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ADSORPTION CHARACTERISTICS OF SUBMICRON POROUS CARBON PARTICLES PREPARED FROM RICE HUSK

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Abstract

This study aims to investigate adsorption properties of submicron porous carbon particles prepared from rice husk. In the experimental procedure, to produce porous carbon particles, the following steps were done: (1) washing rice husk, (2) burning rice husk through two stages of heating process at temperatures of 200 and 600°C, (3) saw-milling process of the burned rice husk to obtain submicron sized carbon particles, and (4) porous structurization by dissolving the silica component from the saw-milled product using Sodium Hydroxide solution. Then, to analyze the adsorption properties, the prepared porous carbon particles were put into the curcumin solution under various conditions (i.e., initial amount of carbon, curcumin concentration, and adsorption time). Experimental results showed that although the prepared carbon particles were agglomerated, having sizes of about 800 nm, they were efficient for being used as an adsorbent. The analysis confirmed that the adsorption phenomena followed the Freundlich adsorption isotherm, describing the characteristics of multilayer and heterogeneous adsorption types. This is because of the existence of porous structure in the carbon adsorbent. This study demonstrates the importance of porous structures in the adsorption process, making the more adsorbate diffusion into the surface site and better adsorption efficiency.

Keywords: Adsorption, Isotherm Langmuir and Freundlich Porous carbon, Rice husk.

1. Introduction

Porous carbon material is one of the most unique and attractive materials because of its extraordinary characteristics, such as having a large surface area, high volumes of mesopore, and high electrostatic charge on the surface [1]. These porous structure in the carbon have been found in microporous (less than 2 nm), mesoporous (between 2 to 50 nm) and macroporous ranges (more than 50 nm) [2]. Porous carbon has been widely applied as a protective mask of harmful gases, absorbs odors, fillers in rubber material, and catalysts [3].

There are several ways to make porous carbon, such as sol-gel method and carbonization polymer. Although many reports have suggested various methods using various raw materials, most of the reports limited their study on the successful synthesis route. Almost no report discussed about what phenomena happen during the applications of carbon, specifically on the adsorption process. In fact, this information is important for practitioners, specifically when they want to apply this material for further uses [4-7].

Here, the purpose of this study was to investigate adsorption properties of submicron porous carbon particles. As a model of the porous carbon particles, we prepared carbon from rice husk. Rice husk is selected because it has high carbon content (about 10-40%) [8, 9]. The content of silica that can reach 50% gives additional benefits. Specifically, when silica is removed, it will create porous structure in the carbon product [10]. In addition, understanding this study will bring advantages for further development of carbon materials.

2. Materials and Method

Several chemicals were used: Rice husk (purchased from the Jaya Makmur Agriculture Shop, Bandung, Indonesia) and Sodium Hydroxide (NaOH, Bratachem, Indonesia). In short, to produce carbon particles, rice husk was saw-milled (using the equipment similar to previous study [11]), washed by water (to remove impurities), dried at 200°C for 2 hours (to remove water and to convert into carbon), and carbonized at 600°C for 2 hours (to obtain stable carbon material). The two steps of heating processes (i.e., drying and carbonization) were done in the electrical furnace in the room atmosphere.

The process was not done under a flow of gas since flowing a gas (such as air) can make incomplete carbonization. The flow gas can allow the organic component in the material to be converted into carbon dioxide and/or carbon monoxide (instead of carbon). Then, the produced carbon was washed using centrifugation (15000 rpm for 5 minutes; washed with water for several times). The washing process was done until the clear filtrate was obtained. The washed carbon was then put into porous structurization process, by adding NaOH solution (concentration of 0.07 M) at 70°C for 2 hours to remove silica components in the rice straw [10]. The porous structurization process was then followed by washing process (using centrifugation) and drying at 100°C to remove water.

To determine the adsorption characteristics of porous carbon particles, curcumin solution was used as a model of organic component. Detailed information of the synthesis of curcumin solution is reported in our previous study [12]. In short, the adsorption analysis was done by adding various amounts of porous carbon

particles (from 0.010 to 0.050 g) into 200 mL of curcumin solution with various concentrations (from 5 to 100 ppm).

