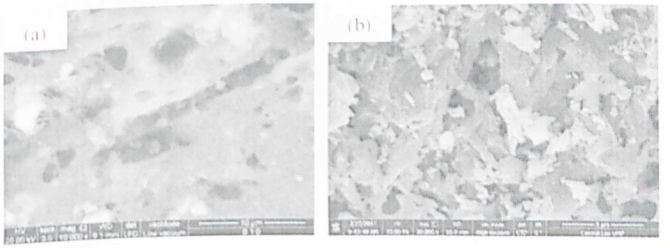

Fig. 2 (a) and **(b)** show the SEM micrographs of (a) untreated CNAC and (b) acid treated CNAC samples.

Fig. 3 shows the spectrum of the activated carbon samples (CNAC and de-ash CNAC). Both activated carbons developed a similar spectrum and exhibit similar peaks. There is no reduction in both spectrums between 3500 and 800 cm^{-1} except for a very weak band at 1570 cm^{-1} in (a), which was disappeared in (b). Result indicated that the acid treatment was not significant in altering the surface functional groups in the CNAC.

Fig. 3 (a) and (b) show the SEM micrographs of (a) untreated CNAC and (b) acid treated CNAC samples.

Batch Adsorption Studies

The adsorption isotherm shows the distribution of adsorption molecules between MB and the de-ash CNAC at an equilibrium state. The adsorption data was fitted to Langmuir, Freundlich and Temkin isotherm models to determine the suitable adsorption model (Rahimi and Vadi, 2014). The amount of MB adsorbed at the equilibrium time specifies the maximum adsorption uptake of the de-ash CNAC as shown in Fig. 4. This happened because of the abundant vacant sites on the adsorbent surface that were available for adsorption during the initial stage (Ahmad et al., 2012).

The adsorption data were investigated using Langmuir, Freundlich and Temkin isotherms. These isotherm models were explained by equation (3), (4) and (5), respectively (Abdel-Ghani et al., 2016):

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{1}{Q_o} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

$$q_e = \ln K_T + B \ln C_e \tag{5}$$

Using the linear form of the equations, the MB adsorption equilibrium of Langmuir, Freundlich and Temkin have been successfully plotted as shown in Fig. 5, 6 and 7, respectively. Table 2 summaries the values of MB isotherms constants calculated from the developed plots.

The essential characteristic of the Langmuir-type adsorption process can be signified with the dimensionless constant or separation factor, R_l which has a value of $0 < R_l < 1$, where lower R_l value indicates a favorable isotherm adsorbate adsorbent (Ahmad *et al.*, 2012). The R_l is defined by equation (6) (Chowdury *et al.*, 2011):

$$R_l = \frac{1}{1 + K_L C_i} \tag{6}$$

where K_L is the Langmuir constant (L/mg) and C_i is the highest initial concentration (mg/L).

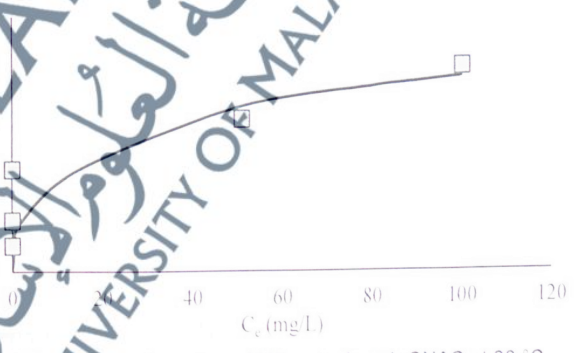

Fig. 4 Equilibrium adsorption of MB onto de-ash CNAC at 30 °C.

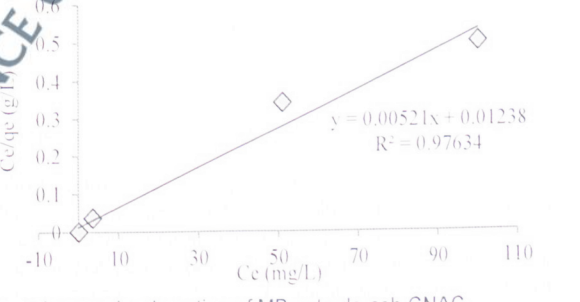

Fig. 5 Langmuir adsorption of MB onto de-ash CNAC.

