

## Preparation and characterisation of activated carbon from rambutan seed (*Nephelium Lappaceum*) by chemical activation

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### ABSTRACT

*Activated carbons were prepared from rambutan seed by chemical activation with ZnCl<sub>2</sub> as dehydrating agent. In order to find its characteristic, different impregnation ratio of ZnCl<sub>2</sub> to rambutan seed (0.5 and 2) and carbonization temperature (450 °C and 650 °C) was employed. The carbonization occurred in a tube furnace with nitrogen flow at rate of 0.5 L/min. The results showed that at higher impregnation ratio and carbonization temperature produced a wider BET surface area of activated carbon that was 9.8761 m<sup>2</sup>/g. Total pore volume also increased with increases of these two factors. However, activation yield was decreased with increasing of carbonization temperature. Activated carbon then were tested on synthetic wastewater with pH 11 to study its pH reduction upon contact time and adsorbent dosage. Reduction of pH ranging 6.2 to 6.8 with employment of 2g/100ml adsorbent dosage at 180 minutes contact time.*

**Keywords** - *Activated carbon, Carbonization temperature, Impregnation ratio, BET surface area.*

### INTRODUCTION

Activated carbon (AC) is a porous carbon material which has a high adsorption capacity to be used as adsorbent in industries for the purpose of liquids and gasses purification and also as catalyst and catalyst support (Oliveras-Marin et al., 2006). Such industries that employed AC in their treatment process are food and beverages industries, pharmaceutical, automobile and mining (Chandra et al., 2009). Some of natural adsorbent found on earth such as zeolite and clay mineral also has been used widely in wastewater treatment. Clinoptilolite is one of the zeolite families that widely used in the world (Wang and Peng, 2010). AC with high surface area and pore volume can be prepared with any carbonaceous material such as almond shell (Nabais et al., 2010), avocado kernel seeds (Elizalde-Gonzalez et al., 2007), bamboo charcoal (Wang et al., 2010) and plum stones

(Nowicki *et al.*, 2010). Among these, coal and coconut shell are the sources for industrial practice (Chandra *et al.*, 2009).

AC is used as an adsorbent for metals and organic contaminants because of its porous nature and large specific surface area (Alhamed and Bamufleh, 2009). A good AC is the one that can adsorb many pollutants because of its large surface area and pore volume. The factors influencing this characteristic are the nature of that material itself and activation method. Activation methods can be in two which are physical and chemical. Physical activation involving two steps: carbonization at 500 °C to 600 °C followed by activation using mild oxidizing gas such as CO<sub>2</sub> at 800 °C to 1000 °C. The first step is to eliminate the bulk of volatile matter while the second step is to develop porosity and surface area of AC (Mohan and Pittman Jr, 2006). Meanwhile in chemical activation involves one step only where precursor has to incorporate with chemical agent before carbonization. The chemicals such as ZnCl<sub>2</sub> and KOH preventing formation of tar and reducing evolution of volatile matter, thus resulting in high precursor to carbon conversion (Chandra *et al.*, 2009). Carbonization temperature for chemical activation is between 200 °C to 800 °C.

People nowadays tend to have awareness towards the environmental issues such as climate change and try their best to protect our environment. Thus, the utilization of agriculture waste as precursor for AC is focused by researchers. AC from agricultural waste has two main advantages. First is to convert the waste into a valuable material that is adsorbent to remove pollutants in wastewater in a lower cost (Imamoglu and Tekir, 2008). Second is to treat wastewater from metals and organic chemicals by using produced AC. Some AC produced by agricultural waste such as hazelnut shell, apricot stone and walnut shell (Imamoglu and Tekir, 2008).

Rambutan is a seasonal fruit growing in Asian countries such as Malaysia and Indonesia. However, the effort of Malaysia Agricultural Research and Development Institute (MARDI) to conduct research to this species resulted in its production throughout year (MARDI, 2011). The main growing area of rambutan in Malaysia is Kelantan, Johor, Terengganu, Pahang and Kedah that covered 26, 946 hectare and able to produce 86, 085 metric tons of fruits in 2011. Rambutan is blooming in March to July and can be harvested from July to November. There are two types of rambutan based on its peel color. It is yellow rambutan and red rambutan. In Perak, there is a light industry which using rambutan for jam making. The seed of rambutan as waste will be thrown away on landfill. The rambutan seed (RS) of this industry will be utilized to produce AC.