All the processes were done in the 400 mL capacity of borosilicate photochemical batch glass reactor (dimensions of 10 and 8 cm for height and diameter, respectively) at room temperature and pressure. The adsorption process was done in the range of 0 to 100 minutes, and the reaction was terminated by taking and putting the samples into centrifugation process (11000 rpm for 5 minutes, to separate carbon and curcumin solution. The concentration of curcumin in the filtrate was measured by checking the filtrate from the centrifugation process in the visible spectroscopy (Model 7205 JENWAY; Cole-Parmer; US; analyzed at maximum wavelength in the range of between 280 and 600 nm).

The concentration was then compared with the Langmuir and the Freundlich adsorption isotherm models. Both model used the adsorbate concentration (C_e; in mg/L) and the amount of adsorbed substance per gram of adsorbent (Q_e; in mg/g). The suitability of the adsorption model was taken by comparing the value of R^2. If the value of R^2 approaches 1, it shows that the data is fit.

The first model is the Langmuir adsorption model, informing the monolayer adsorption. There is a homogeneous surface and there is no interaction between the adsorbed molecules and free adsorbates. There is also no displacement of the adsorbate on the surface area of the adsorbent [13]. Equation (1) can be written as [13]

$$\frac{1}{Q_e} = \frac{1}{Q_{\max} K_L} \frac{1}{C_e} + \frac{1}{Q_{\max}} \tag{1}$$

where K_L is the Langmuir adsorption constant and Q_{max} is the monolayer adsorbent capacity (mg/g).

The second model is the Freundlich adsorption isotherm model, informing multilayer adsorption. This type of adsorption occurs in heterogeneous surface areas. Interactions between the adsorbed molecules occur [14]. The Freundlich model, Eq. (2), is shown as [14]

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \tag{2}$$

where k_f and n are the Freundlich constants.

To support the analysis, we conducted characterizations in the following: Fourier Transform Infrared (FTIR-4600, Jasco Corp., Japan), Energy Dispersive Spectroscopy (EDS-7000/8000; Shimadzu Scientific Instrument Inc., Japan), Scanning Electron Microscopy (JSM-6360LA; JEOL Ltd., Japan), and X-Ray Diffraction (XRD; PANalyticalX'Pert PRO; Philips Corp., The Netherland).

3. Results and Discussion

3.1. Characterization of porous carbon

The SEM result of the prepared porous carbon particles is shown in Fig. 1. The results showed that the prepared particles were agglomerated. Ferret analysis showed that the particles had mean sizes of about 800 nm. Most of the particles are spheres.

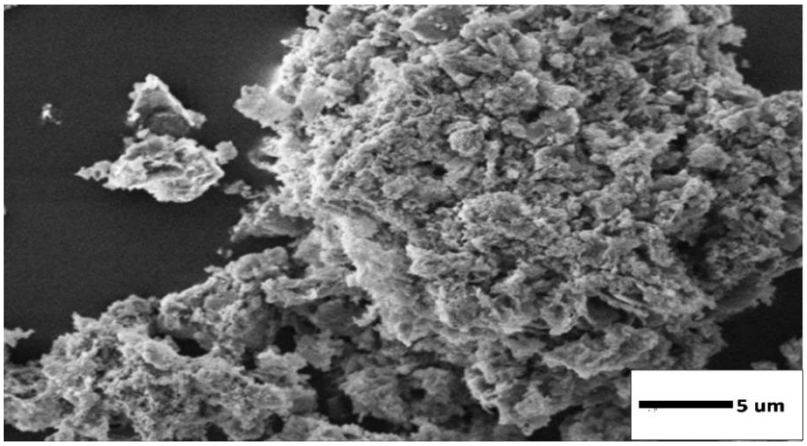


Fig. 1. The SEM image of porous carbon.

Figure 2 is the result of FTIR characterization. The presence of typical absorption bands of carbon at wavelengths between 900 to 1700 cm^{-1} were identified. Peaks at wavelengths of 862.76; 1057.04; and 1633.34 cm^{-1} were corresponding to *C-H* bonds, *C=O* bonds from lactones, and *C=C* bonds, respectively. The absorption band at wavelengths of 3205.24 and 3455.62 cm^{-1} shows the *O-H* bond. This informs that there are trapped water molecules in the carbon porous [15-17].

