Charcoal from Coat of Para Rubber Seeds Uniquely Exhibits a High Level of Porosity with an Excellent Property in Adsorbing Chemicals

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Abstract

Para rubber trees (*Hevea brasiliensis*) grow well in many parts of Thailand. Rubber latex and the rubber wood have been widely used for the production of many materials and furniture. However, there are other parts of this plant that are yet to be explored for their values. We are interested in making charcoal from its seed coats and studying the chemical properties of the charcoal. The charcoal from seed coats were made by using a pyrolysis carbonization reactor at 400 ºC for 20 hr. and having a N_2 flow at a rate of 100 mL/min. The resulted charcoal has a high level of porosity as revealed by a scanning electron microscope (SEM). Pore sizes range from 1.7 to 15.0 µm with the most abundant pore size around 7.8 µm. X-Ray microanalysis (EDX) showed that the charcoal contained C at the highest level of 86.1 %, followed by O, K, and Al at, 12.7, 1.1, and 0.1 %, respectively. The charcoal could remove methylene blue (MB) from a solution rapidly with high capacity. The objective of this study is to convert agricultural waste into charcoal for the adsorption of harmful chemicals.

Keywords: rubber seed coat, charcoal, adsorption

Introduction

In many industrials, charcoal is used for many types of industry, for examples, in medical, manufacturing and agro industries. The charcoal can be made from biomass and agricultural wastes such as bamboo[1], coconut[2], walnut shell[3] and almond shell[3]. It has been used for general illnesses like nausea and diarrhea. Moreover, there is research showing that activated charcoal could be used to reduced LDL-cholesterol in patients with hypercholesterolaemia [4]. Charcoal is not only for medical treatments but also environmental treatment in order to improve quality of sand[5] and remove the impurities of water from the industrial waste[6].

Nowadays, one of the most important problems in the world is water pollution. Many industries such as in textile[7], food processing[8] and paper-making[9] industries produce pollutants which contaminate water. In several industries, one of the dye utilized in the production process is methylene blue (MB). This dye is used in various applications such as coloring paper, temporary hair colorant, dyeing cottons and wools[10]. It has been reported that the contamination of MB in water is harmful to aquatic organisms and human[6]. Receiving this compound into body can cause harmful effects such as nausea, vomiting, profuse sweating, painful micturition, eye burns, mouth burns, and methemoglobinemia[6]. According to these detrimental effects on human, removing MB dye from the water before releasing it into water resources will help the environment to be more sustainable and safe.

Natural rubber has been one of Thailand's most important agricultural products for decades. Thailand is the largest world exporter of natural rubber[11]. Many parts of Para rubber trees can be used for many purposes, for instances, the barks containing latex. However, seed coats of Para rubber tree are wastes. Therefore, this research will focus on applying seed coats of Para rubber to make the benefit from unused agricultural products. One chosen application is producing charcoal for removing environmental-harmful chemicals like methylene blue from water. The objective of this research is to investigate the physical and chemical properties of charcoal produced from the seed coats of Para rubber tree. There are many aspects for validation of the characteristic of charcoal, for examples, the percentage of oxygen groups[12], microwave adsorption[13], the porosity[14] and the pore size[15]. For this work in the present study, the physical properties of charcoal which are the level of porosity, the pore size, the components of charcoal as well as the adsorption capability were determined. Scanning electron microscope (SEM) shows the appearance of the sample surface, so the level of porosity and the size of pore in the charcoal can be considered by this technique. To consider the percentages of elements in samples, X-Ray microanalysis (EDX) is used to quantify elements present in our samples. The adsorption property is examined by the MB adsorption experiment. This can be achieved by measuring the absorbance of MB in solution using UV-visible spectrometer. The kinetics and adsorption properties of MB by the charcoal were carried out using this method. The results will allow us to understand the kinetics of adsorption and isotherm model to support the adsorption behavior of the charcoal.

