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

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Article Info

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Received: March 23, 2017**Accepted:** April 4, 2017**Published:** April 10, 2017

Citation: Nikman KA, Ahmad F, Hassan MS, Nikman K, Ahmad MA. Adsorption of Chemically Prepared Cocoa Nibs Based Activated Carbon Onto Methylene Blue: Equilibrium and Kinetic Studies. *Int J Petrochem Res.* 2017; 1(1): 15-18. doi: 10.18689/ijpr-1000104

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Published by Madridge Publishers

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 out at 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 w_c 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 Lagergren [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]:

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

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.

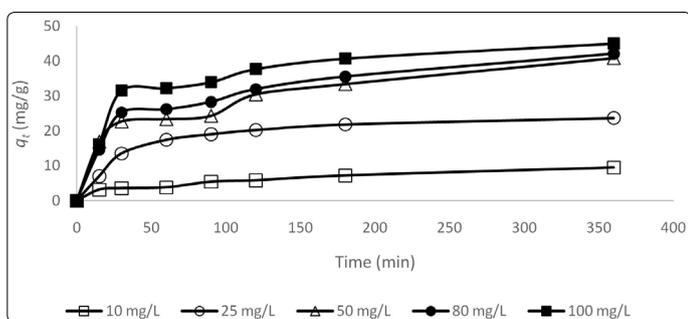


Fig. 2: Effects of contact time of MB onto CNAC

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.

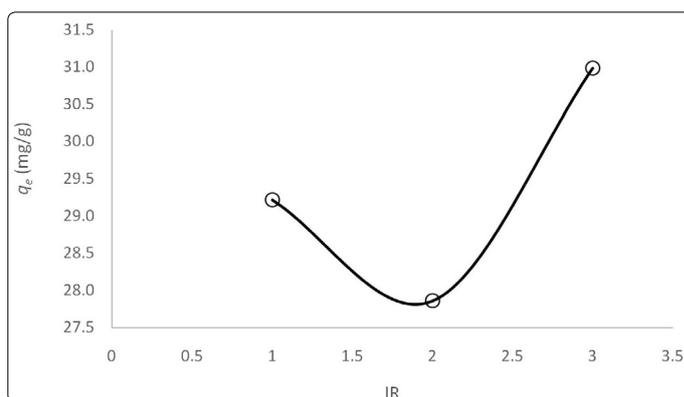


Fig. 1. Effect of IR on MB uptake

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 isotherm models.

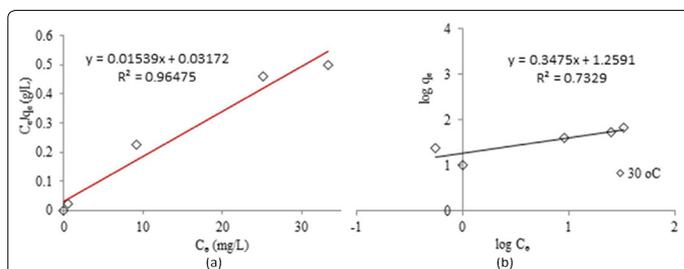


Fig. 3: Linear plots of (a) Langmuir and (b) Freundlich adsorption models

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.

MB concentration	Pseudo-first-order			Pseudo-second-order		
	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.

Acknowledgment

The authors are grateful for the funding from Solid Waste Management Cluster, USM (1001/CKT/870023) and research grant from Ministry of Science, Technology and Innovation (MOSTI), Malaysia.

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