Preparation and Characterization of Microporous Activated Carbon from Chemical Activation of Rubber Seed Shell

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Abstract

Preparation of porous and activated carbon of rubber seed shell adsorption has been conducted in this study. Rubber seed shell relatively known as sustainable, eco-friendly, and a low cost that can be formed as an activated carbon. Porousness of the rubber seed shell can be enhanced by two methods which are chemical and physical activation. Next, the rubber seed shell was activated by using chemical activation and was further process under high temperature and absence of inert media. The study was conducted at a low oxygen content by applying the raw material for consuming oxygen inside the double crucible method (char of rubber seed was wrapped with aluminum foil) as to prevent intrusion of oxygen. The results of this study shows that activated carbon of seed shell was prepared successfully without using any inert media and the optimum temperature for this study is around 500^0C. This is because the adsorption rate of methylene blue that shown on Ultraviolet-Visible (UV-Vis) is increasing as the contact time increasing from 30 min to 120 min which are 3.592 cm^{-1} to 3.596 cm^{-1}. The adsorption ability of the material has increased due to activation with zinc chloride compared to using raw rubber seed shell. It is concluded that rubber seed shell could be prepared in normal conditions instead of using an inert media. The study shows a method and possibility of producing sustainable, eco-friendly and a low cost activated carbon and it could be scaled up for commercial production.

Keyword: Activated carbon, rubber seed shell, adsorption

1. Introduction

Malaysia has large rubber plantation especially in Johor which cover 66% of the total cultivated area in the nation. A large amount of by-product which is rubber seed-shell was usually burned resulting serious environmental contamination. These solid wastes were left unutilized on the field, causing significant environment and disposal problem (Ngah & Hanafiah, 2008). One solution for this problem is to reuse this waste to produce activated carbon which is widely used materials due to its low cost and exceptional adsorption properties (Ioannidou & Zabaniotou, 2007). The versatility of high surface area, porous structure and surface adsorption capacity which can be approximately modified by physical and chemical treatment, are among the reasons for the use of such adsorbent (Azry Borhan, 2012).

Activated carbon in the industry is produce from coal-based materials which is non-renewable and expensive. Due to this condition, activated carbon from agriculture waste has receive interest for alternative current activated carbon production. Rubber seed shell is one of the agriculture waste that can undergoes chemical activation to produce low cost microporous activated carbon. There are many agriculture waste can be precursor for activated carbon such as rice husk, pumpkin seed hull, oak sawdust, banana peels and others. But, the focus of this study solely on the preparation and characterization of microporous activated carbon from chemical activation of rubber seed shell.

Several studies have been developed to search for sustainable, eco-friendly and low cost of activated carbon from agriculture waste. Agriculture has produce vast amount of by-products with the increase of the agricultural activity.

These by-products can provide an alternative for low cost and eco-friendly activated carbon to overcome the expensive coal-based activated carbon. Rice husk, bamboo, oil palm fiber, pecan shell and rubber seed shell are examples of the by-products that left unutilized. Besides, in recent years, the rubber seed shell has begun to attract more attention for use in producing activated carbon and bio composites (Ioannidou & Zabaniotou, 2007).

There are two methods for the activation of carbonized rubber seed shell which is chemical and physical activation. Physical activation is a two-step process. It involves carbonization of carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixture (Ioannidou & Zabaniotou, 2007). The activation gas is usually CO_2, since it is clean, easy to handle and it facilitates control of the activation process due to slow reaction rate at temperatures around 800^0C (Zhang et al., 2004). As for the chemical activation process, the two steps process are carried out simultaneously, by mixing rubber seed shell with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a single step, combining carbonation and activation, performed at lower temperature and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed (Ioannidou & Zabaniotou, 2007). Besides, part of the added chemicals such as zinc salts and phosphoric acid, can be easily recovered (Zhang et al., 2004).

The aim of this study is to prepare activated carbon from rubber seed shell by chemical activation with $ZnCl_2$. The properties of the activated carbon were analyzed with Fourier-Transform Infrared (FTIR). By using rubber seed-shell as precursor, characterization of the activated carbon was evaluated by using Ultraviolet-Visible spectrophotometer (UV-Vis) and its adsorption on methylene blue capacity were studied.