The aim of this research is to prepare AC from RS by chemical activation with ZnCl<sub>2</sub> and characterized based on its BET surface area, total pore volume and activation yield. The influence of carbonization temperature and impregnation ratio to its characteristic was analyzed.

## MATERIALS AND METHODS

### Materials and preparation of AC

Raw RS were washed with distilled water and oven-dried for 24 hour at 104 °C. Then they were cut into size of 6-7 mm before soaking in 0.1 N of sulfuric acid for 24 hours. RS then were washed with distilled water until residual liquid reaching pH 6.

Impregnation of RS was based on mass ratio of zinc chloride to RS. For 2:1, 100 g of solid zinc chloride was mixed with 50 g of RS in 500 ml of distilled water. For 1:2, 25 g of solid zinc chloride was mixed with 50 g of RS in 500 ml of distilled water. The solution was kept agitated for 1 hour at 80 °C. The slurry then was filtered and RS were oven-dried for 24 hour at 104 °C.

Carbonization of RS was take part in 450 °C and 650 °C in a tube furnace. The heating rate was 10 °C/min involving two heating ramps. First were heated from room temperature to 350 °C. Then it was heated to desired temperature ( 450 °C and 650 °C) with nitrogen flow at rate of 0.5 L/min. Samples were held at final temperature for 1 hour for carbonization before cooling down under nitrogen flow.

These AC then were washed with boiled solution of distilled water and 0.5 N of hydrochloric acid. They were washed with hot and cold distilled water alternately until pH solution reached 6.5. They were then dried in an oven at 104 °C for 24 hour before crushing to obtain powder form of AC with size <150 µm. Samples were indicated with aRSACb where a is the impregnation ratio and b is the carbonization temperature. RSAC stands for rambutan seed activated carbon.

### Characteristics

The activation yield of an AC is expected to be high. To calculate activation yield, it is the percentage of mass of AC after carbonization process.

$$\text{Activation yield} = \frac{\text{activated carbon weight}}{\text{raw material weight}} \times 100$$

The surface area of samples was obtained by application of Belsorp Adsorption/Desorption data analysis software with the instrument. The BET surface area was obtained by means of standard BET equation applied in the relative pressure range from 0 – 0.5. Total pore volume also obtained from this analysis.

The pH of adsorbent was measured by mixing of 3 g RSAC with 30 ml of distilled water and agitated for 24 hour as recommended by Acharya et al., (2009). The pH value of solution was measured after 24 hour by using a pH meter.

### Preparation of Synthetic Wastewater Sample

A stock solution of 0.01 M NaOH was prepared by dissolving 0.02 g of NaOH solid in 500 ml volumetric flask. The stock solution was then diluted with deionised water to obtain pH 11.

### Experiment in pH Reduction

In order to investigate the ability in reducing pH of RSAC, it was tested with synthetic sample of pH 11 NaOH. The adsorbent dose was kept constant that was 1g/100ml. The manipulated variable was the contact time. Samples were agitated for 30, 60, and 120 until 540 minutes to observe its reduction in pH. Second experiment was to manipulate the adsorbent dose. The dosage used was 0.4, 0.8, 1.2, 1.6 and 2g/100ml. Agitation speed for both experiments was 180 rpm.

## RESULTS AND DISCUSSION

Table 1 shows the general characteristics of AC obtained from rambutan seed. The characteristics to be discussed are activation yield, BET surface area ( $S_{BET}$ ), total pore volume and pH of RSAC.

Table 1: Characteristics for RSAC samples

Characteristics	0.5RSAC450	0.5RSAC650	2RSAC450	2RSAC650
Yield (%)	25.3	22.2	35.9	28.6
BET surface area (m <sup>2</sup> /g)	1.1403	9.8761	1.1706	6.8941
Total pore volume (cm <sup>3</sup> /g)	6.009E-03	1.652E-02	7.1170E-03	1.3327E-02
pH value	5.6	5.8	5.2	5.6

In producing commercial AC, high yields of products are expected. Activation temperature is a crucial factor on activated carbon yield (Chandra et al., 2009). Figure 1 shows the effect of carbonization temperature on activation yield at different impregnation ratio. Carbonization temperature at 650°C gave less activation yield compared to activation at 450°C.

