Chapter 11
Synthesis and Characterization of Silica Aerogel from Rice Husk Ash with Ambient Pressure Drying Method for Methylene Blue Removal


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Abstract
Rice husk is an abundant agricultural by-product that is rich in silica which is about 60%. Rather than dumped or burnt it in the open areas, this by-product can be used in the production of silica aerogel as an economically viable raw material. Silica aerogel from rice husk ash (RHA) was prepared through sol-gel method and dried by using ambient pressure drying method. The silica RHA was extracted with sodium hydroxide solution to produce sodium silicate solution and neutralized with sulphuric acid to form silica gel. A small amount of Tetraethyl Ortho-silicate (TEOS) was added to the silica gel to strengthen the gel network and increase the porosity of gel. The gel was aged to ensure all of the gel is completely formed and was washed carefully with pure water and dried with ethanol under ambient pressure to form silica aerogel. SEM and FTIR analyses revealed the synthesized silica aerogel has fibrous morphology and indicates similar trend with previous researches. For adsorption testing, the silica aerogel able to adsorb 89% to 97% when the contact time was raised from 1h to 2h from aqueous solution. This study affirmed that silica aerogel was successfully synthesized using RHA and applied as an efficient adsorbent for MB removal.

Keywords: Rice husk ash, Ambient Drying Pressure Method, Silica Aerogel, FTIR, Adsorption

Introduction
Textile industries plays an important role in the economic development especially for developing countries. However, textile industries creates serious effect which produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes (Aljeboree, Alshirifi, & Alkaim, 2017). Numerous of these dyes are carcinogenic, mutagenic, and teratogenic and possibly disturb the ecosystem. Moreover, it also toxic to human beings, fish species, and microorganisms. Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia and hypertension (Pathania, Sharma, & Singh, 2017). Hence, their removal from aquatic wastewater is important.

Adsorption technique is a very attractive and effective separation technique for producing high quality colorless effluents. It also superior to other dye removal methods in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances (Pathania et al., 2017). For researchers and environmentalists, dyes removal in an economic way remains an important...
In this study, the feasibility of using silica aerogel for adsorption of a methylene blue (MB) has been tested. The characteristics of the silica aerogel are highly microporous in the structure with both have high internal surface area and porosity (Mishra, 2007). Thus, rich in porosity can be used as an adsorbent for the removal of organic and inorganic pollutants from various sources such as water and air streams (Mishra, 2007). Considering cost effectiveness in silica aerogel production, researchers developed different precursors from abundant waste materials, such as oil shale ash, fly ash, bagasse ash and rice husk ash (Zhu et al., 2018). In this study, rice husk ash (RHA) was used as the main raw material since it has been thrown away and ends up either being dumped in open area or burned in open spaces (Bakar, Yahya, & Gan, 2016). Therefore, the aim of this research is to synthesis and characterize of silica aerogel from RHA using ambient pressure drying (APD) technique for methylene blue (MB) removal.

**Materials and synthesis methods**

The rice husk is dry at 50°C, and grounded to pass the 150 µm sieve. The rice husk is put into a muffle furnace at different calcination temperatures (400 – 800 °C) with holding time length (5h) are carried out for different samples. The calcination mixture is then immersed in 1M H$_2$SO$_4$ solution with a certain ration of 8 mL/g. The silica sol is obtained after vacuum filtration, with the residues for further characterization. The silica sol with a certain volume was then put into the oven, and gelation occurred after calcined 12 h under 60 °C. The hydrogel is aged for 1 d, after which 1 M H$_2$SO$_4$ solution is performed to remove the impurities inside the skeleton at room temperature. The hydrogel is then immersed into EtOH for solvent exchange at room temperature, after which hexane is used to substitute the ethanol inside the pores. Surface modification is then carried out by soaking the wet gel in a mixture with a volume ratio of hexane: TMCS:EtOH=8:2:1 for 24 h at 40 °C. After a complete surface modification, the silica wet gel is suspended in a liquor and bailed out. The modified silica wet gel is then dried under room temperature for 3 h, and then it is heated at 100 °C and 200 °C for 2 h, respectively, to obtain the super hydrophobic silica aerogel.

