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Preparation and Characterization of Activated Carbon from the Sea Mango (Cerbera Odollam) with Impregnation in Phosphoric Acid (H_3PO_4)

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The properties of the activated carbon from Sea Mango (*Cerbera Odollam)* prepared from chemical and physical activation was studied. The sample was impregnated with phosphoric acid (H_3PO_4) at the impregnation ratio of precursor to activant as 1:2 and followed by thermal activation at 500 °C with different flowing gas i.e. nitrogen (N_2), carbon dioxide (CO_2), steam and at the absent of any gases for duration of 2 hours. The sample experienced two different steps of preparation which were Method 1 and Method 2. In Method 1, the precursor will be thermally heated after the chemical activation process, and the samples were denoted as RIHM1-N, RIHM1-CO_2, RIHM1-S and RIHM1-A which utilize either N_2, CO_2, steam and absent of any gases, respectively. Meanwhile in Method 2, the carbonization process with N_2 flow at 200 °C was done prior to chemical and thermal activation. This type of treatment method was denoted as RCIHM2-N, RCIHM2-CO_2 RCIHM2-S and RCIHM2-A, which use the same flowing gases as described previously. The surface area of the activated carbon was determined using standard method (ASTM) of iodine test. A higher iodine number reading was given by the sample prepared via Method 2 i.e. 1021.74 mg/g, 1069.98 mg/g 902.40 mg/g and 1040.58 mg/g for sample RCIHM2-N, RCIHM2-CO_2, RCIHM2-S and RCIHM2-A, respectively. For sample prepared via Method 1, the iodine number measurement for sample RIHM1-N, RIHM1-CO_2, RIHM1-S and RIHM1-A were 896.480 mg/g, 810.900 mg/g, 973.70 mg/g and 856.217mg/g, respectively.

Keywords : Sea Mango (Cerbera Odollam), activated carbon, phosphoric acid, yield, surface area.

INTRODUCTION

Activated carbons are one of the most widely used adsorbent. They were derived from a versatile material for a wide range of applications including gas purification, gold purification, metal extraction, medicine, catalyst, water purification, recovery solvent and many others applications (Arami-Niya *et al.* 2010, Adinata *et al*. 2007, Budinova *et al*. 2006). The past decade has seen the rapid development in production of activated carbon from a variety of raw materials and different method of processing. Traditional examples as raw material for activated carbon production were: wood, coal and coconut (Girgis *et al*. 2007). However, the used of this precursor are having a serious effect to the environment and food security. Therefore exploring the economical supplies for the production of activated carbon is necessary. A low-cost forest and agricultural waste were recognized. A number of research has been reported on the production of activated carbon from agricultural waste, such as acorn shell (Sahin and Saka 2013), local peach stone (Girgis *et al*. 2007), empty fruit bunch (Foo and Hameed 2012) and jackfruit peel waste (Prahas *et al*. 2008).

Activated carbons with a high porosity and surface area were prepared by either physical, chemical activation or combination of both activation step using appropriate precursor through optimizing the activation process condition (Srinivasakannan and Bakar 2004). Physical activation involved two stage processes of carbonization of the raw material and activation of the char at high temperature, while chemical activation involve impregnation of the precursor with appropriate activation agent followed by pyrolysis in inert atmosphere (Budinova *et al*. 2006). Normally activating agents used are phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), and alkaline metal compounds like potassium hydroxide (KOH) and sodium hydroxide (NaOH). Usually, H_3PO_4 and $ZnCl_2$ are used for the activation of lignocellulosic material which not been carbonized previously; while KOH are used for the activation of char. H_3PO_4 is most preferred compared with $ZnCl_2$, KOH and NaOH because of the environmental disadvantage related with $ZnCl_2$ (Srinivasakannan and Bakar, 2004). While KOH and NaOH are not preferable as activation agent because of hazardous, expensive and corrosive factors (Adinata *et al*. 2007).

