

Preparation and Characterization of Activated Carbon from Gelam Wood Bark (*Melaleuca cajuputi*)

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Abstract. In this study, Gelam wood bark (*Melaleuca cajuputi*) was used as precursor to prepare the activated carbon. The preparation process consisted of $ZnCl_2$ impregnation followed by carbonization in nitrogen at 500°C for 3 hours and carbon dioxide for 1 hour. The optimum surface area was obtained at 25 % of $ZnCl_2$, which is 1213 and 1443 m^2/g for BET and Langmuir, respectively. The activated carbon shows acidic properties and low ash content. Other characteristics of the resulting activated carbon are also discussed.

Abstrak. Dalam kajian ini, kulit kayu gelam (*Melaleuca cajuputi*) telah digunakan sebagai bahan mentah untuk penyediaan karbon teraktif. Proses penyediaan merangkumi impregnasi dengan larutan $ZnCl_2$ diikuti dengan pengkarbonan dalam aliran nitrogen pada suhu 500°C selama 3 jam dan karbon dioksida selama 1 jam. Luas permukaan yang optimum telah diperolehi pada 25% $ZnCl_2$ iaitu 1213 dan 1443 m^2/g masing – masing bagi BET dan Langmuir. Karbon teraktif ini menunjukkan sifat keasidan dan mempunyai kandungan abu yang rendah. Sifat – sifat lain bagi karbon teraktif yang dihasilkan turut dibincangkan.

Keywords : Activated carbon, surface area, porosity

Introduction

Activated carbon is a black solid substance resembling granular or powdered charcoal. It is a processed carbon material with a highly developed porous structure and a large internal specific surface area¹.

The preparation of activated carbon with different pore sizes can be achieved by using physical or chemical activation process. In both methods, the development of porosity is different in term of practical procedures and mechanism. In physical activation the generation of porosity took place via selective elimination of the more reactive carbon of the structure and further gasification led to the production of the activated carbon with the sought pore structure.

In chemical activation process, the precursor is mixed with a chemical such as $ZnCl_2$ or H_3PO_4 , carbonized and washed to produce the activated carbon. Following the thermal decomposition of the precursor, the chemical reacts with the product causing reduction in the evolution of volatile matter and inhibition of the particle shrinkage. Once the chemical is removed by exhaustive washing, a large amount of porosity is formed [1,2].

In determining the surface area and pore structure, adsorption of N_2 gas at $-196^\circ C$ is used and the isothermal equilibrium data is fitted using either Langmuir or BET equations [1]. However, other method such as adsorption of methylene blue [3] or iodine [4,5] has been employed to perform such task. In this study, wood bark from a tropical tree (Gelam) was used as a precursor to produce activated carbon. This plant could be found in swampy ground near coasts of Malaysia. Gelam is a medium size single stem tree, which is also known as paper bark tree. The bark is whitish or light grey in colour, layered and papery. The bark is used for caulking boats whereas the wood is a useful source of fuel in places where mangrove wood is not easily available.

Experimental

Sample preparation

Gelam wood bark was cut into small pieces (0.5 – 1.0 cm in length), washed with distilled water and oven dried at 120 °C overnight. A series of 10 grams of the sample was mixed with 100 ml of $ZnCl_2$ solution of various concentrations (5 - 40 % w/w). The impregnation process was performed at 70 °C in an oil bath until the excess water had evaporated. The impregnated sample was dried in an oven at 120 °C

overnight. The sample was placed inside a quartz tube and inserted horizontally into the middle of a tubular electric furnace. The carbonization and activation were carried out at 500 °C under N₂ gas flow for 3 hours followed by CO₂ gas flow for 1hour. The resulting activated carbon was washed with 0.05 M HCl followed by distilled water until traces of chloride ions were no longer detected.

The activated carbon was characterized by its surface area, porosity, surface topography, adsorption of iodine, adsorption of methylene blue, pH and ash content. The determination of surface area and porosity were performed by adsorption of nitrogen at -196 °C using Micromeristic ASAP 2000 instrument. A scanning electron micrograph of the samples was made by means of the JEOL JSM-35C instrument.

In determining the iodine number, 10 ml of 5 % by weight HCl was added to 1 g of activated carbon and was allowed to boil. After the solution was cooled to room temperature, 100 ml of 0.1N iodine solution was added. The content was shaken vigorously and filtered. 25 ml of the filtrate was titrated with 0.1 N sodium thiosulphate in the presence of starch as indicator. To determine the decolorizing power of the resulting activated carbon, 50 ml of 200 ppm methylene blue solution was shaken for 30 minutes in a 250 ml Erlenmeyer flask containing 0.1 g activated carbon and then filtered using a membrane filter. The color of the filtrate was compared with a control using Shimadzu UV-160A Spectrophotometer.

