

The Use of Activated Carbon Prepared from Jackfruit (*Artocarpus heterophyllus*) Peel Waste for Methylene Blue Removal

Devarly PRAHAS, Yoga KARTIKA, Nani INDRASWATI, and Suryadi ISMADJI*

Department of Chemical Engineering, Widya Mandala Surabaya Catholic University
Kalijudan 37, Surabaya 60114, Indonesia

Abstract

Jackfruit peel waste which has no economic value has been utilized for activated carbon preparation. The preparation of the activated carbon was carried out using chemical activation with phosphoric acid as activating agent. The impregnation ratio was 4:1 (g H₃PO₄/g raw material) and semi carbonization process was conducted at 200°C and followed with carbonization at 550°C. The applicability of this adsorbent for organic pollutant removal purpose was then evaluated using Methylene Blue adsorption in aqueous solution. Langmuir and Freundlich equations were used to model the adsorption equilibria data, and pseudo-first order and pseudo-second order models were used to correlate the kinetic data. The Langmuir equation gave better correlation for methylene blue adsorption onto activated carbon produced from jackfruit peel. The kinetic adsorption data follows pseudo-second order model.

Keywords: Activated carbon; Adsorption; Jackfruit peel; Phosphoric acid; Surface Chemistry; Methylene Blue.

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Introduction

Colored wastewater could be generated from several industries such as textile, ceramic, rubber, paper, leather, printing, plastic, cosmetics, *etc.* These industries commonly use synthetic dyestuff as their colorant [1-3]. Discharge of this dye-containing-wastewater into environment can contaminate surface water and ground water system [4]. The presence of dyes even in very small amounts in water system is undesirable since dyes are highly visible and can result in a hazard to the aquatic life [5]. Furthermore, some of dyes have been reported to be mutagenic and carcinogenic especially for human [1, 6]. Several methods are available to remove dyes from wastewater before it safely discharged into environment, and the most widely used technique is adsorption using activated carbons since it can remove dyes even in trace amount [1, 2, 4].

However, commercially available activated carbons are expensive so they may not be economical for wastewater treatment purpose. If an activated carbon for a specific purpose such as for wastewater treatment can be produced

from low-cost or waste materials, than its use as an adsorbent should be economical. The use of activated carbon prepared from jackfruit peel using sulphuric acid as activated agent for heavy metal removal has been reported by Inbaraj and Sulochana [8]. In the present study we used phosphoric acid as activating agent for activated carbon preparation using jackfruit (*Artocarpus heterophyllus*) peel waste as the precursor [7]. Here we used the activated carbon from jackfruit peel to remove methylene blue from aqueous solution. The adsorption equilibria and kinetic of methylene blue onto activated carbon prepared from jackfruit peel waste were also studied.

Methylene Blue (MB) is one of frequently used dyes. MB is a dark green powder or crystalline solid which can dissociates in aqueous solution like electrolytes into Methylene Blue cation and the chloride ion [5]. This cationic dye is usually selected as a model compound to evaluate the capacity of activated carbon due to its vast field of application, i.e. for coloring paper, temporary hair colorant, dyeing cottons and wools, and coating for paper stock, etc [3]. Furthermore, as an indicator for evaluation for activated carbon in liquid phase adsorption, MB has

* To whom all correspondence should be addressed. Dr. Suryadi ISMADJI; E-mail: suryadiismadji@yahoo.com, Tel: 62-31-3891264, Fax: 62-31-3891267.

stable color toward a pH change in the solution compared with other dyes, for example Congo Red, which is affected by the pH of solution [1].

Experimental Technique

Activated carbon preparation

In this section we just give a brief description about the activated carbon preparation and characterization, detail about the preparation and characterization can be found elsewhere [7].