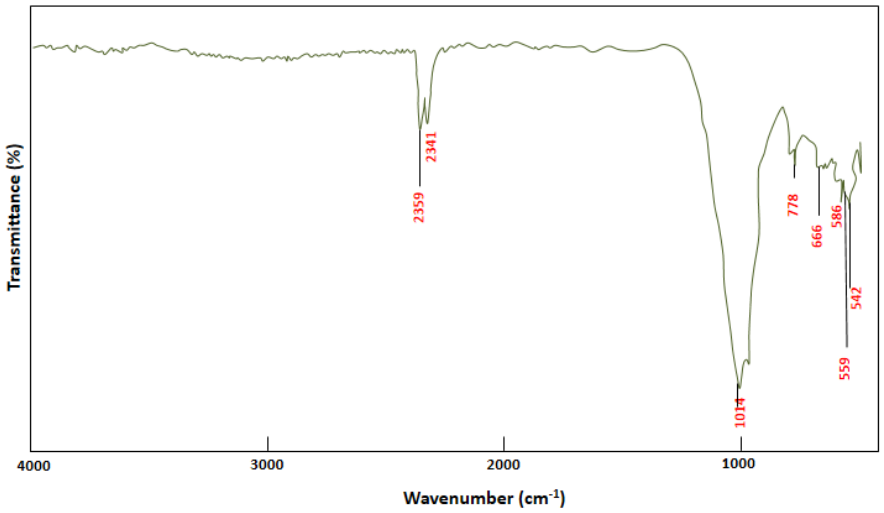
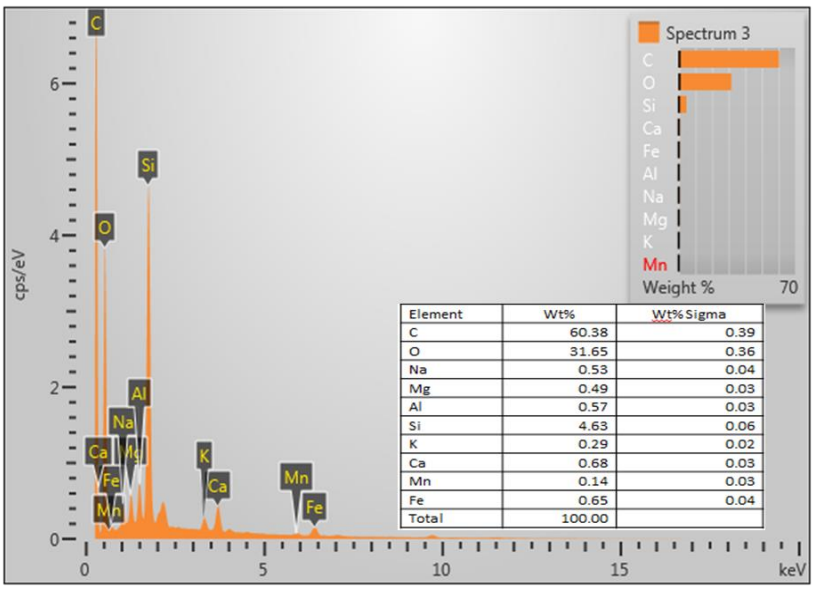


Fig. 2. FTIR analysis result of porous carbon.

Figure 3 shows the EDS analysis result of the prepared porous carbon particles. The characterization results that the elements mostly contained carbon (C) and oxygen (O) elements, reaching 60.38 and 31.65 wt%, respectively. Although other elements were detected, such as sodium (Na), calcium (Ca), and iron (Fe), their amounts are less than 0.60 wt%, informing these elements can be ignored. Other element that is identified is silicon (Si) that has less than 5 wt%. This informs that the extraction of silica from the carbon product is not completed yet. The remained silica should be in the center of the particles. Thus, to remove more silica from the

particles, additional techniques must be added, in which these techniques must allow further particle breakage to make smaller sizes of rice husk ash. Other technique is by changing processing parameters in the extraction process, such making longer processing time or using higher temperature process.



Element	Wt%	Wt% Sigma
C	60.38	0.39
O	31.65	0.36
Na	0.53	0.04
Mg	0.49	0.03
Al	0.57	0.03
Si	4.63	0.06
K	0.29	0.02
Ca	0.68	0.03
Mn	0.14	0.03
Fe	0.65	0.04
Total	100.00	

Fig. 3. EDS analysis of porous carbon.

