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Research Article

Adsorption Studies of Rice Husk-Based Silica/Carbon Composite

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Abstract: Rice husk as a by-product of the rice milling process is a material that can still be processed to be a product that can be used in various applications. The potential for the commercialization of rice husks is still hampered by its low economic value. By using the heating method using an inert gas, rice husk can be converted into a composite which contains mostly silica and carbon, a wellknown component with excellent adsorbent properties. This aimed to study the preparation of rice husk-baased silica/carbon composite and its adsorption behavior. In this research, the utilization of rice husk into silica/carbon composites was done by using three different methods. Common heating under temperature of 800^{o}C, heating process under temperature of 800 ^{o}C using furnace equipped with inert gas, and heating process under temperature of 800 ^{o}C using furnace equipped with inert gas with addition of glucose solution were carried out in order to obtain three different kinds of composite. Analysis and characterization using were performed to observe the properties of the composites. As the result, from Fourier Transform Infra-Red and X-Ray diffraction characterizations, silica/carbon composites were successfully made as both of carbon and amorphous silica spectra appeared in the result. Furthermore, composite made under temperature of 800 ^{o}C using furnace equipped with inert gas with addition of glucose solution has the highest adsorption capacity and Langmuir's model adsorptive behavior with R^2 value of 0.935.

Keywords: adsorption, carbon, silica, composite, rice husk

Introduction

The demand of rice, which is one of the biggest commodities in Indonesia, is increasing every time. Increased rice production certainly brings benefits as well as its own problems because of the waste of rice, one of which is in the form of husk[1-2]. Low prices and large quantities certainly ensure the sustainability of this commodity as raw material to be processed further in order to have a higher economic value [2-7]. Several applications for utilizing rice husks as superior products have been reported such as adsorbents for waste water treatment [3], raw materials for bioethanol and also biogas [4-5] or used as composite materials for polymers or building materials [6-7].

Although it may be a little different for the numbers due to the influence of the planting site or the nutrition on the fertilizer used, it is well known that the majority of the content of rice husks is organic volatile matters and also silica [8]. The existence of these contents makes this rice husk widely explored to be used as a source of activated carbon and also high grade amorphous silica [7]. Both of these materials can be obtained from rice husks through various methods both chemically and physically [9] .Carbon and silica are usually used as ingredients adsorbent either in its own form or as a composite Some previous studies such as experiments conducted by Ahmaruzzaman, Daffalla, and Chandrasekhar have proven that adsorbents obtained from rice husk derivative products have very good performance and potential to be commercialized [10-12].

Carbon and silica have been widely known and used in water purification or waste management treatment because both materials are known to bind various compounds such as various heavy metals (Cu,

Mg, Zn, Ni) or also textile dyes [7, 13]. Besides, carbon and silica also have high porosity and a very large surface area; therefore it has the potential to be developed as a high capacity adsorbent. In addition, the process of obtaining silica and carbon adsorbents is fairly easy which makes many people interested to learn more and also develop these technologies [14-15].

The development that is currently happening, many fabricated adsorbents are made from two or more materials, hereinafter often referred as composites. Composites consisting of silica and carbon which can both be obtained from rice husks can make organic-inorganic composites that have superior properties. Research conducted by Karnib proves that the adsorption ability of silica/carbon composites can surpass the adsorption ability from unmixed activated carbon or silica [16-18]. To our knowledge, there have not been many studies that discuss the making of silica/carbon composites directly from the rice husk, so this study will provide a discussion about the comparison of properties and also the ability of adsorption of silica composites with carbon resulting from three different methods in order to obtain the best way of process for making silica/carbon composites with good adsorption ability.

Materials and Methods

Materials

The materials used in this study were rice husks obtained from farmers in the area of Semarang, Central Java and glucose (food grade). Chloric acid, sodium oxide, and methylene blue were Sigma grade.

Methods

Preparation

Three types of silica/carbon based composite adsorbents were obtained from different heat treatments on rice husk ash. For the preparation process, rice husk is dried in the sun and then burned to obtain rice husk ash. The ash obtained was pounded and then sieved using a sieve tray to get fairly homogeneous size particles.