Chemical activation method using phosphoric acid was used to prepare the activated carbon. 20 grams of jackfruit peel was impregnated by weighing and mixing certain amount of 85 wt % phosphoric acid with occasional stirring. The amount of phosphoric acid solution used was adjusted to give a certain impregnation ratio (weight of activating agent/weight of raw material) of 4:1. The resulting slurry was then kept in a desiccator for 24 hours. After 24 hours, the slurry was then ready to have two-stage activation process with semicarbonisation as first stage [9]. In the first stage, the slurry was put in a horizontal tubular reactor and kept in a muffle furnace to experience semicarbonisation at a temperature 200°C for 30 minutes. After semi-carbonisation, the black and sticky dry powder was heated until certain heat treatment temperature (HTT) was reached. The carbonisation was performed under a nitrogen flow of 100 cm³ min⁻¹ STP for 45 minutes. After activation, the activated carbon product was cooled in a desiccator. The activated carbon product was then repeatedly washed with warm distilled water (70°C) until the pH of the solution close to the initial pH of rinsing water. Finally, the activated carbon was dried in a vacuum oven at 110°C for 24 hours.

The resulting carbon was then characterized its pore structure and surface morphology using nitrogen adsorption, SEM, XRD, Boehm titration, pH Drift and FTIR.

Adsorption procedure

Adsorption experiments were conducted using basic dye, *i.e.* Methylene Blue as an adsorbate and jackfruit peel activated carbon as an adsorbent. Methylene Blue used on this experiment was purchased from Sigma-Aldrich and was used as it is without any further purification. Methylene Blue stock solutions were prepared by dissolving analytically 500 mg of Methylene Blue into 1000 mL of distilled water. Experimental solutions of the desired concentration (50, 100, 150, and 200 mg/L) were obtained by dilutions from stock solutions. Adsorption experiments were conducted by adding 0.1-1.1 gram of activated carbons into a series of 250 mL Erlenmeyer each filled with 100 mL of Methylene Blue experimental solution with each initial concentration. All of the erlenmeyers then covered with aluminium foil and were placed to a thermostatic shaker bath (Memmert Type W-

350) and shaken for 72 hours. After equilibrium time had been reached, activated carbon was separated from the solution by centrifugation at 3000 rpm for 5 min. The absorbance of clarified supernatant solution was analyzed using spectrophotometer (Shimadzu 8400S) at the maximum wavelength of the Methylene Blue observed, which was 664 nm.

Results and Discussions

Physical Characteristic of Jackfruit Peel Activated Carbon

Yield of jackfruit peel activated carbon (JPAC) used in this study was found to be 42.15 %. The yield here was calculated as final weight of activated carbon produced after activation, washing, and drying, divided by initial weight of raw material; both on a dry basis [10]. Pore characteristic of the activated carbon was determined by N₂ adsorption. The nitrogen adsorption/desorption isotherms of the jackfruit peel activated carbon is illustrated in Figure 1.

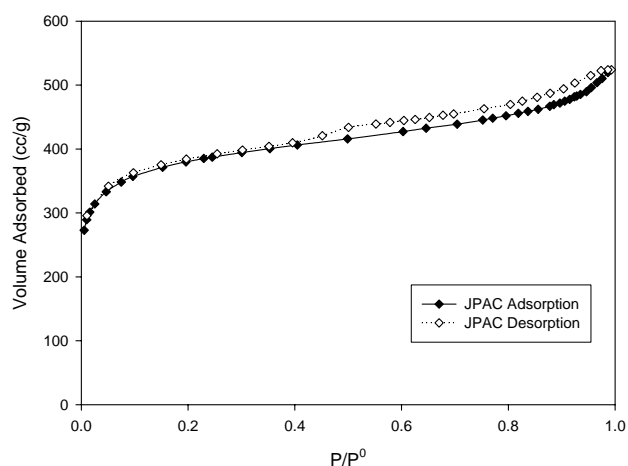


Figure 1. Nitrogen adsorption/desorption isotherm of jackfruit peel activated carbon.

The activated carbon possessed combination of type I and type II of IUPAC isotherm, indicating simultaneous presence of micropores and mesopores. This isotherm also exhibited a type H4 hysteresis loop, characteristic of slit-shaped pores. The pore characteristics of jackfruit peel activated carbon are given in Table 1. The present of micropores and mesopores in the activated carbon prepared from jackfruit peel waste also indicated by the pore size distribution as depicted in Figure 2.

Table 1. Pore characteristic of jackfruit peel activated carbon.