Materials and Methods

Charcoal preparation

Charcoal was made from the Para rubber seed coats collected from rubber trees in Kamnoetvidya Science Academy, Rayong province, Thailand between latitudes 12º 42' 27.8"N and longitudes 101º 08' 50.5". The formation of charcoal was achieved by a carbonization reactor by carrying out a pyrolysis at 400 °C for 20 hr. while having N_2 flow through at a rate of 100 mL/min. The resulted black charcoal was grinded into small pieces and then the grinded charcoal was sieved through the wire mesh with the pore size of 1 mm^2.

Preparation of methylene blue (MB) stock solution

Methylene blue was ordered from Sigma-Aldrich. The stock solution of MB was prepared to be at the concentration of 255 mg/L. This methylene blue solution was used to study the kinetics of adsorption and adsorption isotherm to fit the model of the adsorption.

Adsorption study

Kinetics study

This study was set out to determine the rate of adsorption of the 50 mL of 2.55 mg/L MB onto 50 mg charcoal. The contact time between charcoal and MB were varied from 0, 20, 40, 60, 80, 100, 120, 140, 160 to 180 minutes. The flask was shaken at 4.0 rev/s by orbital shaker (Heidolph Unimax 1010) to allow all the surface area of charcoal to contact with MB. Absorbance of samples were measured at 663 nm using spectrophotometric probe. (SpectroVis Plus) connecting with data logger (LabQuest2). The percentage of charcoal adsorption is calculated as

$$\% \text{ Adsorption} = \frac{(C_i - C_f)}{C_i} * 100$$

Where C_i and C_f are the initial and final concentration (mg/L) of MB, respectively.

Batch experiments and adsorption isotherm

This study was to determine the adsorption isotherm of MB onto charcoal. The amount of charcoal was varied from 10, 20, 30, 40, 45 to 50 mg while that of MB are constant at 50 ml of 2.55 mg/L MB. The flask was shaken at 4.0 rev/s by orbital shaker (Heidolph Unimax 1010). After equilibrium was reached the concentration of MB was determined by measuring the absorbance at 663 nm using spectrophotometric probe. (SpectroVis Plus) connecting with data logger (LabQuest2). The amount of MB adsorbed onto charcoal (mg/g) was calculated as

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

Where C_i and C_e are the initial and equilibrium concentration (mg/L), respectively, V is the volume of the solution (L) and m is the mass of the adsorbent (g).

Scanning Electron Microscope and X-Ray microanalysis

The black charcoal was chopped into small pieces of about 3 x 3 x 2 (w x l x h) mm before attaching to an aluminum stub via conductive carbon tape. The specimens were then examined under a Tabletop Hitachi Scanning Electron

Microscope Model 3030Plus without metal sputtering. The specimen was positioned at 4.5 mm below the BSE detector and examined at 15 keV. The Scanning Electron Micrographs were taken under the mixed mode of BSE and SE. X-ray microanalysis was achieved by using the built-in silicon drift detector (SDD) to obtain elemental compositions of the samples. EDX spectrum was obtained using sensitive mode with the scanned time of 3 min. The identification of the elements was done using auto identification against the built in elemental database library. Mapping of elements of the charcoal samples were done by accumulating characteristics X-ray energy of elements for 6 min.

Results and Discussion

Kinetics Study

Figure 1 shows the percent MB removed with respect to time. At the beginning, the rate of the adsorption increased rapidly, went up slightly and then remained constant at the end when it reached equilibrium. The findings illustrated that the charcoal made from para rubber trees adsorb MB quickly within 20 min and the equilibrium of adsorption is reached at 140 min.