Synthesis of composites

Method I : A total of 90 g of rice husk ash in the previous process was put in a cubicle to be heated at 800^{o}C for 2 hours.

Method II : A total of 90 g of rice husk ash obtained from the previous process was put in a furnace column equipped with an inert gas (nitrogen) flow. Heating was carried out in the furnace for 2 hours at a temperature of 800^{o}C.

Method III : A total of 90 g of rice husk ash obtained from the previous process was mixed with 200 mL of 0.3 N glucose solution and then put in a furnace column equipped with an inert gas (nitrogen) flow. Heating was carried out in the furnace for 2 hours at a temperature of 800^{o}C.

Analysis and Characterization

In this experiment, three adsorbents were obtained with the conditions as can be seen in Table 1. Samples obtained were then characterized using FTIR to observe its functional groups and XRD to determine the crystallinity. Furthermore, the adsorption ability was tested using a solution of Methylene Blue (MB) and a UV-Vis spectrophotometer was used to measure the levels of MB that can be absorbed by the adsorbent. The adsorption test was carried out by inserting 2 grams of sample in 200 mL of MB solution (20 ppm). The solution was stirred at room temperature (30^{o}C) and then at the specified time, absorbance measurements were carried out using a UV-Vis spectrophotometer (λ = 663 nm). In the adsorption test, chloric acid and sodium oxide (0.1 N each) were used as pH regulators in order to adjust the pH level of the adsorption test environment.

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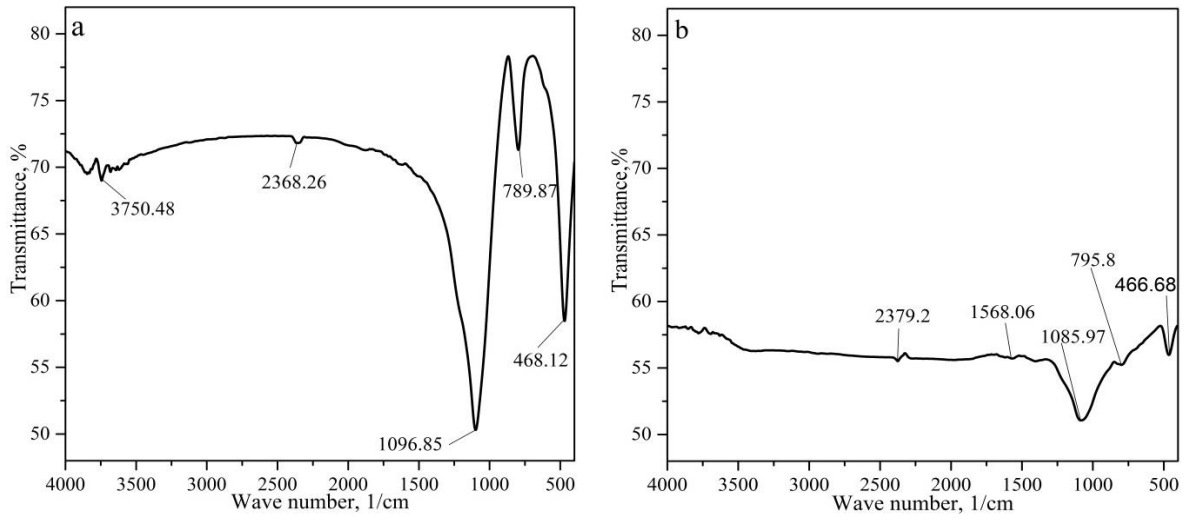
Table 1. Sample Identification

Sample Code	Description
S	Composite obtained from method 1
CS	Composite obtained from method 2
CSL	Composite obtained from method 3