**Characterization**

The morphology of the synthesized silica aerogel was determined using Scanning Electron Microscopy (SEM Jeol). The functional groups were examined by Fourier Transform Infrared (FTIR Spectrometer Bruker Vertex 70) in the range of 4000 to 400 cm$^{-1}$.

**Adsorption process**

A batch adsorption experiments were conducted in a set of conical beakers at initial concentration MB is 50 mg/L. 1 g/L of silica aerogel was added to the MB solution under constant stirring (300 rpm) at ambient temperature with different contact time. Then, the samples were collected, centrifuged (3000 rpm, 2 min), and analysed using UV-vis spectroscopy at 665 nm. The amount of MB removal percentage was computed using following equation:

$$\text{Removal (\%)} = \frac{\text{Concentration inlet} - \text{Concentration outlet}}{\text{Concentration inlet}} \times 100$$

**Results and Discussion**

*Characterization of silica aerogel synthesized of RHA*

Figure 1 shows the SEM image of silica aerogel synthesized from RHA. As illustrated from the figure, the pore size and porosity distribution was uneven. The SEM image of the synthesized
The functional groups present in silica aerogel synthesized from RHA were analyzed using FTIR, as shown in Figure 2. Firstly, rice husk (RH) consists of O-H bonds due to the existence of cellulose, hemicellulose, and lignin contents. Ramesh (2016) observed the broad band at 3328.98 cm\(^{-1}\) representing the cellulosic materials which contain a various number of O-H bonds. 2896.95 cm\(^{-1}\), 1635.56 cm\(^{-1}\), 1074.30 cm\(^{-1}\), and 790.78 cm\(^{-1}\) respectively contain C-H stretching vibrations, hemicellulosic subtraction and C-O-C stretching for glucose rings (or C-O stretching single bond). Unlike raw RH, FTIR spectra of RHA (400°C, 600°C, 800°C) illustrate less absorption peaks since most functional groups disappeared. According to the previous researches, the functional groups from the raw material spectrum which mostly is cellulose (Wang, Li, Barford, Hellgradt, & Mckay, 2016) were as volatile matters when heat was provided (Deshmukh, Peshwe, & Pathak, 2012). As the temperature getting higher to 800°C, the broad peak becomes greater due to the SiO\(_2\) transformed to crystalline form. The characteristics of band at 1074.30 cm\(^{-1}\) and 798.49 cm\(^{-1}\) for silica aerogel are allied to Si-O-Si asymmetric and O-Si-O symmetric bond stretching vibration respectively (Wörmeyer, Alnaief, & Smirnova, 2012). This finding is also quite similar to Fan, Wu, Xu, & Sun, (2016).

**Adsorption Performance of Silica Aerogel Synthesized from RHA**

Figure 3 exhibit the adsorption performance of silica aerogel synthesized from RHA on MB removal. Silica aerogel was proven to have a high feasibility as adsorbent for MB removal as demonstrated in its high removal percentage (89%) for contact time 1h and continue rising to 97% when the contact time is increased to 2h, owing to its favourable structural properties. This indicates that during absorption process, it started of with MB molecules penetrating onto the boundary layer of adsorbent. Then, MB molecules diffused into the absorbent surface and are adsorbed onto the surface pores of silica aerogel by weak forces of intermolecular cohesion (B. H. Hameed, A. L. Ahmad, 2007). Hence, with a longer contact time, more molecules of MB have more chances to interact and be attached to the silica aerogel surface and finally increased the MB removal efficiency (De, Azargohar, Dalai, & Shewchuk, 2013).
**Conclusion**

The potential of silica aerogel synthesized from rice husk ash (RHA) was tested on methylene blue (MB) removal from aqueous solution. A simple sol-gel method together with an ambient pressure drying technique has been used to synthesis one kind of high performance and flexible silica aerogel (800°C). The characterization analysis (SEM and FTIR) of synthesized silica aerogel in conformity with literature, signifying the successful formation of silica aerogel structure from RHA. The performance studies showed that the silica aerogel from RHA has a good performance in MB removal from aqueous (89% to 97%).

**References**