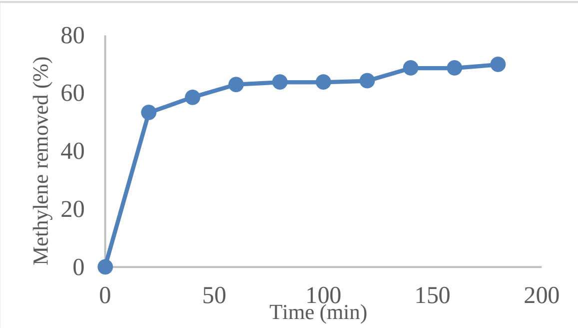

Figure 1: Kinetic of MB adsorption

Adsorption Isotherm

Isotherms are used to describe the adsorption behavior. There are many adsorption methods however the simple adsorption isotherms such as Langmuir and Freundlich were chosen in this study. The Langmuir isotherm indicates characteristic of adsorption where the surface containing the adsorbing sites are perfectly flat plane with no corrugations. All sites are equivalent, each site can hold at most one molecule and there are no interactions between adsorbate molecules on adjacent sites. It is expressed in an equation by

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{C_e}{q_{max}}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbed per amount of adsorbent at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g) and K_l is adsorption equilibrium constant which is related to the energy of adsorption (L/mg). The Freundlich isotherm is an empirical adsorption that is characteristic for the heterogeneous surface. It is expressed in an equation by

$$\ln q_e = \ln K_f - \frac{1}{n} \ln c_e$$

Where q_e is the amount of adsorbed per amount of adsorbent at equilibrium (mg/g), K_f and n are constant and c_e is the equilibrium concentration (mg/L).

The results were used to investigate the adsorption behavior of MB onto the charcoal using Langmuir and Freundlich isotherms. Figure 2 shows The Langmuir isotherm linear graph of c_e/q_e with related to c_e of the MB adsorption with q_{max} is equal to 13.210 mg/g and R^2 is 0.9424. And figure 3 shows The Freundlich isotherm linear graph of $\ln q_e$ with related to $\ln c_e$ of the MB adsorption with R^2 is 0.8069. From both graphs, the adsorption of MB onto Charcoal from coat of Para rubber Seeds is best fit in Langmuir adsorption isotherm.

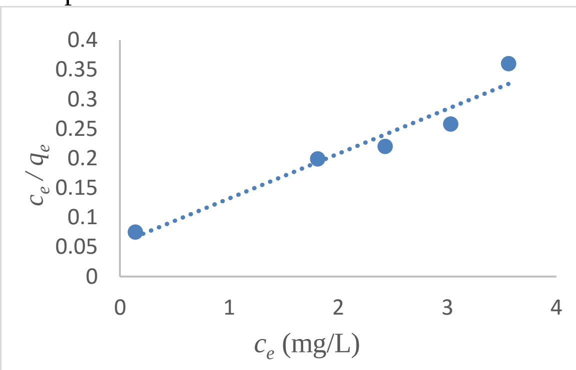

Figure 2: The Langmuir isotherm graph of methylene blue adsorption

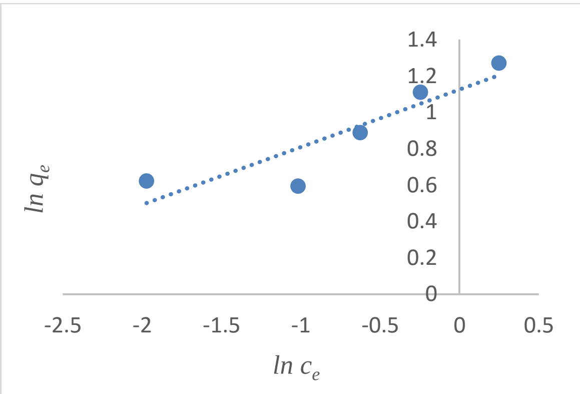

Figure 3: The Freundlich isotherm graph of MB adsorption

Scanning Electron Microscope and X-Ray Microanalysis

SEM images as shown in Figure 4 show that the charcoal has a high level of porosity as revealed under a scanning electron microscope (SEM). Pore sizes range from 1.7 to 15.0 µm having the most abundant pore size around 7.8 µm. And X-Ray microanalysis (EDX) showed that the charcoal contained C at the highest level of 86.1 %, followed by O, K, and Al at 12.7, 1.1, and 0.1 %, respectively as shown in Figure 5.