In this study, two types of preparation step were studied. The sample was impregnated with phosphoric acid (H_3PO_4) at the impregnation ratio of precursor to activant as 1:2 and followed by thermal activation at 500 °C with different flowing gas i.e. nitrogen (N_2), carbon dioxide (CO_2), steam and at the absent of any gases for duration of 2 hours. The sample experienced two different steps of preparation which were Method 1 and Method 2. In Method 1, the precursor will be thermally heated after the chemical activation process, for the meantime in Method 2, the carbonization process with N_2 flow at 200 °C was done prior to chemical and thermal activation.

In the present investigation, Sea Mango (*Cerbera Odollam*) was used as precursor in preparation of activated carbon by followed either Method 1 or 2. In this study the feasibility of the preparation of high quality activated carbons by using different method of preparation via combination of chemical activation with H_3PO_4 and physical activation with several flowing gases. The surface area of the new carbon sorbent was investigated using iodine number.

MATERIAL AND METHODS

Raw Material Preparation

The non-edible fruit; Sea Mango (*Cerbera Odollam)* was collected along the road side of Kompleks Pusat Pengajian Jejawi 3, Jejawi situated in Perlis. The seeds were removed from its fibrous shell, whilst the fibrous shell was washed, crushed and dried in an oven 105°C for 24 hours in order to remove the moisture content. The precursor was ground and sieved into fine particle of 1-2 mm in size. Then, the fine particles were divide into two categories, to either follow Method 1 or 2. Phosphoric acid (H_3PO_4) was diluted using distilled water to prepare 50% H_3PO_4 solution.

Preparation of Activated Carbon

Method 1

In Method 1 the accurate of the sample weight was directly impregnated with phosphoric acid impregnation ratio precursor to activant 1:2, and dehydrated in a drying oven at 110 °C overnight. Then, the sample was activated thermally at 500 °C for 2 hours duration with nitrogen gas at flow rate 1.5 L/min. After the heat activation, the sample was washed a few times with hot distilled water. Finally, the activated carbon was dried and kept in air tight closed container. All the steps were repeated with different flowing gas i.e. N_2, CO_2, steam and absent of any gases. The sample in Method 1 denoted as RIHM1-N, RIHM1-CO_2, RIHM1-S and RIHM1-A, respectively. The preparation of activated carbon from Sea Mango via Method 1 is simplified in Figure 1.

Method 2

In Method 2, as simplified in Figure 2, the sample was carbonized at the early stage with N_2 flow at 200 °C for 30 minutes. The sample was cooled in the desiccators until it reached room temperature. Next, the sample will be treated according to the procedure in Method 1. The samples were denoted as RCIHM2-N, RCIHM2-CO_2, RCIHM2-S and RCIHM2-A, respectively.