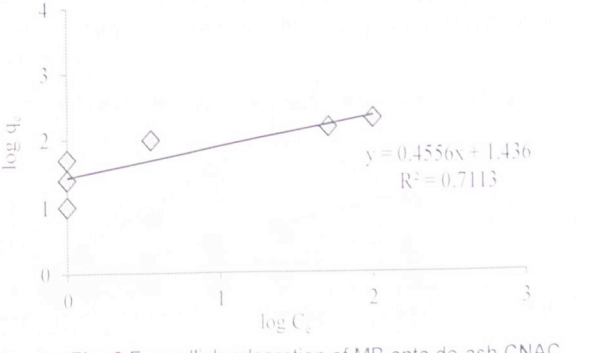

Fig. 6 Freundlich adsorption of MB onto de-ash CNAC.

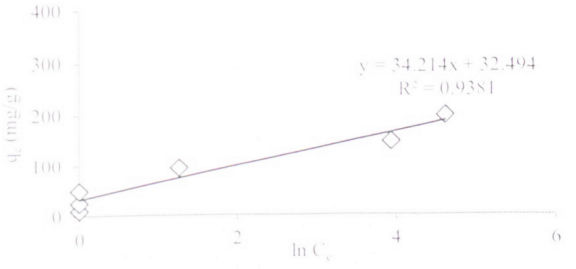

Fig. 7 Temkin adsorption of MB onto de-ash CNAC.

The adsorption data were well fitted with Langmuir isotherm model where the correlation coefficient, R^2 value is close to 1 (0.9763). The higher correlation coefficient of 0.9763 for the Langmuir isotherm predicts the monolayer coverage of MB on the de-ash CNAC particles. A high value of K_L (0.4208) and a low value of R_L (0.0232) indicated a favorable solute adsorbent adsorption process (Joseph and Xavier, 2013).

The Freundlich isotherm did not fit the data well, as the R^2 value is far from 1. The R^2 value for Temkin isotherm is higher than Freundlich but lower than Langmuir, indicating agreement with the experimental data (Ahmad *et al.*, 2012).

Table 2 Isotherm constants for adsorption of MB by CNAC.

Langmuir	R^2	q_m (mg/g)	K_L (L/mg)	R_L
	0.97634	191.94	0.4208	0.0232
Freundlich	R^2	1/n	n	K_F ((mg/g)(mg/L)$^{1/n}$)
	0.7113	0.4556	2.1949	4.2038
Temkin	R^2	A (L/g)	B	-
	0.9381	2.585	34.214	-

The fact that the Freundlich isotherm did not fit the experimental data well may be due to a result of homogeneous distribution of active sites onto the cocoa nib-based activated carbon surface rather than heterogenous distribution. The Freundlich equation assumes multilayer adsorption on the surface as well as heterogeneous adsorption (Dogan *et al.*, 2006). That is why the data were well fitted with Langmuir but not Freundlich isotherm model.

Table 3 lists other adsorbents with maximum monolayer adsorption capacity of MB. It can be observed that the de-ash CNAC had a relatively moderate adsorption capacity of 191.94 mg/g and nearly similar with cocoa shells (212.77 mg/g).

Table 3 Comparison of the maximum monolayer adsorption of Methylene Blue onto various adsorbents.

Adsorbent	Maximum monolayer, q_m (mg/g)	Reference
Cocoa shell	212.77	Ahmad *et al.*, 2012
Pecan nutshell	400.00	Bello-Huitle *et al.*, 2010
Crescentia cujete fruit shell	66.67	Joseph and Xavier, 2013
Jatropha curcas fruit shell	499.17	Tongpoothorn *et al.*, 2011
Pistachio hull	389.00	Moussavi and Khosravi, 2011
Ricinus communis epicarp	62.50	Santhi and Manonmani, 2009
Cola nuts hell	87.12	Nsami and Mbadcam, 2013
Cocoa nibs	191.94	This work

Adsorption Kinetic Studies

The pseudo-first-order and pseudo-secondorder kinetic models were applied to evaluate the kinetic of adsorption of MB on de-ash CNAC. The pseudo-first-order and pseudo-second-order kinetic models were applied to evaluate the kinetic parameters of the adsorption process (Lagergren, 1998). The pseudo-first-order and the pseudo-second-order equations based on equilibrium adsorption are expressed as in equation 7 and 8, respectively (Ho and McKay, 2000):

$$ln\,(q_e - q_t) = ln\,q_e - k_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Fig. 8 demonstrates the pseudo-first-order kinetic model to predict sorption kinetics. The values of K_1 and correlation coefficient, R^2 obtained from the plots for MB adsorption on the activated carbon are given in Table 4. The experimental q_e values were not in agreement with the calculated values obtained from the linear plots. In addition, lowest initial concentration (10 mg/L) did not achieved high R^2 (0.812) values for MB adsorption.