Sample	S_{BET} , m ² /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g
JPAC	1260.61	0.471	0.262

Scanning electron micrograph of the surface morphology of jackfruit peel activated carbon is given in Figure 3. It is obvious that the activated carbon produced have already had cavities on their external surface. It seems that the cavities on the surfaces of carbons resulted from the evaporation of the activating agent in this case is phosphoric acid during carbonization, leaving the space previously occupied by the activating agent.

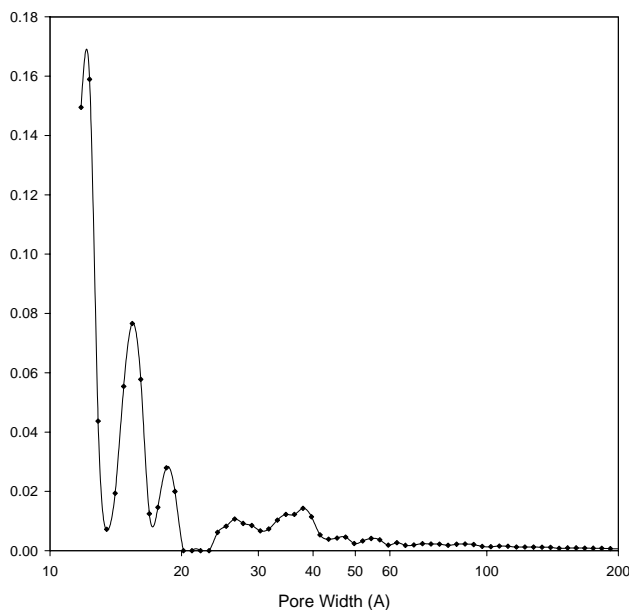


Figure 2. Pore size distribution of jackfruit peel activated carbon.

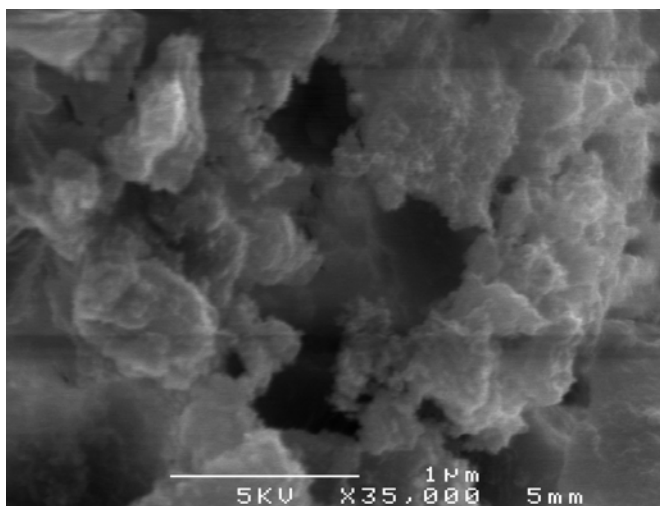


Figure 3. SEM image of jackfruit peel activated carbon.

Activated carbon can be crystallographically characterized by means of X-Ray Diffraction (XRD). XRD spectrum for jackfruit peel activated carbon is given in Figure 4. Here, the XRD analysis was measured by CuK α with wavelength of 0.154 nm. From the XRD spectrum, the interlayer spacing d_{002} can be determined using the Bragg equation:

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

where λ is the X-ray wavelength and θ is the scattering angle for the peak position. The crystallite size along c-axis, L_c , and the size of the layer planes, L_a , are determined from the half-width of the diffraction peak using the Scherrer equation:

$$L = \frac{K\lambda}{B \cos \theta} \quad (2)$$

where L is L_c or L_a , B is the half-width of the peak in radians, and K is the shape factor. The quantities L_c and L_a are named stack height and stack width, respectively. The (002) and (10) peaks are used to calculate L_c and L_a , respectively. The shape factor $K = 0.9$ and $K = 1.84$ are used for calculation of L_c and L_a , respectively [11]. The values of d_{002} , L_c , and L_a of activated carbon prepared from jackfruit peel are given in Table 2.

Table 2. Nanographitic structures of jackfruit peel activated carbon.