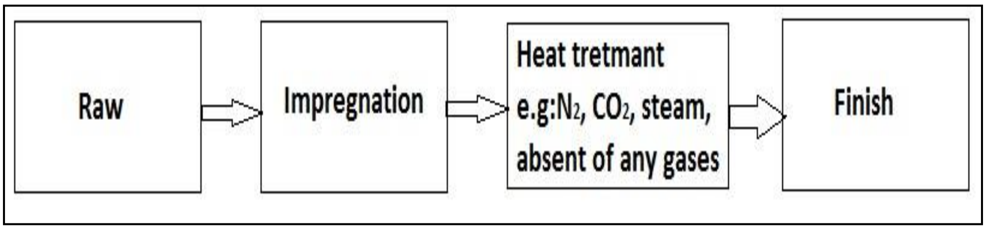

Fig.1 : Preparation of Sea Mango activated carbon via Method 1

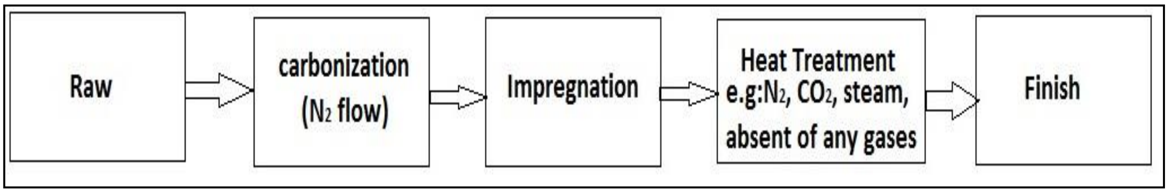

Fig.2 : Preparation of Sea Mango activated carbon via Method 2

Characterization of Activated Carbon

The characterization in term of surface are of activated carbon samples was carried out using Iodine Number Test. The production of activated carbon was further discussed in term of yield and ash content percentage.

Yield is defined as the ratio of the weight of activated carbon obtained to the weight of the initial sample taken for activation, both based on dry weight. While, the ash content of activated carbon was determined by using ASTM Designation: D2866-11, “Standard Test Method for Total Ash Content of Activated Carbon”. Approximately 1 gram of sample was transferred to a crucible and placed in a muffle furnace and heated slowly to a temperature of 650±25°C for 3 hours.

The Iodine Number of activated carbon was determined by using the ASTM designation D4607-94 (reapproved 2011), “Standard Test Method for Determination of Iodine Number of Activated Carbon”. An adsorption Isotherm was needed to plot for every test, so at least 3 different suitable weights of carbon (ranging from 0.7-1.2g) was used for this purpose. A known weight of sample was placed in a 250 ml Erlenmeyer flask. 10.0 ml of 5% (v/v) hydrochloric acid was added to the flask so as to completely wet the sample. The content was gently boiled for 30±2 s to remove any sulphur which may interfere with the results. It was then cooled to room temperature. 100.0 ml of standardized iodine solution (0.100N) was added to the flask, which was stopped immediately. The flask was shook vigorously for 30±1 s and subsequently filtered through Whatman 2V filter paper. The first 20-30ml of filtrate was used for rinsing the pipette and then discarded. 50.0 ml of the remaining filtrates was titrated with a standardized $Na_2S_2O_3$ solution using starch solution as indicator. Iodine Number is defined as the iodine adsorbed (in milligram) per gram of carbon at a residual iodine concentration of 0.02N.

RESULT AND DISCUSSIONS

Product Yield

Two different methods of preparation were applied which were known as Method 1 and Method 2 and the product yield was measured. In addition, four different gases flowed during thermal activation at 500 °C for each method; N_2, CO_2, steam and absent of any gases. The samples were denoted as RIHM1-N, RIHM1-CO_2, RIHM1-S and RIHM1-A for Method 1 route of preparation. Samples were denoted as RCIHM2-N, RCIHM2-CO_2, RCIHM2-S and RCIHM2-A was prepared according to Method 2. Different methods of preparation illustrated several results in terms of yield, ash content and iodine adsorption as shown in Table 1.

Table 1. Characteristic of tested activated carbon

Sample[a]	**Yield (wt.%)**	**Ash Content (wt.%)**	**Iodine Number (mg/g)**
Raw	-	2.09	-
Raw Carbonized	-	2.03	-
RIHM1-N	22.04	14.86	896.48
RIHM1-CO_2	22.90	14.67	810.90
RIHM1-A	22.23	14.20	856.22
RIHM1-S	18.44	10.14	973.70
RCIHM2-N	16.89	24.80	1021.74
RCIHM2-CO_2	19.68	14.12	1069.98
RCIHM2-A	17.46	3.73	1040.58
RCIHM2-S	21.89	5.13	902.40

[a] *Note:* RIHM1-*a* denote Raw-Impregnate(50% H_3PO_4)-Heat Thermal (500°C, 2h durations)-Method 1-flowing gas (nitrogen, carbon dioxide, absent of any gases or steam); RCIHM2-*a* denote Raw-Carbonized (200°C, Nitrogen flow)-Impregnate (50% H_3PO_4)- Heat Thermal (500°C, 2h durations)-Method 2-flowing gas (nitrogen, carbon dioxide, absent of any gases or steam).

