Synthesis of mesopore silica composite from rice husk with activated carbon from coconut shell as absorbent methyl orange color adsorbent

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Abstract. The aim of this study is to synthesize mesoporous silica composites with activated carbon by utilizing rice husk waste and coconut shell as absorbent to absorb methyl orange dyes. Rice husk ash was hybridized with PEG into silica-PEG, then PEG was released by solvothermal extraction using DMG (dimethyl sulfoxide) as solvent to obtain mesopore silica. Composites are formed by homogenizing mesoporous silica and activated carbon with methanol. Composites were successfully synthesized based on SEM-EDX data which showed the distribution of carbon, silica and oxygen in surface morphology with content of 76.99%, 5.08% and 17.93% respectively. The results showed that the adsorption of composite adsorbent reached the adsorption capacity of 0.470 mg.g⁻¹ in a pH 2 solution with 30 minutes of contact time. The occurrence of methyl orange adsorption is monolayer because it matches the Langmuir adsorption isotherm equation.

1. Introduction
Adsorption is a common method, in which the process of fluid molecules touches and attaches to the surface of solids, there are some researchers who conduct research on the adsorption of dyes with various materials, methods and types of dyes that are diverse, such as research on adsorption of textile dyes with activated carbon from apricot waste conducted by Basar [1-3], a study of adsorption of textile dyes with pine cone conducted by Mahmoodi [4], adsorption of textile dyes with activated carbon from orange peels conducted by Azami [5], a study of adsorption of textile dyes with carbon from rice husk ash by Lakshmi [6], adsorption of textile dyes with bio-silica, chitosan and silica-chitosan nanocomposite conducted by Cheshmeh [7], adsorption of methyl orange with mesoporous carbon conducted by Mohammadi [8]. Most of the above research is conducted based on waste, so this method is used to demonstrate the cost-effectiveness of solving wastewater treatment problems. The most commonly used adsorbents are activated carbon and silica because they are good absorbers [9].

This research innovates in the preparation and the use of mesoporous silica composite adsorbents from rice husks with activated carbon from coconut shells to absorb methyl orange dyes from aqueous solutions.

The silica used is based on rice husk ash. The silica that has been taken from rice husk ash were made into mesoporous silica which can be used as an adsorbent [2], Yusmaniar found the raw material of activated carbon from coconut shells [10]. Most of coconut shells are only considered as waste from the coconut processing industry, their abundant availability is considered as an environmental problem, but
it is renewable and cheap. Besides that, this coconut shell charcoal can still be processed into products that have high economic value as activated carbon or activated charcoal. This activated carbon will later be combined with mesoporous silica as a composite to increase the adsorption of adsorbent. The aim of this study is to synthesize mesoporous silica composites with activated carbon by utilizing rice husk waste and coconut shell as adsorbent to absorbs methyl orange dyes

2. Experimental method

Rice husk ash (RHA) as much as 10,00 grams sifted and ashed with the furnace at 700°C for 4 hours. The silica from the isolation was mashed, then added by 4M NaOH then was refluxed for 1 hour, the mixture was filtered. The filtrate was obtained namely is sodium silicate. PEG 1,00 g was dissolved aqua demineralization. Then added 45 mL of 1M HCl while stirring to form an acid-PEG solution. Furthermore, the acid-PEG solution was put into 30 mL of sodium silicate solution and added HCl until pH 4. The residue was dried in an oven at 100°C for 24 hours and mesoporous-PEG silica solid is formed, then it was characterized by FTIR. The mesoporous-PEG silica solid was wrapped up by filter paper and inserted to a soxhlet. 5% DMSO solvent was added into the flask. The solvent was heat until the DMSO boiling point is reached. Then silica that has been released from PEG was dried at 100°C for 12 hours. Mesoporous silica was then characterized by FTIR, and SAA.

Mesoporous-activated carbon silica composites are synthesized by dissolving 5.00 g of mesoporous silica in 100 mL methanol while stirring for 30 minutes. Then was add 5.00 grams of activated carbon, stirred with a homogenizer with a stirring speed of 1000 rpm for 30 minutes. Then silica-activated carbon was poured into a beaker, where the solid was stored for 10 minutes to form a gel. The gel was dipped in methanol and hushed up for 5 days at room temperature and the gel as a mesoporous-activated carbon silica composite. Then the gel was filtered and the residue were heated in an oven at 200°C for 2 hours. The mesoporous-activated carbon silica composites were characterized using FTIR and SAA.

