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Preparation of Hierarchical Porous Carbon Derived from *Averrhoa Bilimbi* and Its Diffusion Properties

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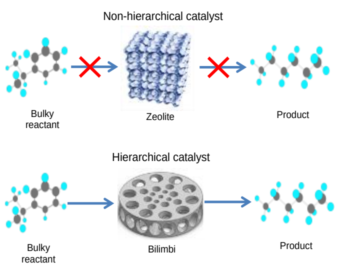
Graphical abstract



Abstract

In this study, a hierarchically porous carbon was prepared from a natural material, *Averrhoa bilimbi*, also known as bilimbi. The bilimbis were cut into preferred shape and size before drying by freeze drying method. The bilimbis were then subjected to pyrolysis at temperature of 400°C and transformed to porous carbon. Scanning electron microscopy (SEM) revealed that the bilimbis have a hierarchically porous structure in the macro-range. The diameter of the porosity decreased inwards from 30 to 8μm. Different types of motor oil, which were used to represent bulky molecules, were employed to test the diffusivity of these molecules from the bilimbi. It was found that the oils were able to diffuse through the hierarchically porous bilimbi in 2 to 3 hours, depending on the viscosity of the oils. Therefore, it can be concluded that, *Averrhoa bilimbi* possesses hierarchical porous structure with interconnected pores and capability to diffuse bulky molecules.

Keywords: Hierarchically porous carbon; diffusion limitation; bulky molecules; viscosity

Abstrak

Dalam kajian ini, karbon berliang hierarki telah disediakan daripada bahan semula jadi iaitu *Averrhoa bilimbi* atau lebih dikenali sebagai bilimbi. Bilimbi dipotong mengikut bentuk dan saiz pilihan sebelum dikeringkan menggunakan kaedah pengeringan sejuk beku. Bilimbi kemudiannya dipirolisis pada suhu 400°C untuk ditukarkan kepada karbon berliang. Mikroskopi elektron pengimbas (SEM) menunjukkan bahawa bilimbi yang disediakan mempunyai struktur berliang hierarki dalam julat makro. Diameter menunjukkan penurunan dari 30 μm di luar kepada 8 μm di dalam. Pelbagai jenis minyak motor yang mewakili molekul-moleku besar digunakan untuk menguji kebauran molekul melalui bilimbi ini. Didapati bahawa, minyak-minyak ini dapat membaur melalui liang hierarki bilimbi di dalam masa 2 hingga 3 jam, bergantung kepada kelikatan minyak yang digunakan. Oleh itu, dapat disimpulkan bahawa, *Averrhoa bilimbi* mempunyai struktur berliang hierarki dengan liang yang saling berkait dan mampu untuk membaur molekul besar.

Kata kunci: Karbon berliang hierarki; had pambauran; molekul besar; kelikatan

1.0 INTRODUCTION

Hierarchically structured porous material is defined as materials with multiple levels of interconnected pores in the range of micro (< 2 nm), meso (2–50 nm) to macropores (> 250 nm). The combination of different pore-size systems within one material can give huge benefits in the field of catalysis. The micro and mesopores will provide a large surface area for the dispersion of active sites while the macropores can act as an efficient mass transport [1]. For conventional catalysts such as zeolite, the sole presence of micropores inhibit the diffusion of bulky molecules due to restricted access and slow mass transport to the active sites located in the catalyst. The negative impact of the diffusion constrain is not only shown on the activity but also on the selectivity and stability of the catalyst [2]. Therefore, by introducing hierarchical porous catalyst, it is possible to significantly minimize the diffusion limitation and enhance the catalytic performance over that of a catalyst without hierarchical pores [3].

Hierarchically porous material can be synthesized by different methods such as microphase separation, self-assembling of surfactant, macroscopic hard template and others. However, these methods required high cost and it is difficult to control the synthesis conditions [4]. Therefore, as an alternative, a rich variety of biological materials with complex hierarchical morphologies can be used as the source of hierarchical porous materials.

Averrhoa bilimbi is one of the species that belongs to the *Averrhoa* genus and oxalidaceae family. It is a seasonal fruit which are widely cultivated in tropical countries. Figure 1 shows the physical appearance of raw *Averrhoa bilimbi* fruits. The fruits are crisp when unripe and turn green to yellowish when riped. The bilimbi's skin is thin and glossy while the green flesh is very juicy and extremely acidic due to the oxalic acid content. Previous research showed that bilimbi contains high minerals such as calcium, phosphorus, iron and potassium [5]. Besides that, it is also rich in vitamin C and a potential good antioxidant.