2. EXPERIMENT PROCEDURES/METHODOLOGY

2.1 Char Production

Initially the rubber seed shell was smashed with a mortar to separate the shell and seed of the rubber as the seed is in the shell. Then, rubber seed shell waswashed with water thoroughly in order to remove dirt and other impurities that may stick at the inner layer of the shell. The seed shell was put on a big tray and enters the oven at 105°C for 24 hours. The shell was preserved in air tight container which can prevent further absorption of moisture. The shell was heated in the oven to remove the moisture surface of shell for 24 hours. Next, the rubber seed shell was grinding into powder by using a blender and mortar and sieved the powder into micro-size particle. After that, the micro-size shell was put into a porcelain crucible and later to be put into muffle furnace. The shell was left in the muffle furnace for an hour with temperature of 500°C. The shell will be carbonized in the furnace. The carbonized shell then will be preserved and cooled.

2.2 Chemical activation of rubber seed shell

For the chemical activation process, the rubber seed shells that have been sieved into micro-size particles were soaked into the zinc chloride ($ZnCl_2$) for about 24 hours. The samples were washed with water and it were filtered by using filter funnel. Then, the rubber seed shells were placed in a crucible to be turn into char for about 500°C. A pH test was done after the activation. Then, soaked micro-sized shell was put into the oven again at 105°C for 24 hours. The dried samples were preserved in a vacuum container to avoid further absorption of moisture which will affected the char.

2.3 Preparation of activated carbon

In general, all activated carbon is prepared by the presence of argon or nitrogen gas which is to make the condition to inert properties. However, the procedure is inaccessible in general at local condition. So another alternative was found which is to make the activated carbon by using double crucible method. A double crucible method is a method where the char of the rubber seed shell was placed in a small crucible covered with a lid on it. Next, the small crucible containing the char are put into a bigger crucible. However, due to the shortage of crucible, the small size crucible was replaced with aluminium foil. The aluminium foil was make into small container to fill the char. The gap between the small and aluminium foil container are replaced with raw material which is rubber seed shell in order to reduce the oxygen content inside the crucible. Thus in this process, the bulk of volume which is occupied by the raw material is heated up and the volume expanded and a portion of those air comes out from both of the crucible. The volatile part of the rubber seed reacts with the oxygen and it is assumed that all oxygen has been reacted inside the crucible.

2.4 Experimental treatments for preparation of activated carbon

To produce a high quality activated carbon, rubber seed shell was used to investigate the activated carbon preparation with the temperature of 400°C, 500° and 600°C. After the rubber seed shell that turned into micro-size particles was activated by using zinc chloride, washed with water and filtered by using filter funnel, then, it was weighed using digital balance (Model: OHAUS) and divided into 3 samples with the weight of 5g each. This rubber seed shell char was heated at the duration of 30 to 120 min and with the interval of 30 min. The activated carbon at different temperature level and different ratio of level char was prepared.

2.5 The adsorption test for the activated carbon

To ensure that the activated carbon can be used properly, first, the activated carbon was evaluated through adsorption test using methylene blue dye. There are 3 different temperatures that used in this experiment as the main objective of this experiment was to study the effect of temperature toward activated carbon during preparation of char in muffle furnace at the temperature of 400°C, 500°C and 600°C. After that, the rubber seed char was weighed using digital balance (Model: OHAUS) for 0.10 g for each of the sample and then they will be mixed with 100 ml of 0.0004 M of methylene blue solution. Then, they will be stirred using incubator stirrer at different contact time which are for 30 min, 60 min and 120 min. Next, the solution will be filtered by using filter funnel to separate the rubber seed shell char and methylene blue dye solution. The methylene blue absorbed will be measured by using UV-VIS spectrophotometer and FTIR.