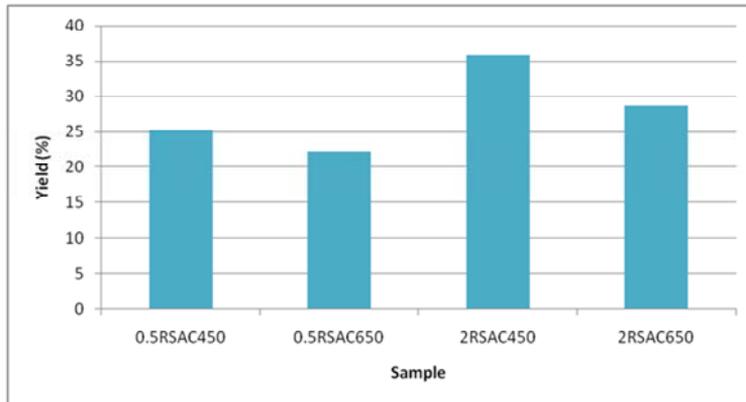


Figure 1: Percentage of activation yield for each sample

RSAC carbonized at 450°C with 2 impregnation ratio gave the highest activation yield that was 35.9% while 25.3% activation yield obtained at 0.5 impregnation ratio. At 650°C carbonization, 2RSAC produced 28.6% of yield higher than 0.5RSAC that was 22.2%. In increasing of activation temperature will decrease activation yield as the weight loss rate is higher initially because of the easiness of volatiles released with higher temperature (Chandra et al., 2009). Carbonization time does not much effect on activation yield rather than carbonization temperature (Sudaryanto et al., 2006). So 1 hour of carbonization time selected in this research.

Figure 2 depicts the effect of carbonization temperature to  $S_{BET}$ . At 650°C,  $S_{BET}$  was wider compared to carbonization at 450°C. This is because as the temperature increasing, surface area increased due to generation of the new micro- and mesopores (Kalderis et al., 2008). Surface area of carbonized RSAC at 650°C was 6.8941 m<sup>2</sup>/g and 9.8761 m<sup>2</sup>/g for impregnation ratio of 0.5 and 2 which is higher than carbonization at 450°C.

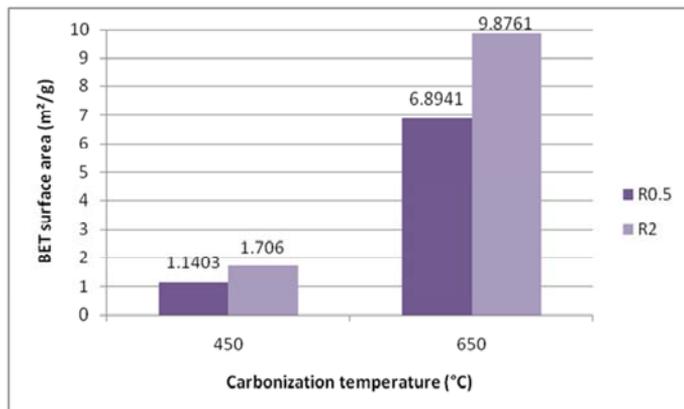


Figure 2: Effect of carbonization temperature to BET surface area

The effect of impregnation ratio towards  $S_{BET}$  also can be referred at Figure 2. At higher impregnation ratio had the wider surface area for RSAC because the chemical agent widening existing micropores and development of new micropores occurs simultaneously and leading to higher  $S_{BET}$  (Chandra et al., 2009). Sample 2RSAC had wider surface area compared to 0.5RSAC that was 1.1706  $m^2/g$  compared to 1.1403  $m^2/g$  at 450°C carbonization.

Total pore volume also influenced by impregnation ratio and carbonization temperature. As increasing of temperature and impregnation ratio, the total pore volume also increased as a large amount of micropore was created (Chandra et al., 2009). Sample 2RSAC650 had the highest total pore volume that was 1.332E-2  $cm^3/g$ .

The adsorbent pH may influence the efficiency in pH reduction. With higher impregnation ratio gave higher pH value. 0.5RSAC for both temperatures had higher pH value compared to 2RSAC samples. At higher carbonization temperature also gave higher pH value. Overall pH of samples was acidic.