Figure 1 Mature fruits of Averrhoa bilimbi

To the best of our knowledge, there has been no study on the potential of *Averrhoa bilimbi* fruits as a hierarchical porous carbon. Therefore, in this work the morphology porosity and the diffusion properties of the bilimbis as hierarchical porous carbon are studied.

2.0 EXPERIMENTAL

2.1 Pretreatment of Averrhoa Bilimbi

The *Averrhoa bilimbi* was first washed with distilled water before being cut into preferred shape with about 0.5 cm thickness and 1 cm in diameter. Then, the bilimbi was submerged in liquid nitrogen before freeze-dried for 48 hours using a laboratory freeze-dryer, Alpha 1-4 LD plus. Later, the freeze dried bilimbi (BBP) was pyrolysed in a stainless steel vertical furnace under nitrogen gas flow (100 mL/min). The pyrolysis time and temperature used were 1 hour and 400°C with heating rate of 5°C/min.

2.2 Characterization

Fourier transform infrared (FTIR) spectra were obtained by KBr method using a Thermo Scientific iS50 spectrophotometer with a spectral resolution of 2 cm^{-1} and scan 10 s at temperature of 20°C. Scanning electron microscopy (SEM) analyses were carried out using a JEOL JSM-6390LV instrument with an accelerating voltage of 15 kV. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA-DTA STAR SW.8.10 thermal analyzer with a heating rate of 10°C/min and temperature range of 0 to 800°C.

2.3 Hydrophobicity Test

The hydrophobicity test was done by using water adsorption technique. In a typical experiment, the pyrolysed bilimbi (BAP) was dried in an oven at 110°C for 24 hours to remove all the physically adsorbed water. After dehydration, the bilimbi was exposed to water vapor in a closed desiccator at room temperature for 12 hours. 3/4 of the desiccator was first filled up with distilled water for overnight. The weight of the BAP was taken every 30 minutes. The percentage of adsorbed water as a function of time was determined by $((m_t - m_0)/m_0)) \times 100$ %, where m_t represents the sample mass after adsorption of water and m_0 represents the initial mass of the sample. The hydrophobicity of the bilimbi was compared to those of silica and pyrolysed bilimbi covered with polystyrene (BAP-polystyrene).

The types of silica used for the comparison was fumed silica. The BAP-polystyrene was prepared by the polymerization of styrene in 30% aqueous hydrogen peroxide (H_2O_2) together with pyrolysed bilimbi (BAP). 0.1 mL of H_2O_2 was added to 5 mL of styrene. The mixture was stirred slowly at 125 rpm with temperature of 90 °C. The BAP was then added to the mixture and stirred continuously for 3 hours. After 3 hours, the BAP was taken out from the mixture and heated in oven at temperature of 110 °C for overnight.

2.4 Kinematic Diffusion Test

The kinematic diffusion of the bilimbi was tested with different types of lubricants; water, motor oil grade SAE 40 and motor oil grade SAE 30. The motor oil grade SAE 40 and SAE 30 represents bulky substrates due to their high kinematic viscosity, meanwhile water, which is low in kinematic viscosity, represents non-bulky substrates. The main purpose of the diffusion test is to know the potential of prepared bilimbi as a hierarchical porous catalyst, which can diffuse bulky molecules. About 0.1 mL of each lubricant was dropped onto the surface of the pyrolysed bilimbi. The size of BAP used was 1 cm in height and 1 cm in diameter. The diffusion time of each lubricant was taken when the lubricant is spotted on the filter paper at the bottom of the pyrolysed bilimbi. The test was done in an open condition at room temperature. The kinematic diffusion test was repeated thrice as to ensure constant diffusion time.

3.0 RESULTS AND DISCUSSION

The main purpose of using freeze drying method is to remove all the water content in bilimbi, which then leave the porous structure in its original morphology [6]. Although thermal drying method can also be used to remove the water, it will produce undesirable shrinkage and changes the morphology of the bilimbi [7]. Therefore, freeze drying is the best method to remove water content and retain the morphology of the bilimbi.

Figure 2 shows the SEM images of the freeze-dried bilimbi (BBP), the pyrolysed bilimbi (BAP), pore structure of the bilimbi after pyrolysis at the outer part and pore structure of bilimbi after pyrolysis at the center. After the removal of all the water by freeze drying method, SEM images showed that the bilimbi has porous structures. Further pyrolysis of the bilimbi revealed that the porous structure in the bilimbi becomes more defined and clear. With magnification, it is shown that the pore diameter at the center part of the BAP is around 25 µm, which is smaller compared to the pore diameter of the outer part. The pore diameter at the center part of the bilimbi is around 6 to 12 µm whereby the pore diameter at the outer part is around 25 to 30 µm.

Therefore, from the SEM images it is proven that *Averrhoa bilimbi* possesses hierarchical porous structure.