Figure 4 is the result of XRD characterization. This analysis is important to confirm the presence of phases in the porous carbon structures. The results detected wavelength 2θ at 21°, confirming the existence of carbon in the form of crystals. A sharp peak identified at 26° confirmed the carbon in the amorphous form, and a weak peak at 44° showed the presence of crystal shaped carbon. A small shift in the wavelength compared with the references was obtained. This is because of the presence of chemical activation used in the porous structurization, which can damage the carbon crystalline structure of rice husks [16, 18].

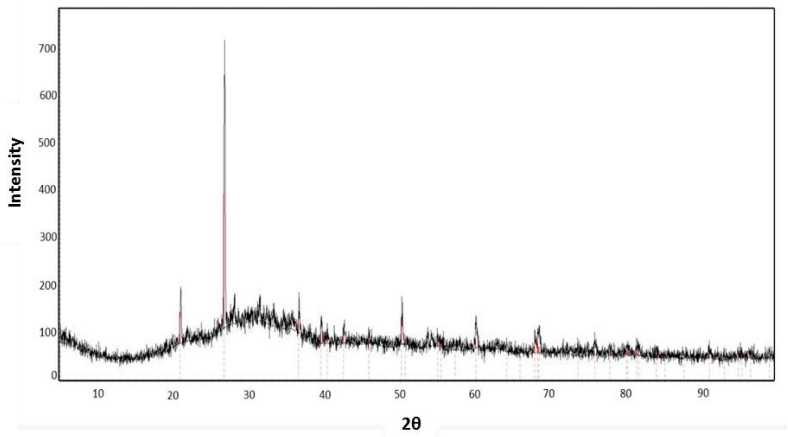


Fig. 4. Result XRD of porous carbon.

3.2. Characteristic adsorption of porous carbon

Prior to analyzing the effect of other parameters in the adsorption process, the first analysis is to understand the optimum amount of adsorbent. The result showed that the optimum amount was 0.022 g when using the concentration of curcumin of 30 ppm. Increasing the mass of adsorbent (more than this value) will make in the decreases in the adsorption ability, resulting in the inefficient adsorption process. This is because the accumulation of carbon particles can create more agglomeration. Too crowded porous carbon particles allowed the surface inefficient [19].

Figure 5 shows the effect of adsorption time on the adsorption ability. The analysis was done using 30 ppm of curcumin solution. The result showed a parabolic curve. Effective adsorption time was obtained at 20 minutes. When the time exceeds the optimal time, the adsorption efficiency is lowered because the adsorbent is no longer able to absorb more organic waste. The surface area of the adsorbent is in saturation and the entire surface is filled with adsorbates [20].

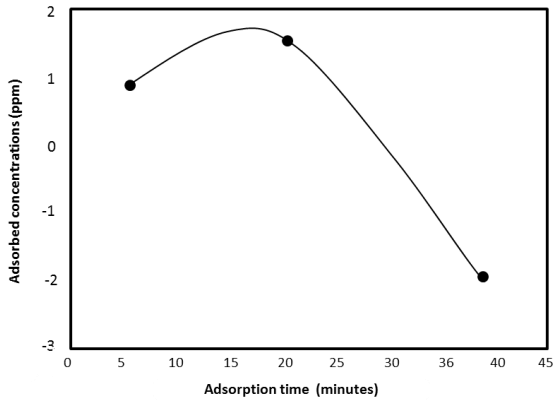


Fig. 5. Efficiency of adsorption time in the adsorption test.

Figure 6 shows effect of adsorbate concentration on the adsorption efficiency. In short, the analysis was done using curcumin concentration of 15, 30, 45, and 60 ppm. The results showed that that the efficiency increased with increasing initial concentration of curcumin. The higher concentration of curcumin dissolved in water makes the more porous carbon adsorbs. However, it should be the saturation condition where the concentration of the absorbed substance will not change or decrease because there is an equilibrium between the substance adsorbed with the remaining substances [20].