To calculate the concentration of methylene blue adsorbed this equation was used, which is:

$$C_e = \frac{A}{E} \qquad (1)$$

Where C_e = concentration of methylene blue solution adsorbed; A = absorbance of Vis UV, cm^{-1}; E = coefficient of extinction 65 280 L $M^{-1}cm^{-1}$. After that, the amount of methylene blue adsorbed by the activated rubber seed char was calculated using this equation:

$$q_e = \frac{(C_0 - C_e) \times W}{m}$$

where q_e = uptake of methylene blue solution by adsorbent, mg g^{-1}; C_o = initial concentration of dye, M L^{-1}; C_e final concentration of methylene blue solution, M; V = volume of methylene blue solution, L; m = weight of activated carbon, g; W = mole weight of methylene blue solution (319.86 x 1000), mg/mole. Lastly, calculate the specific surface area from amount of methylene blue adsorbed by using this equation:

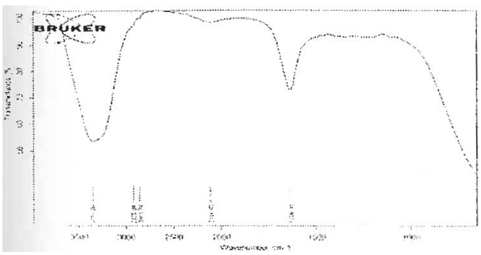
$$S_s = \frac{q_e \times Av \times A_{mb}}{W \times 10^{20}} \quad (3)$$

Where S_s = specific surface area, m^2g^{-1}; q_e = amount of methylene blue adsorbed, mg g^{-1}; W = molecular weight of methylene blue, mg/mole; Av = Avogrado's number (6.02×10^{23} per mole); A_{mb} = area covered by one molecule of methylene blue (130 A^2).

3. RESULT AND DISCUSSION

3.1 Fourier Transform Infra-Red (FTIR) test

In this study, a test has been run by using Fourier Transform Infra-Red (FTIR) through 9 samples of methylene blue dye solution after adsorption of rubber seed shell activated carbon. The 9 samples were from different parameter which are temperature of the rubber seed shell char in the muffle furnace (400⁰C, 500⁰C and 600⁰C) and contact time between rubber seed shell char and methylene blue (30 min, 60 min and 120 min). The purpose of this experiment was to study the effect of temperature and contact time of activated carbon towards methylene blue solution.



a) Temperature (400⁰C), Contact time (30 min)

b) Temperature (400⁰C), Contact time (60 min)

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c) Temperature (400⁰C), Contact time (120 min)

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d) Temperature (500⁰C), Contact time (30 min)

e) Temperature (500^0C), Contact time (60 min)

f) Temperature (500^0C), Contact time (120 min)

g) Temperature (600^0C), Contact time (30 min)

h) Temperature (600^0C), Contact time (60 min)

i) Temperature (600^0C), Contact time (120 min)

Figure 1: FTIR band for methylene blue solution at different temperature and contact time

Based on the graph shown in all of the figure above, this FTIR equipment shows that the wavelength (cm^{-1}) peak of the 9 samples do not have much different between each other. For example, when the temperature at 400^0C, the wavelength peak at contact time 30 min is 3346.41 cm^{-1}, at 60 min is 3342.63 cm^{-1} and at 120 min is 3348.15 cm^{-1}. For temperature of 500^0C, the wavelength peak at contact time 30 min is 3345.22 cm^{-1}, at 60 min is 3348.16 cm^{-1} and at 120 min is 3343.09. Lastly, at temperature of 600^0C, the wavelength peak at contact time 30 min is 3345.94 cm^{-1}, at 60 min is 3344.43 cm^{-1} and at 120 min is 3345.90 cm-1. This is because the FTIR was usually used to find the percentage of certain component but with different type of solution. However, in this experiment, methylene blue solution is the only solution that used to calculate the wavelength peak and the only factors that differentiate this 9 samples are their temperature and contact time. This explain why the graph peak from our result does not have too much different between each other. However, through this test, the functional bonds of carbon-hydrogen-oxygen bond in methylene blue solution after the adsorption by activated carbon was observed. The purpose of using FTIR in this study was to determine the percentage of O-H that is present in the char. So it is found that the components of O-H bonds were reduced as the char was produced in inert media (no presence of oxygen) have been adsorbed from methylene blue solution.