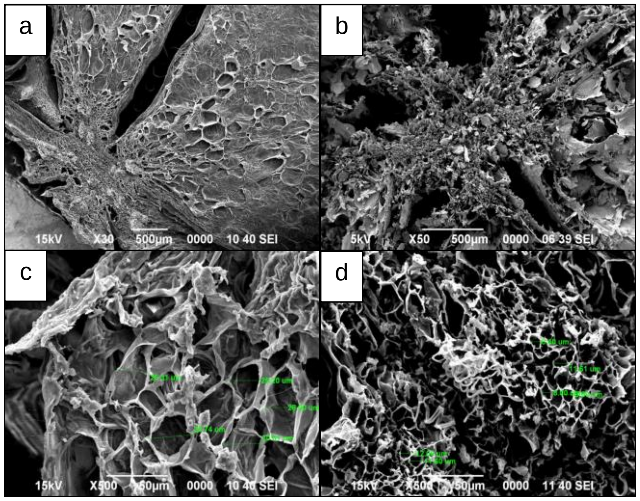


Figure 2 SEM images of (a) freeze-dried bilimbi, (b) bilimbi after pyrolysis, (c) pore structure of bilimbi after pyrolysis at the outer part and (d) pore structure of bilimbi after pyrolysis at the center

The FTIR spectra of freeze-dried bilimbi (BBP) and pyrolysed bilimbi (BAP) are presented in Figure 3. In BBP, the characteristic absorption bands at 3420, 1661 and 1263 cm^{-1} originated from the streching mode -OH, bending mode -OH and -C-O, respectively. These peaks confirmed the cellulose nature of the *Averrhoa bilimbi*. After pyrolysis, all the FTIR peaks assigned to cellulose were diminished. The absorption band at around 2934 cm^{-1}, which is assigned to C-H stretching, has disappeared. However, the BAP's spectrum still shows the strong absorption band of $–CH_2$ scissoring at 2934 cm^{-1}. This shows the complete elimination of cellulose from bilimbi and only the carbon structure was left after pyrolysis.

The prepared bilimbi was pyrolysed in order to remove all of the impurities. Pyrolysis is a thermochemical method which decomposed organic material at elevated temperature in the absence of oxygen. The thermogravimetric (TG) curves of BAP and BBP are depicted in Figure 4. The TG curve of BBP showed a three-stage weight loss. The first-stage is desorption of water and adsorption of gas molecules (<130°C) followed by high percentage of weight loss (60%) from 130 to 350°C which due to the decomposition of organic compounds and mineral contents. While in the last stage, the weight loss around 20% was caused by the decomposition of other organic compounds and mineral contents which evaporate at temperature higher than 350°C. On the other hand, the TG curve of BAP showed a two-stage weight loss. In the first-stage, the weight loss around 4% was due to desorption of water and adsorption of gas molecules (<200°C). While in the second stage, the weight loss around 40% was caused by the decomposition of carbon residues and organic compounds which evaporate at temperature higher than 350°C.

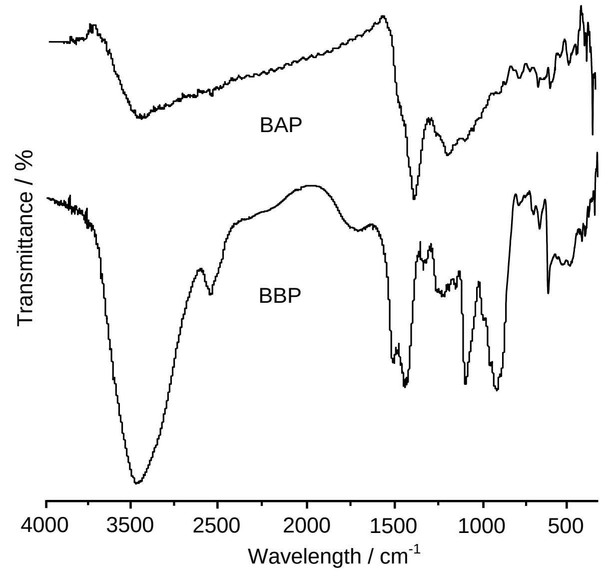


Figure 3 FTIR spectra of pyrolysed bilimbi (BAP) and freeze-dried bilimbi (BBP)