Results and discussion

Molecular Bonding

Characterization using FTIR was carried out with the aim to find out the functional groups that exist on the composite so that the interactions that occur or that exist in the intra-particle can be observed. The result of FTIR characterization is presented in a form of spectrum images as reported in Figure 1. The peak at 3750 cm^{-1} indicates the stretching vibration of silanol groups and the hydrogen bonds (OH) between water and the silanols. The presence of asymmetrical stretching vibration of Si-O-Si is also ensured as there is a very sharp peak area around wave number 1096.85 cm^{-1}. Whereas in the low wave number area, peaks were also detected at 789.87 cm^{-1} and 468.12 cm^{-1}, which means that the sample has amorphous silica. Chemical bonds in CS and CSL samples can be seen in Figures 1b and 1c. The results from FTIR show that the spectrum is almost the same for both images. In order to see the difference more clearly, in Figure 1d the two spectra are placed side by side with the spectrum at the top is CS and the lower spectrum belongs to CSL. As previously shown in Figure 1a, a peak of transmittance appears in the wave number area 400-800 cm^{-1} is a typical characteristic of amorphous silica spectrum. The peak at 466.68 cm^{-1} indicates the existence of vibration of the oxygens which is perpendicular to Si–O–Si planes. The CSL also obtained a peak at 677.12 cm^{-1} which was assigned to strongly polarized Si-O symmetric stretch. The presence of more absorbance and shifting from peak 1096.85 at S to 1085.97 is due to the characteristics of the Si-O-Si asymmetric stretch. A small peak in the area of 1400-1460 cm^{-1} indicates the presence of $-CH_3$ groups. In addition, the presence of carbon in the composite (C = O and C = C) is also marked by the peak that appears in the region of the wave number 1610-1680 cm^{-1}.



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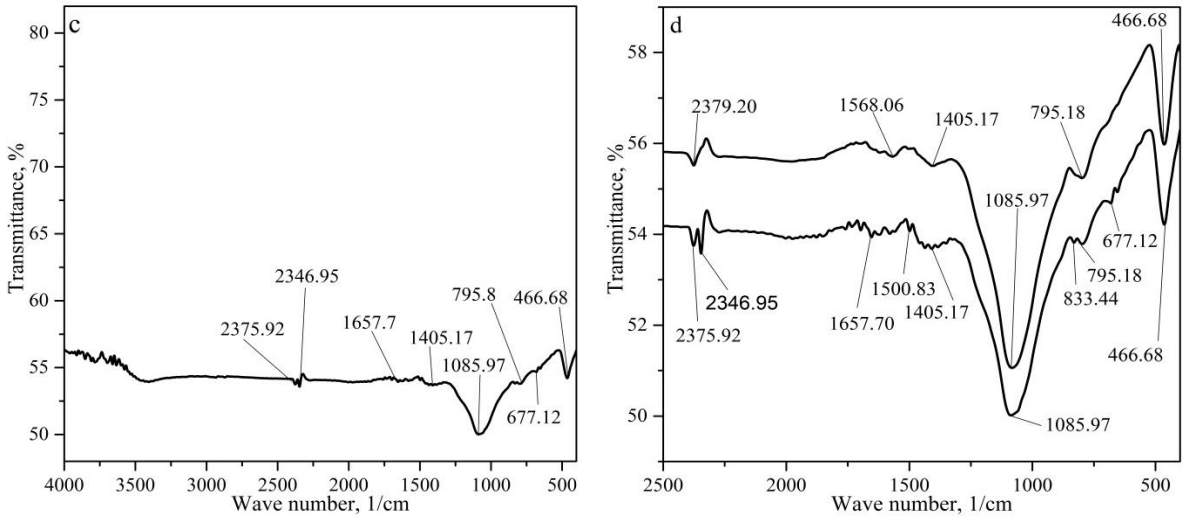

Figure 1. FTIR Spectra of: a. S; b. CS; c. CSL; d. Comparison of CS and CSL

Phase Properties

Crystal or amorphous phase determination can be detected using XRD equipment. The results of XRD characterization are attached in Figure 2. From the three images listed, it appears that there are differences in sample S with CS and CSL samples. In Figure 2a, it can be seen that there is a sharp peak at 2θ = 23°C as well as at 35°C assigned to crystalline silica form. While in figures 2b and 2c, the peak has decreased in intensity but the area is getting bigger. This is caused by the amorphous nature of silica and also because of the carbon present in the sample [13-14].