Determination of pH was performed by gently boiling 100 ml of distilled water in an Erlenmeyer flask containing 0.1 g activated carbon for 5 minutes. The pH was measured after the solution was diluted to 200 ml and cooled to room temperature. In determining the ash content, 0.1 g of the activated carbon was heated at 500 °C for 4 hours, cooled in a desiccator and weighed.

Results and Discussion

Impregnation of activated carbon

Figure 1 showed that the yield increased as the concentration of ZnCl₂ impregnating solution increased. It approached an optimum point at 15 % of ZnCl₂ with 64 % yield. A further increase in ZnCl₂ loading led to a decrease in yield, which may be attributed to the incomplete carbonization of Gelam wood bark.

Surface area and porosity

Temperature has been reported to play an important role in producing optimum surface area of activated

carbon. Preliminary works have shown that by heating a material at 500 – 700°C for 3 hours would lead to the formation of activated carbon with large surface area [5, 6]. These experimental conditions were adopted in the activation process of this study.

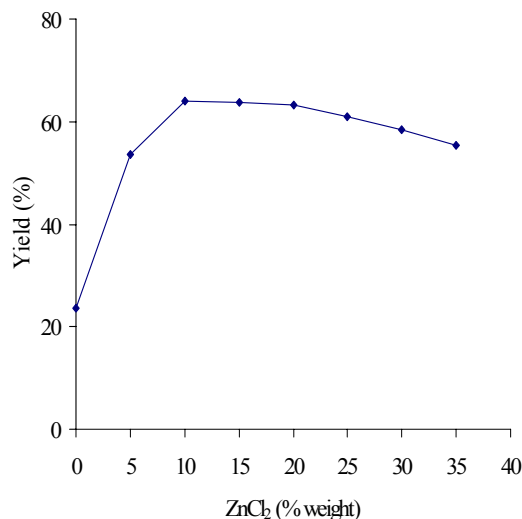


Figure 1 : The effect of the concentration of ZnCl₂ impregnation solution on the yield of the resulting activated carbon

One of the foremost important properties of activated carbon is that they are highly microporous and have large surface areas. These properties could be affected by varying the amount of activation reagents and other reaction parameters such as temperature and reaction time.

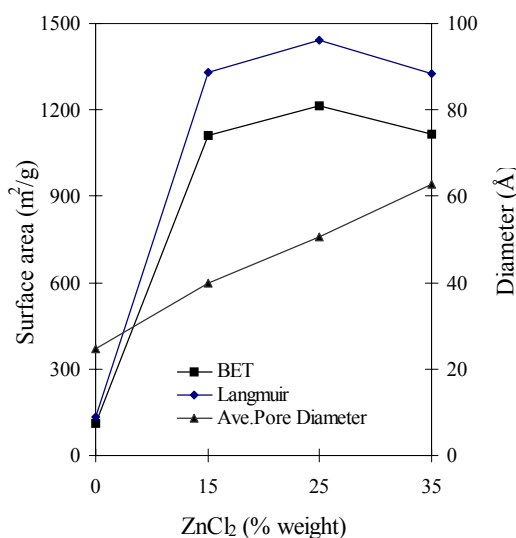


Figure 2 : The effect of the concentration of ZnCl₂ impregnation solution on the surface area and average pore diameter of activated carbon

The surface areas of the resulting activated carbon prepared from gelam wood bark impregnated with various concentration of $ZnCl_2$ solution is given in Figure 2. The BET surface area of the physically activated carbon (0 % w/w $ZnCl_2$) is much lower compared to that of chemically activated carbon. It increased dramatically upon the introduction of $ZnCl_2$ and reached a maximum value of $1213 \text{ m}^2/\text{g}$ at 25 % w/w $ZnCl_2$. A slight decrease in the surface area was

observed with a further increase of $ZnCl_2$. Similar phenomenon was observed for the Langmuir surface area although the values were slightly higher compared to that of BET. The micropore surface area increased with increasing percentage of zinc impregnation solution. It reached a maximum value at 15 % w/w $ZnCl_2$. Above this concentration; a slight decrease in the micropore area was detected.