Figure 7 shows the analysis of adsorption based on two adsorption models. Figure 7(a) is the Freundlich, whereas Fig. 7(b) is the Langmuir adsorption model. Based on the experimental results compared to the above adsorption models (taking into account the value of R^2, the analysis showed that the porous carbon particles are fit to the Freundlich adsorption model (with a value of $R^2 = 0.9722$)). Measuring the Freundlich adsorption parameters, it obtained $K_f = 2.8674$, $1/n = 0.7051$. From the Freundlich adsorption model, the value of n is obtained to be more than 1. In short, if $n < 1$ then the process involves chemical adsorption. If $n = 1$, the process that occurs is linear adsorption. If $n > 1$, the process involves physical adsorption. Since the n value was 1.4181, we can conclude that the adsorption process involved physical adsorption.

The sorption analysis show interactions between adsorbed molecule layer and free adsorbates. Interactions between molecules occur because of the physical force. The physical force should be from the van der walls force. The other possible force is a tensile force between molecules that is not firmly bound to the surface. This type of force is a reversible process. We also obtained that a physical adsorption process with a heterogeneous surface area of adsorbent interaction [21, 22].

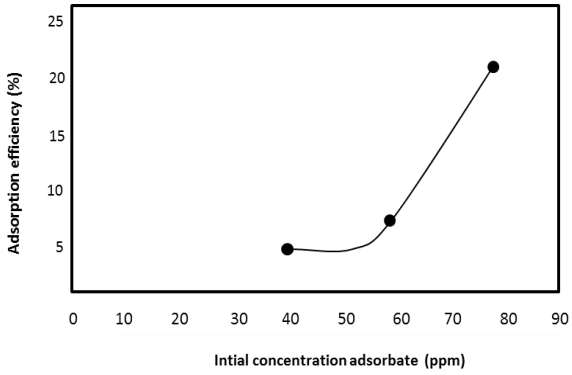


Fig. 6. Variation of adsorbate concentration on adsorbents.

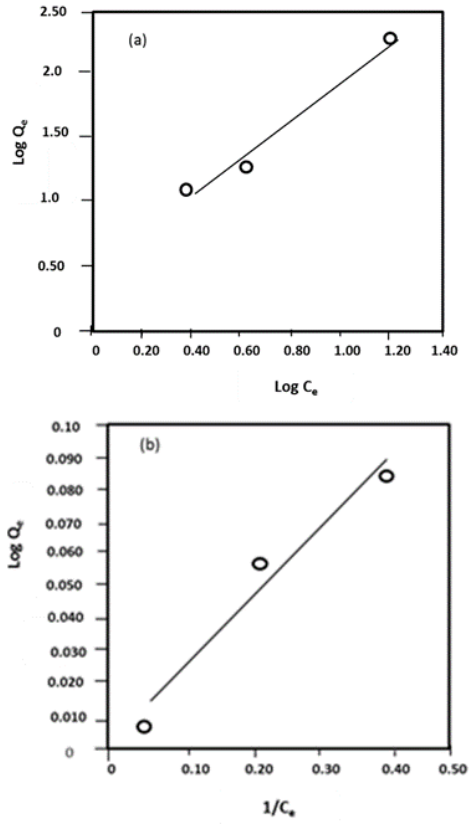


Fig. 7. (a) Model Freundlich adsorption and (b) Model Langmuir adsorption.

The results showed that in the porous structure, all sites can contribute to the adsorption process. The volume and size of porous carbon affect the ability to do adsorption. The porous structure in the carbon affects the ability of particles to do more adsorption. In our research, we used particles with sizes of submicrometers. Thus, we obtained suboptimal adsorption process [19]. Indeed, to understand in detail for the size and porosity, additional nitrogen sorption analysis (such as Brunauer Emmett Teller (BET)) is important. And, this will be done in our future work

4. Conclusion

The present study has demonstrated the adsorption properties of submicron porous carbon particles prepared from rice husk. Experimental results showed that although the prepared carbon particles were agglomerated, having sizes of about 800 nm, they were efficient for being used as an adsorbent. The analysis confirmed that the adsorption phenomena followed the Freundlich adsorption isotherm, describing the characteristics of multilayer and heterogeneous adsorption types. This result is in a good agreement with our hypothesis since the present carbon has porous structure. This study demonstrates the importance of porous structures in the adsorption process, making the more adsorbate diffusion into the surface site and better adsorption efficiency.

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