Adsorption of methyl orange by adsorbents was studied using batch techniques. The effect of several parameters was studied in this adsorption process, such as contact time, adsorbent mass, concentration and pH of methyl orange solution. The results studied were used to determine the optimum conditions for measuring adsorption capacity. Percent loss of adsorbate was calculated using the formula:

\[ \% E = \frac{Co - Ce}{Co} \times 100 \]

Where,

- \( E \) = Number of dyes absorbed
- \( Co \) = initial concentration
- \( Ce \) = final concentration

Determination of adsorption isotherms was determined at room temperature with optimum mass, pH and contact time conditions. 25 mL of methyl orange solution with several concentrations, that are 2, 4, 6, 8 and 10 ppm were put into an Erlenmeyer flask contained an amount of adsorbent with the optimum mass of mesoporous-activated carbon silica composites. Then was stirred using a magnetic stirrer with a speed of 550 rpm for a predetermined optimum time. The solution was filtered and the filtrate were analyzed using Ultra Violet spectroscopy at 462 nm a wavelength of 462 nm.

3. Results and discussion

The results of FTIR silica isolation shown in Figure 1, can be seen in the silica spectrum measured at wavelengths of 4000-400 cm\(^{-1}\) there is a typical peak of silica that is the peak widens around 3217.27 cm\(^{-1}\) which indicates the existence of vibration strain OH group, and there are a peak 1629.85 cm\(^{-1}\) which indicates the existence of vibration OH buckling from silanol (Si-OH), the emergence of these peaks due to the adsorption of water during the isolation process. Then there is a peak of 1107.14 cm\(^{-1}\) indicating the strain vibration from Si-O-Si [11]. Another peak was found in the fingerprint region of 804.32 cm\(^{-1}\) peak indicating the structure of the tetrahedral silica SiO\(_4\) ring [12]. Then found peaks of 688.59 cm\(^{-1}\) and 468.7 cm\(^{-1}\) indicate the existence of bending vibrations from the Si-O-Si group. Results
Characterization of SAA silica isolation showed a BET surface area of 26.0954 m$^2$g$^{-1}$ with type IV adsorption isotherm pattern.

The Silica-PEG hybrid produced is then characterized by FTIR. The spectra resulting from the silica-PEG hybrid FTIR shown in Figure 1, found a widening peak at wave number 3406.29 cm$^{-1}$ indicating the presence of the -OH group of silanol (=Si-OH), then a new peak at wave number 2920.23 was found. cm$^{-1}$ which is the -CH$_2$ group of PEG. It was found that peaks of 1631.78 cm$^{-1}$ and 1471.69 cm$^{-1}$ were thought to indicate the presence of buckling -OH vibrations from silanol (=Si-OH), a result of spectral shifts due to strong interactions between the two components showing hybrid nature [13,14].

Mesoporous silica, which was produced was characterized by FTIR, and SAA. In Figure 1 we can see the loss of the peak of 2920.23 cm$^{-1}$ indicating the release of PEG from silica. Furthermore, there is a peak of 3284.77 cm$^{-1}$ indicating the presence of the -OH silanol group (= Si-OH). It was found that the peak of 1629.85 cm$^{-1}$ was the bend -OH vibration of a water molecule. The -OH buckling vibration of Si-OH at wave number 1458.18 cm$^{-1}$ and the bending vibration of Si-OH at wave number 1352.10 cm$^{-1}$. The peak at wave number 1093.64 cm$^{-1}$ was found as an asymmetric stretching vibration of Si-O from siloxane (=Si-O-Si=), there was a peak of 952.84 cm$^{-1}$ which was the vibration of Si-O stretching on silanol (=Si-OH). There is a peak of 800.46 cm$^{-1}$ which is symmetrical stretching vibration of Si-O in siloxane (=Si-O-Si=), found a peak of 565.14 cm$^{-1}$ and 474.49 cm$^{-1}$ is the bending vibration of the group siloxane (=Si-O-Si=).

![Figure 1. The result of FTIR Silica, silica-PEG, and silica mesopore.](image1)

The results of activated carbon by SEM characterization after chemically activated by soaking ZnCl$_2$ are presented in Figure 2, showing that there are too much pores. The results of the SAA characterization of activated carbon showed a surface area of BET 234.7908 m$^2$g$^{-1}$ with type IV adsorption isotherm pattern.