Sample	$d_{002}(\text{nm})$	$L_c(\text{nm})$	$L_a(\text{nm})$
JPAC	0.35	1.02	1.30

As shown in Table 2, it can be seen that the value of d_{002} was close to that of graphite (0.335 nm) and still in the range for activated carbon of 0.34-0.36. L_c and L_a values were also of the order 1-3 nm, typical of activated carbon. For this activated carbon, the diffraction profiles exhibited broad peaks at around 24 and 42° which are assigned to the reflection from (002) and (10) planes, respectively. The occurrence of broad peaks at these 2 θ indicated a regularity of crystal structure and resulting in better layer alignment [12].

Surface chemistry characteristic of jackfruit peel activated carbon

The carbon matrix does not consist of carbon atoms alone, but is also formed by other heteroatom like hydrogen, oxygen, nitrogen, halogen, sulfur, phosphorus, etc. These heteroatoms bonded to the edges of the carbon layers, which govern the surface chemistry of activated carbon. The surface chemistry of carbon materials is

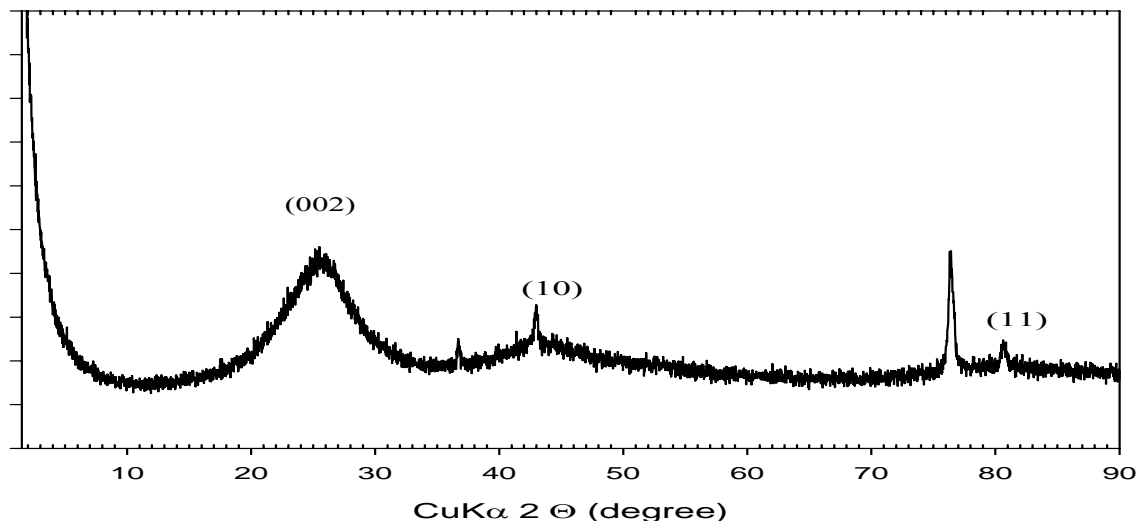


Figure 4. XRD spectrum of jackfruit peel activated carbon.

basically determined by the acidity and basicity of their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, *etc.*, has been postulated as constituting the source of surface acidity. Whereas the basic properties of activated carbon is associated with two types of structures: (i) the presence of oxygen containing groups, *i.e.* pyrone, chromene and carbonyl structures, at the edge of carbon crystallite; and (ii) oxygen free Lewis basic site on the graphene layers. The Lewis basicity of delocalized π electrons is influenced by the aromatic system on the carbon surface [13].

Table 3 shows quantitative surface chemistry analyses, which consist of the amount of acidic and basic functional groups of jackfruit peel activated carbons. Low pH_{PZC} value was consistent with Boehm titration result, which indicated a dominance of acidic group at the surface of the activated carbons. While quantitative analysis of the surface chemistry was given by Boehm titration and pH drift method, a qualitative analysis of activated carbon can be carried out by FTIR spectrum. The spectrum of jackfruit peel activated carbon is illustrated in Figure 5. As shown in Figure 5, it can be interpreted that there is broad absorption band around $3400-2400\text{ cm}^{-1}$. A peak around 1710 cm^{-1} shows the presence of stretching vibration of C=O in ketones, aldehyde, lactone, and carboxyl. The presence of broad band around $3400-2400\text{ cm}^{-1}$ and peak around 1710 cm^{-1} indicates the presence of carboxylic acid [14,15]. Very weak peak around 2900 cm^{-1} is C-H