Table 1 : Surface Areas of the Resulting Activated Carbon

Samples $ZnCl_2$ (% w/w)	Surface area (m^2/g)			Micropore Volume (cc/g)	Ave. pore diameter \AA
	BET	Langmuir	Micropore		
0	111	135	53	0.0207	25
15	1113	1329	385	0.1558	40
25	1213	1444	326	0.1306	50
35	1114	1327	313	0.1248	63

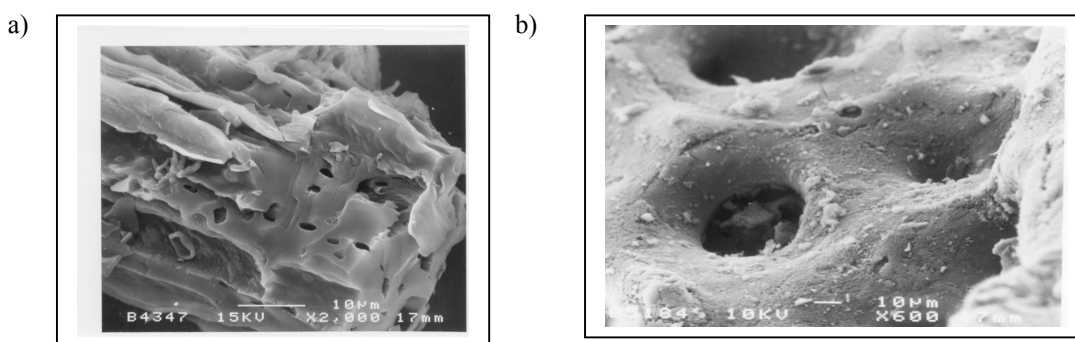


Figure 3 : Scanning electron micrographs of activated carbon impregnated with (a) 0 % (b) 25 % $ZnCl_2$

These results indicate that $ZnCl_2$ plays an important role in increasing the surface area of the activated carbon. The increment of surface area may be achieved via the creation of new micropores as indicated by the rise in micropores surface area and volume (Table 1). It should also be noted that the increase in micropore area was accompanied by an increase in average pore diameter. Hence, indicating that, up to 15 % w/w $ZnCl_2$, the increase in surface area may be attributed to the formation of new micropores and the widening of the micropore sizes. At 25 % w/w $ZnCl_2$, where the maximum surface area for BET and Langmuir was achieved, a slight decrease in micropore surface area was noted along with the further increase in pore size.

Therefore, further increase of the BET and Langmuir surface area is attributable to the widening of the pore sizes. The drop in micropore surface area and volume is also an indication to another role played by $ZnCl_2$ i.e. converting micropores to mesopores. This phenomenon is substantial at higher $ZnCl_2$ loading which also lead to a decrease in the BET and Langmuir surface area. The entire above

phenomenon are consistent with those observed by other researchers [7, 8]. Rodriguez *et al.* [2] offered some explanation to the development of porosity of activated carbon. During impregnation, the present of $ZnCl_2$ led to some hydrolysis reactions and the swelling of the particle but prevent the formation of tar during heat treatment.

At low concentration, the small amount of $ZnCl_2$ can be distributed uniformly with high dispersion throughout the interior of the particle hence, after washing, produced a uniformly microporous carbon. At higher concentration, a larger swelling of the particle was produced but the distribution of $ZnCl_2$ throughout the interior of the particle was poor. Thus, the pore volume increased with heterogeneous pore size distribution. Figure 3 represents the morphology of the resulting activated carbon prepared via physical and chemical activation methods. Both micrographs showed original pores from the starting material. The presence of mesopores and micropores, although supported by the findings from the BET surface area, was not visible from the micrographs.

Iodine adsorption and methylene blue decolourizing power.

Iodine adsorption is a simple and fast adsorption method to determine the adsorptive capacity of activated carbon, also known as iodine number. The amount of iodine adsorbed increased rapidly with the increased in ZnCl₂ and reached a maximum at 15 % w/w. Further increase in ZnCl₂ concentration led to an insignificant increase in the iodine adsorption. The iodine number value is also an indication to the surface area of the activated carbon according to Puri and Bansal [3]. Another solute that has been used to determine the surface area and the pore size distribution of activated carbon is methylene blue. The methylene blue value represent the dsorptive capacity of activated carbon for molecules with dimension similar to methylene blue and the surface area which results from the presence of pore sizes greater than 1.5 nm. The adsorptive capacity of methylene blue also increased with the introduction of ZnCl₂ solution and gave a maximum value of 51 mg/g at 30 % w/w.

pH and Ash Content

pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. The presence of acid functional group such as carboxyl, phenolic and others on the surface of carbon may cause the acidic property of activated carbon. The pyrolysis step increased the microporosity of the sample and decreased the negatively charge surface. Activation process increased the surface area and porosity as well as the surface basicity of activated carbon. Ash is non-carbon or mineral additives, which is not chemically combined with the carbon surface. It consists of various useless mineral substances, which become more concentrate during the activation process. It comprises of 1-20 % and primarily depends on the type of raw material.

High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity.

Conclusion

Gelam wood bark can be used as a precursor in the preparation of activated carbon with high surface areas. This study showed that the chemical activator, ZnCl₂ has developed and created the porosity of activated carbon prepared from Gelam wood bark well. Application of concentration of 15 % increased the surface area and achieved the optimum at 25 % of ZnCl₂ impregnation solution.

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