Figure 3 below shows the trend of reduction in pH of prepared alkaline solution. Samples were tested by using alkaline solution with initial pH of 11. An obvious descending trend of curves can be observed from initial to the 180<sup>th</sup> minutes. At 180 minutes, pH value for all samples is in between 6.2 and 6.4. However samples with 2 ratio of impregnation have lower pH value at 60 minutes contact time compared to sample with 0.5 impregnation ratio, which is 7.6 and 7.5 for 2RSAC450 and 2RSAC650 respectively. The obvious decreasing is caused by availability of acidic surface on activated carbon to adsorb hydroxide ions in alkaline solution. After 180 minutes, there is no big change on pH value showing that there is no active adsorption occurred onto activated carbon. 180 minutes has been chose as contact time for adsorbent dose study.

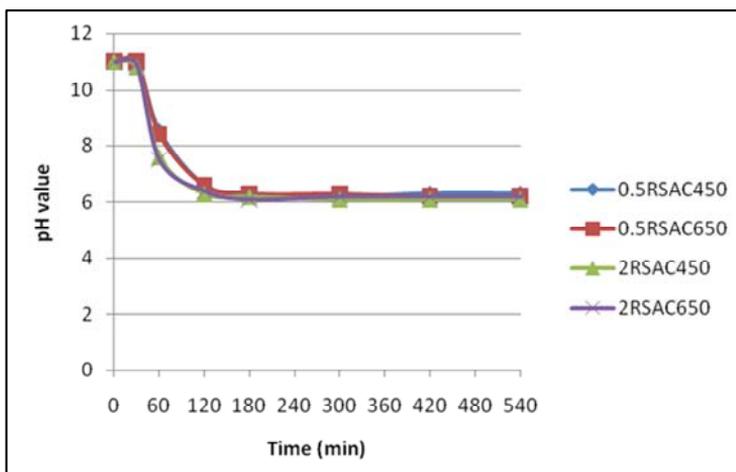


Figure 3: Graph pH value versus contact time

Figure 4 shows the effect of adsorbent dosage on pH reduction. The contact time for this experiment was 3 hours. Graph trend shows that pH reduction increased with increases in adsorbent dose. This happened because much adsorbent dose provides a great availability of exchangeable sites for OH<sup>-</sup> ions in adsorbate (Anandkumar and Mandal, 2009). There was not much difference on pH reduction with usage of all samples. Adsorbent dose of 0.4g/100 ml gave the same pH value that was 10.1 by using all samples. At 0.8g/100ml and 1.2g/100ml dose of 2RSAC450 had reduced the lowest pH among other samples to 9.2 and 8.4. At the end of experiment 2RSAC450 had the greatest reduction that was 6.3 with dose of 2g/100ml. 2RSAC450 had reduced the solution pH the lowest among other samples.

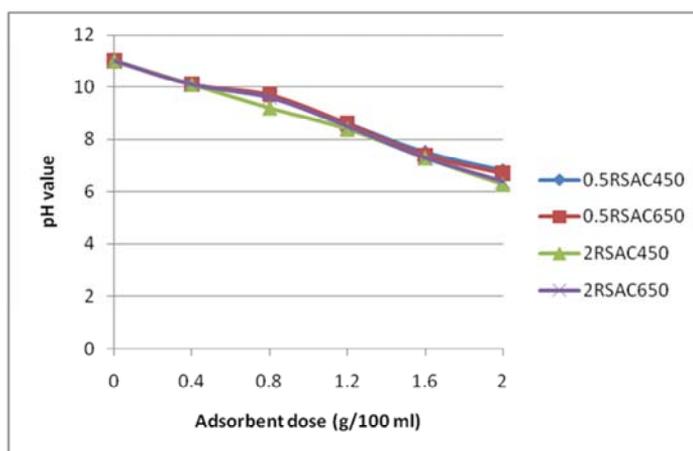


Figure 4: Effect of adsorbent dose on pH reduction

Prepared activated carbons were tested on adsorption of ferum and sulfate ion. However, negative results obtained showing that RSAC not suitable to be used as adsorbent for these ions. Test on reactive red dye removal also gave negative result.

## SUMMARY AND CONCLUSION

Activated carbons were prepared from rambutan seed by activation of zinc chloride at different impregnation ratio and carbonization temperature where significant effect on characteristics of activated carbon produced was studied. The ZnCl<sub>2</sub> to rambutan seed ratio of 2 and carbonization at 650 °C was found to be the best condition to obtain high surface area with 9.8761 m<sup>2</sup>/g. By adjusting the carbonization temperature and impregnation ratio, pore structure of carbon can be altered. However, to remove ferum and sulphate ion by using prepared activated carbon is not suitable. Same goes to removal of reactive red dye.

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