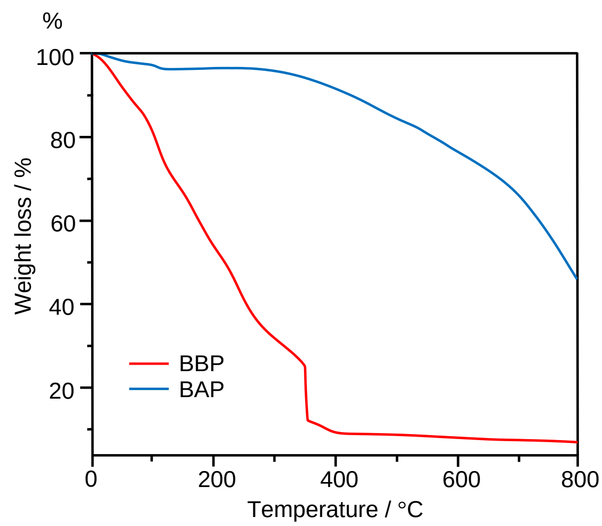


Figure 4 Thermogravimetric analysis curves of freeze-dried bilimbi (BBP) and pyrolysed bilimbi (BAP)

Figure 5 shows the comparison of the percentage amount of adsorbed water for BAP, BAP-polystyrene and silica. As commonly known, silica is hydrophilic due to the silanol (Si-OH) groups on the surface, meanwhile polystyrene is a hydrophobic material. From the figure, it shows that the water capacity in BAP is higher compared to that of silica and BAP-polystyrene. This indicates that BAP possesses more hydrophilic properties compared to silica and BAP-polystyrene.

The diffusivity of water, motor oil grade SAE 30 and motor oil grade SAE 40 through BAP are shown in Figure 6. The motor oil grade SAE 40 with 12.5×10^{-6} m^2/s of kinematic viscosity took longer diffusion time in compared with motor oil grade SAE 30. Meanwhile, water, with 0.29×10^{-6} m^2/s of kinematic viscosity, only took about a few seconds to diffuse through the BAP. Although the high kinematic viscosity for the lubricants took a longer diffusion time compared to water, they are still diffusible due to the hierarchical pores in BAP that are highly interconnected. Therefore, kinematic diffusion test compliments the SEM images of hierarchically porous pyrolysed bilimbi (BAP).

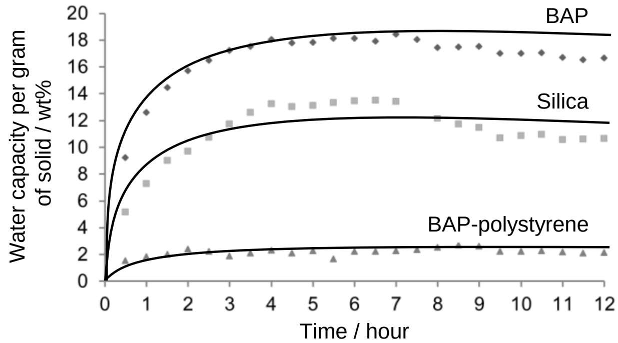


Figure 5 The percentage of water adsorption on the surface of pyrolysed bilimbi (BAP), bilimbi after pyrolysis covered with polystyrene (BAP-polystyrene) and silica

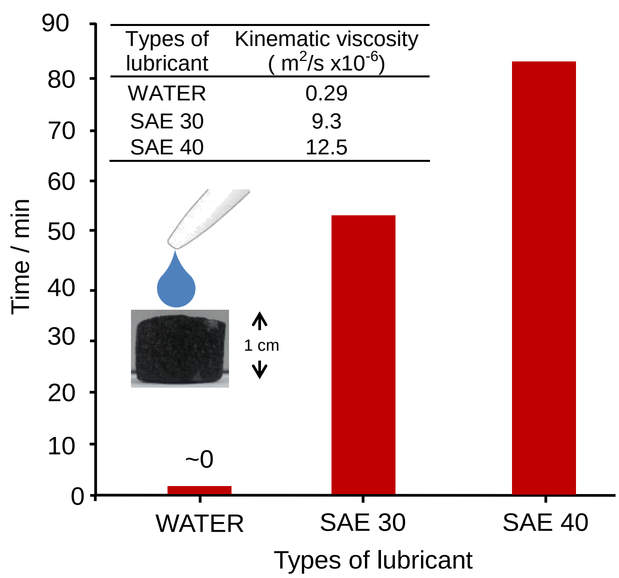


Figure 6 The kinematic diffusion of different types of lubricant through pyrolysed bilimbi (BAP)

4.0 CONCLUSION

The freeze-dried *Averrhoa bilimbi* retained a good morphology after complete removal of water and the pyrolysed *Averrhoa bilimbi* showed a dominant hierarchical porous structure based on the SEM image. The pyrolysed bilimbi also showed hydrophilic properties and good diffusivity of bulky molecules. Therefore, it can be concluded that hierarchical porous carbon of *Averrhoa bilimbi* has potentials to be used as catalysts and can enhance the diffusivity of bulky catalytic reactions.

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