stretching vibration in methyl group [15]. A strong band at 1590 cm^{-1} can be ascribed to C=C aromatic ring stretching vibration enhanced by polar functional groups [16,17]. There is also a presence of broadband between $1300-1000\text{ cm}^{-1}$ with the strong band around 1200 cm^{-1} and a shoulder around 1080 cm^{-1} . According to Puziy *et al* [16,17], the peak at $1220-1180\text{ cm}^{-1}$ may be ascribed to the stretching mode of hydrogen bonded P=O, O-C stretching vibrations in P-O-C linkage, and P=OOH; and the shoulder at $1080-1070\text{ cm}^{-1}$ can be ascribed to ionized linkage $P^+ - O^-$ in acid phosphate esters and to symmetrical vibration in a chain of P-O-P. Surface chemistry characterization by Boehm titration, pH drift, and FTIR spectrum has shown that activated carbons from jackfruit peel waste activated with phosphoric acid are rich in acidic surface functional groups. Therefore, pH_{PZC} value of the jackfruit peel activated carbon was low, *i.e.* 1.9.

Methylene Blue Adsorption

Figure 6a shows the amount of Methylene Blue (expressed as qt, mg/g) adsorbed with time (min). The effect of contact time was observed by having adsorbent dose fixed to 0.3 g/L and initial Methylene Blue concentration of 50 mg/L. The amount of Methylene Blue adsorbed steeply increased at initial progress of adsorption and then reached relatively constant value at later time. Very rapid adsorption was found during the adsorption time of 400 minutes.

Table 3. Quantitative surface chemistry of jackfruit peel activated carbon.

Sample	pH_{PZC}	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Acidic (meq/g)	Basic (meq/g)
JPAC	1.9	0.7807	0.7395	0.2350	1.7552	0.0808

However, the amount of Methylene Blue adsorbed increases with time and reaches a constant value after 3000 minutes. After the equilibrium time, the amount of Methylene Blue adsorbed did not alter with time. Thus, referred to this experiment, the mixing time for the rest of adsorption studies was set to be 72 hours (4320 minutes) to ensure the equilibrium in adsorption and kinetic studies. For higher initial concentration studied, *i.e.* 100,150, and 200 mg/L, it was found that there was no significant change on the equilibrium time at the observed initial MB concentration range. As shown in Figure 6b, the removal efficiency of Methylene Blue decreased from 95 to 41 % by the increase of initial Methylene Blue concentration from 50 to 200 mg/L. Smooth and continuous curves indicates a formation of monolayer coverage on the surface of jackfruit peel activated carbon [1].

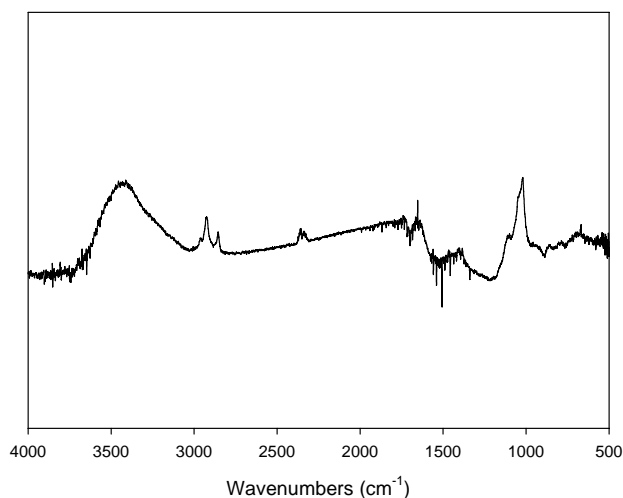


Figure 5. FTIR spectrum of jackfruit peel activated carbon.