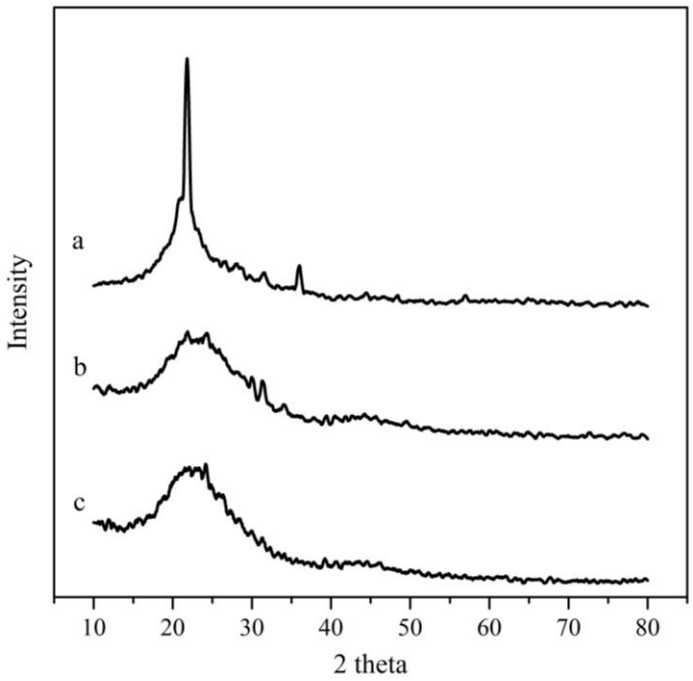

Figure 2. XRD Result of: a. S; b. CS; c. CSL

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Adsorption Ability

Adsorption ability of the sample was tested by using MB as an adsorbate. Comparison of the ability of the three adsorbents produced in this study can be seen in Figure 3. The ability to bind MB is increasing sequentially from S, CS, and the largest is CSL. As for the effect of different acid conditions on adsorption ability, it can be seen in Figure 4. The data in the diagram shows that the best condition for adsorption is found in acidic conditions. And as the pH level increases, the adsorption capacity was decreased. These results are in line with the results obtained by Cowdhurry where it is possible that this happens because of the negative charge neutralization on the surface of the adsorbent which causes an increase in the protonation [15].

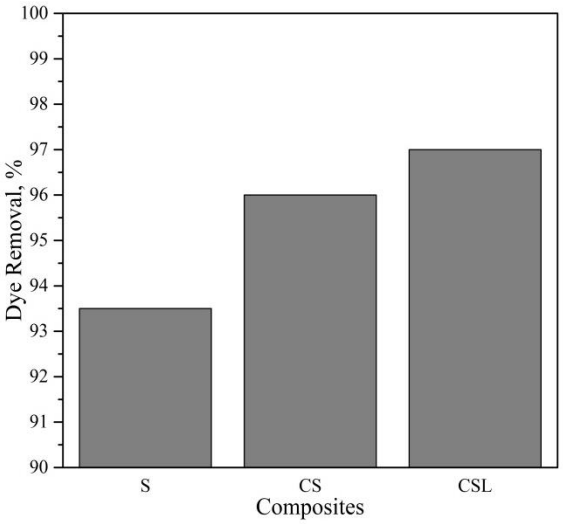

Figure 3. Adsorption capacity of the composites

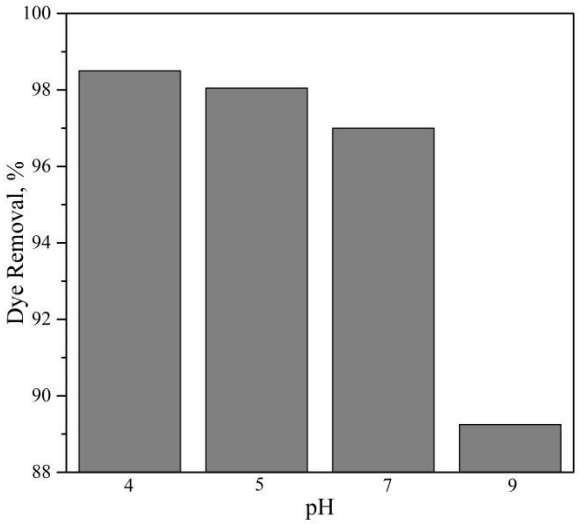

Figure 4. Removal capacity in different pH

Meanwhile, adsorptive behavior from CSL samples was also observed by fitting experimental data with 2 well-known adsorption models, Langmuir and Freundlich. Where the formula for Langmuir's model is as follows:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad \text{(eq. 1)}$$