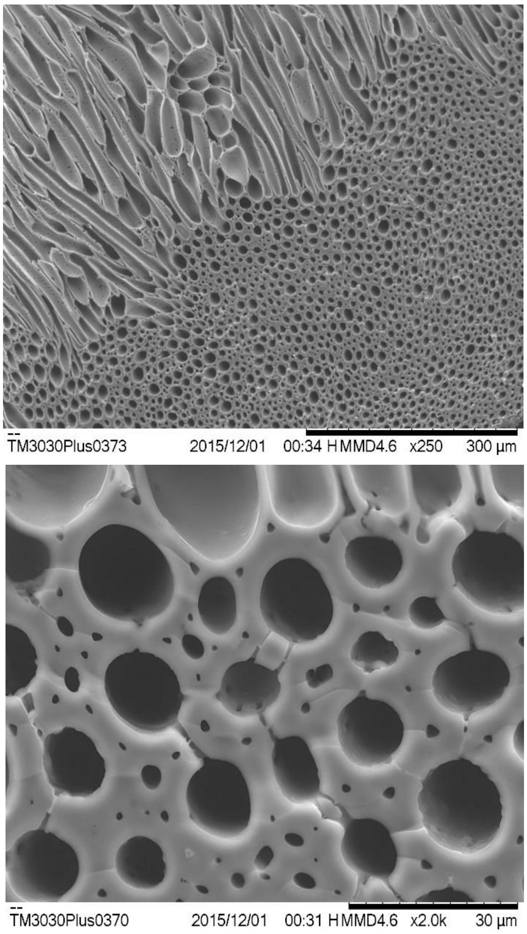

Figure 4: SEM images of Charcoal from coat of Para rubber seeds (a) x250 times (b) x2000 times

Conclusions

The characteristic of charcoal made from seed coat of Para rubber tree can be used as an efficient absorbent due to the good level of porosity and the large pore size (~7.8 µm) as evident from the scanning electron microscopy (SEM) analysis.

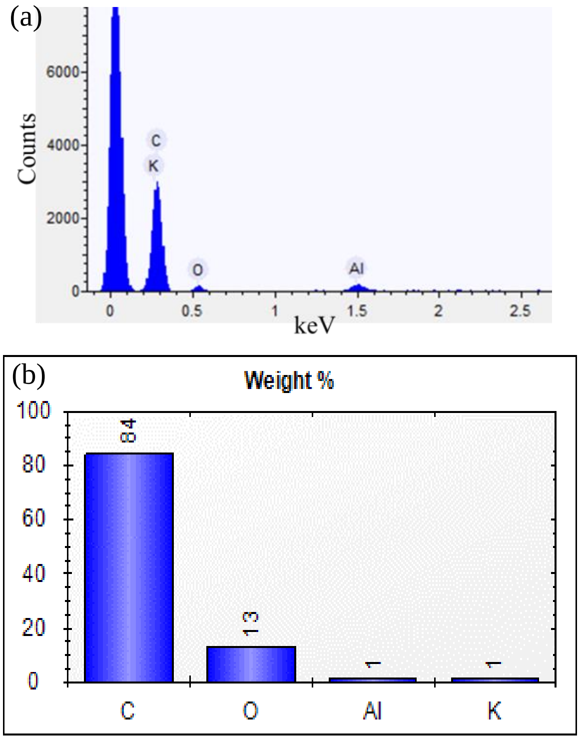

Figure 5: Characteristic X-ray spectrum of elemental composition (a) Peak spectrum (b) Bar charts

From the MB adsorption data, it revealed that firstly, the rate of the adsorption increased rapidly then remained constant when it reached equilibrium because mostly all sites of adsorbent are all occupied. The kinetic results showed a rapid rate of adsorption of MB, when more than 50% of MB was adsorbed by 50 mg of charcoal within 20 minutes. The adsorption isotherm fits with the Langmuir isotherm model, indicating that charcoal can trap MB and does not react further in the next cycle.

From the overall results, charcoal from seed coat of Para rubber tree is one of the effective materials to remove harmful chemicals, like methylene blue, in water. This work has a potential contributing to a more sustainable planet.

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