Effect of pH on Methylene Blue adsorption

Figure 7 shows effect of initial pH of solution on the removal efficiency and amount adsorbed (q_e). The removal efficiency increased from 78 to 98 % and q_e from 232 to 294 mg/g when initial pH range was raised from 1.5 to 10.0. At pH 1.5, which is lower than pH_{PZC} of the JPAC adsorbent, the removal efficiency slightly decrease because of electrostatic repulsion. The repulsion occurred since Methylene Blue is one of cationic dyes so when the pH solution lower than pH_{PZC} the activated carbon surface is positively charged. On the contrary, as the initial pH became higher, ionic interaction between Methylene Blue cation and negatively charged surface of activated carbon enhanced the adsorption. Adsorption of the cationic dye was found to be more favorable at higher pH.

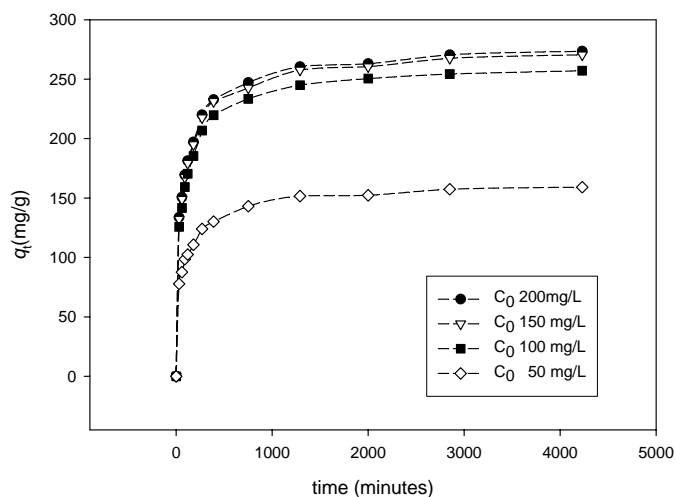


Figure 6a. The effect of contact time on Methylene Blue adsorption at different initial concentration (adsorbent dose = 0.3 g/L).

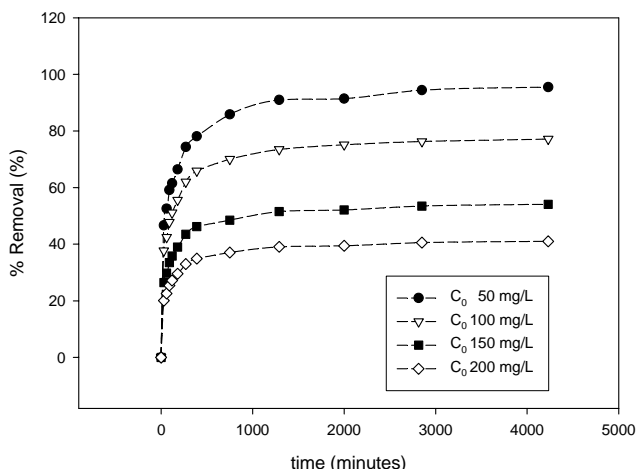


Figure 6b. The effect of contact time on removal efficiency of Methylene Blue at different initial concentration.

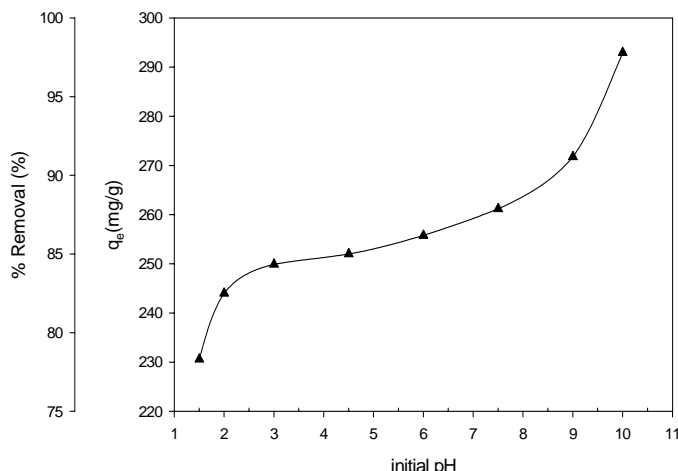


Figure 7. The effect of initial pH solution on Methylene Blue adsorption.