![Figure 2. The result of SEM activated carbon.](image2)
Elemental mapping image of mesoporous-activated carbon silica composites is presented in Figure 3, where the red part is the C element of activated carbon, the blue and green parts are the O and Si elements of mesoporous silica. It can be seen that the particle size of element C from activated carbon is much greater than the particle size of element O and Si from mesoporous silica. Composite samples contained 76.99% C, 17.93% and Si 5.08% elements, from the data proving that mesoporous-activated carbon silica composites were formed and there were no other impurities present. Results Characterization of SAA composites showed a BET surface area of 306.745 m$^2$g$^{-1}$ with a type IV adsorption isotherm pattern.

The percent adsorption graph is presented in Figure 4, explaining that the mass of mesoporous silica adsorbents, activated carbon and composites that best adsorb methyl orange are 0.4 g, 0.2 g and 0.2 g with each percent adsorption of 48%, 51% and 51% and the adsorption capacity in Table 1.

![Figure 4. Determination of optimum mass.](image)

| Adsorbent       | Massa (g) | Percentage of Adsorption (%) | Q (mg/g) |
|-----------------|-----------|------------------------------|----------|
| Mesopore silica | 0.4       | 48.259                       | 0.115    |
| Activated carbon| 0.2       | 50.833                       | 0.235    |
| Composite       | 0.2       | 50.707                       | 0.247    |

The graph (figure 5) explains that the optimum pH of methyl orange for the adsorption process of mesoporous silica adsorbents, activated carbon and mesoporous-activated carbon silica composites are the best to adsorb methyl orange is pH 2 with each percent adsorption of 68%, 88% and 84% and adsorption capacity in Table 2.

![Figure 5. Determination of the optimum adsorbent pH.](image)
Table 2. Percent adsorption and optimum pH adsorption capacity.

| Adsorbent   | Percentage of Adsorption (%) | Q (mg/g) |
|-------------|-----------------------------|----------|
| Mesopore silica | 68,383                     | 0,161    |
| Activated carbon  | 88,317                     | 0,415    |
| Composite        | 84,718                      | 0,398    |

The optimum contact time of each adsorbent with methyl orange presented in Figure 8 is 30 minutes, where the first 30 minutes of the adsorption process reaches about 60% to 86%, which then increases the amount of adsorption at the contact time of 90 minutes to 150 minutes, only an increase The adsorption is very low in activated carbon adsorbents and composites, whereas in mesoporous silica there is a decrease in graph so that it is stated that 30 minutes is the optimum time of adsorbent contact in the methyl orange adsorption process, then it can be re-concluded that the effect of activated carbon on the active silica-carbon composite is adsorbent absorption in the methyl orange adsorption process. The adsorption capacity is presented in Table 3.

Table 3. Percent of adsorption and adsorption capacity of optimum contact time.

| Adsorbent   | Percentage of Adsorption (%) | Q (mg/g) |
|-------------|-----------------------------|----------|
| Mesopore silica | 74,604                     | 0,199    |
| Activated carbon  | 87,769                     | 0,468    |
| Composite        | 88,194                      | 0,470    |

Based on the Langmuir isotherm curve (Figure 7) and the Freundlich isotherm (Figure 8), the most suitable isotherm model for composite adsorbents is the Langmuir adsorption isotherm model. The adsorbent adsorption properties are at the active center of the surface of the adsorbent and form a monolayer layer. The adsorption kinetics presented in Figure 9 shows the third-order adsorption kinetics with a regression value (R²) of 0.9989.

Figure 6. Determining the optimum contact time.

Figure 7. Langmuir isotherm curve.  
Figure 8. Freundlich isotherm curve.
4. Conclusion

Successfully synthesized mesoporous silica adsorbents from rice husk ash, activated carbon from coconut shells and activated mesoporous-carbon silica composites. The optimum mass of mesoporous silica adsorbent is 0.400 g, activated carbon 0.200 g and mesopore-activated carbon silica composite 0.200 g. In all the adsorbent synthesized, work optimally at pH 2 with the optimum contact time is 30 minutes. Activated carbon in mesoporous silica composite adsorbents-activated carbon affects and increases the adsorption power of mesoporous silica and it has successfully adsorbed methyl orange dyes above the adsorption power of activated carbon and mesoporous silica.

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