Besides, it was observed that all initial dye concentrations, except for 10 mg/L, the adsorption data were well represented by the pseudo first-order model only the first 30 to 40 minutes. This result suggests that the MB adsorption onto de-ash CNAC does not conform with the pseudo first-order adsorption model. The similar findings have also been observed in the adsorption of MB onto Crescentia cujete fruit shell (Joseph and Xavier, 2013), kenaf core fiber (Saiab *et al.*, 2011) and palm kernel coat (Oladoja *et al.*, 2009). The model is generally not applicable to be used for the whole range of contact time but only effective over the initial 30 minutes of the adsorption processes (Bulut *et al.*, 2008). The result showed that the adsorption of MB on the cocoa nib-based activated carbon was not first-order.

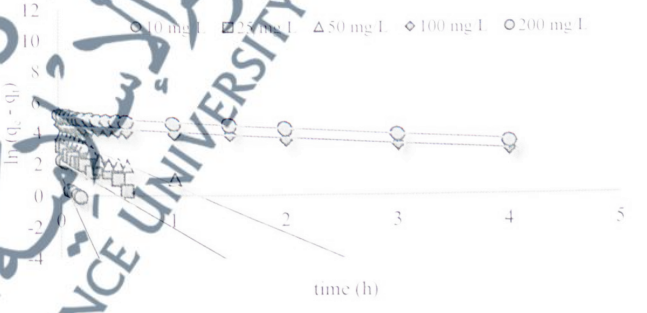

Fig. 8 Pseudo-first-order of MB kinetic adsorption.

Fig. 9 shows a linear plot of t/q_t versus t to represent the pseudo-second-order kinetic model. The graph showed good agreement between the experimental and the calculated q_e values, as addressed in Table 4. The correlation coefficients (R^2) for the linear plots of t/qt against t were observed to be close to 1 indicating the applicability of the second-order kinetic model to describe the MB adsorption process on the de-ash CNAC. It is clearly suggest that the adsorption kinetic of the MB was accurately described by the pseudo second-order adsorption model.

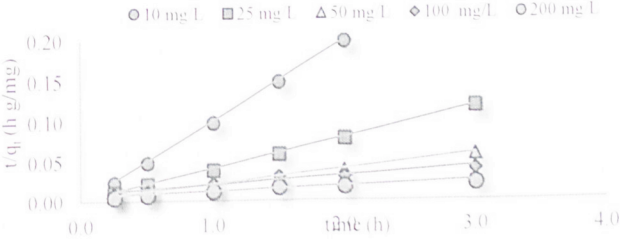

Fig. 9 Pseudo-second-order of MB kinetic adsorption.

From Table 4, it was learn that the R^2 values for second-order model were higher than the first-order model. The higher R^2 value confirmed that the sorption data are well represented by pseudo-second-order kinetics model (Dogan *et al.*, 2004).

Table 4 Kinetics model equation constants and correlation coefficients for MB adsorption.

Initial conc. (mg/L)	Kinetic models					
	Pseudo-first-order			Pseudo-second-order		
	q_e, *cal* (mg/g)	K_1 (1/h)	R^2	q_e, *cal* (mg/g)	K_2 (g/mg h)	R^2
10	8.711	15.369	0.812	10.000	0.000	1.000
25	19.508	4.081	0.916	25.641	0.691	0.995
50	43.654	3.087	0.963	52.356	0.159	0.995
100	83.188	0.390	0.963	87.719	0.014	0.942
200	160.871	0.397	0.969	158.730	0.007	0.945

*conc. - concentration

CONCLUSION

The CNAC was optimised using hydrochloric acid as leaching agent to remove remaining minerals that contribute to ash content. The de-ash CNAC was used to remove MB. The acid treatment was found to significantly increase the adsorption of MB. The treated carbon was characterized by nitrogen adsorption isotherm to determine its BET surface area, mesopore surface area, total pore volume, mesopore volume and average pore size and the values were 1,932.36 m^2/g, 659.60 m^2/g, 290.03 $m2/g$, 2.67 cm^3/g, 42.68 % and 5.52 nm, respectively. The acid treatment process did not influence the composition of functional groups in the CNAC. The adsorption kinetics indicated that pseudo-second-order kinetic model fits the adsorption data, while the adsorption isotherm was well explained by Langmuir and Temkin isotherm models. The results of this study demonstrate that the adsorption capacity of CNAC can be optimized by hydrochloric acid treatment.

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