And for the Freundlich's model is as follows:

$$q_e = K_f {C_e}^n \quad \text{(eq. 2)}$$

Where qe is the equilibrium adsorbent-phase concentration of adsorbate, Ce is equilibrium concentration, qm is the maximum adsorption capacity monolayer, K_L is the Langmuir constant, whereas K_f and n are empirical constants in the freundlich model that is dependent on the nature of adsorbate, adsorbent, and the temperature. The results of the fittings in both models can be seen in Figures 5 and 6 and the parameters obtained can be seen in Table 2.

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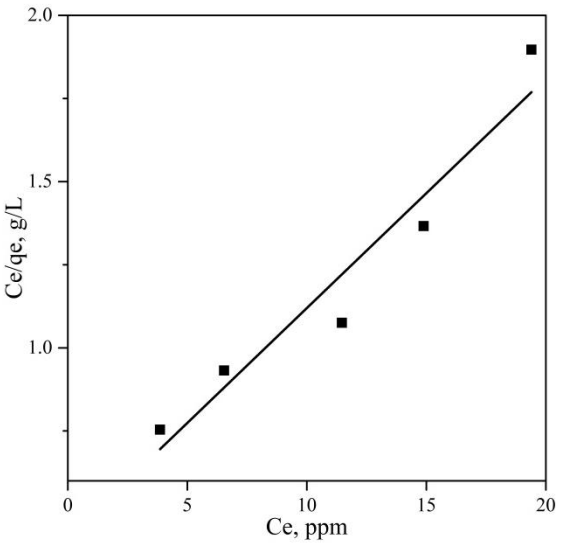

Fig. 5. Linear plot of Langmuir's model

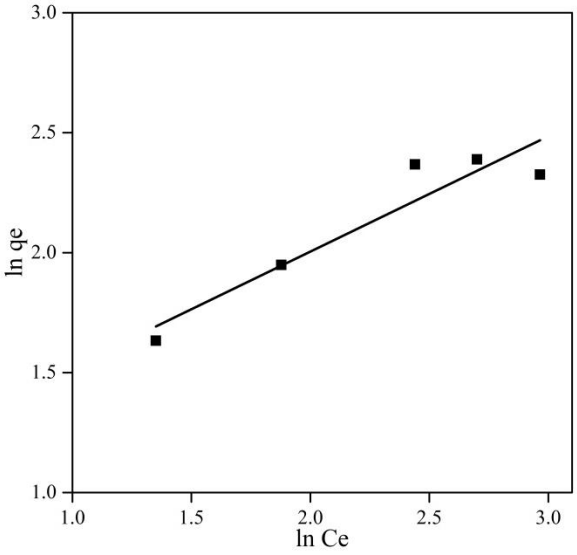

Fig. 6. Linear plot of Freundlich's model

The R_2 parameter of Langmuir's model is closer to 1 which means that the adsorption model can be more described with this model. Fit to the Langmuir's isotherm model means that adsorption process occurs at specific homogeneous sites within the adsorbent. In addition, R_L value (R_L= 1/(1+K_LCo) in the range of 0< R_L <1 means that the adsorption process is favorable [16].

Table 2. Adsorption Parameter Value

Model	K_L	R_L	K_F	n	R^2
Langmuir	0.1612	0.236-0.607			0.935
Freundlich			2.838	2.08	0.8884

Conclusion

Three methods have been successfully carried out to obtain composites with different properties. The best adsorption capacity was obtained by CSL composite. Mathematical model fitting was also reported and it is known that the adsorption process can be explained by the Langmuir model with the value of R^2 is 0.935.

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