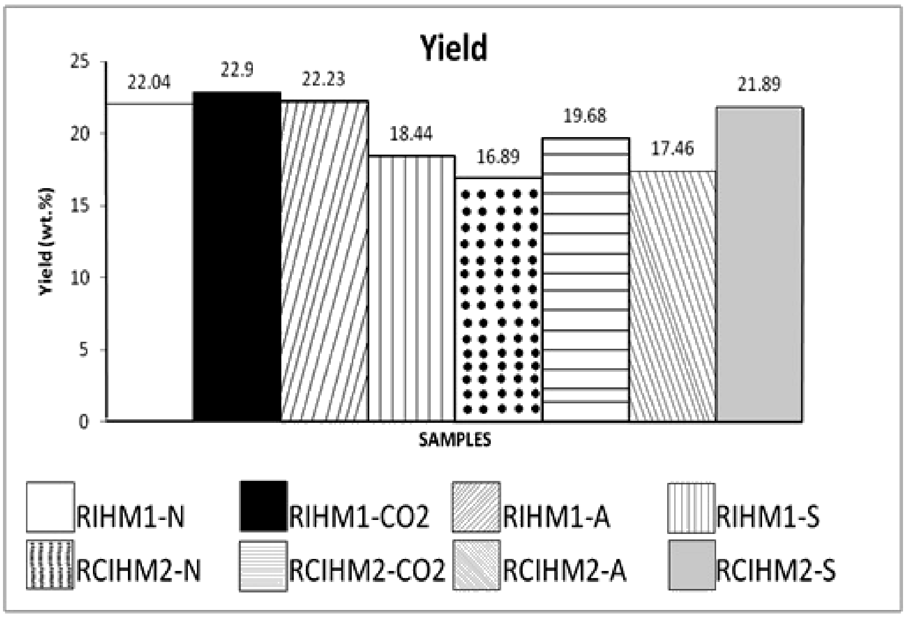

Fig.3 : Sea Mango activated carbon yield prepared at different flowing gas.

As can be seen from Table 1 and Figure 3, the yield for sample RIHM1-N, RIHM1-CO_2, RIHM1-S and RIHM1-A are 22.04 wt%, 22.90 wt%, 18.44 wt% and 22.23 wt%, respectively and sample RCIHM2-N, RCIHM2-CO_2, RCIHM2-S and RCIHM2-A are 16.89 wt%, 19.68 wt%, 21.89 wt% and 17.46 wt%, respectively. It was clearly observed that the range of percentage yield obtained in Method 2 was lower compared to sample prepared from Method 1. This is due to the double heating process occurred during activated carbon preparation according to Method 2. The repetition of heating process at 500°C would reduce the yield of sample in Method 2 as a result of volatile material loss.

Ash Content

The percentages of ash content for each activated carbon were given in Table 1 and Figure 4. The ash contents varied from 3 to 25 wt% for activated carbon samples depending on the activation techniques applied on precursor. Raw and raw carbonized samples show the lowest percentage of ash which are 2.09 % and 2.03% respectively. Lower percentage of ash for this type of precursor shows that Sea Mango has very high and good potential to be an adsorbent and activated carbon. Activated carbon prepared via Method 1 recorded the range of 10 to 15 wt% of ash, while percentage of ash for activated carbon produced via Method 2 is in the range 3 to 24.8 wt%. The lowest and highest ash content was measured in sample RCIHM2-A and RCIHM2-N with 3.73 wt% and 24.8wt %, respectively.

Iodine number

The adsorption capacity was observed via Iodine Number technique through iodine adsorption capacity of activated carbon. This method is based upon three-point isotherm. A standard iodine solution is treated with three different weight of activated carbon under specified conditions. The iodine amount adsorbed per gram of carbon (X/M) is plotted against the iodine concentration in the filtrate (C), using logarithmic axes. If the residual iodine concentration (C) is not

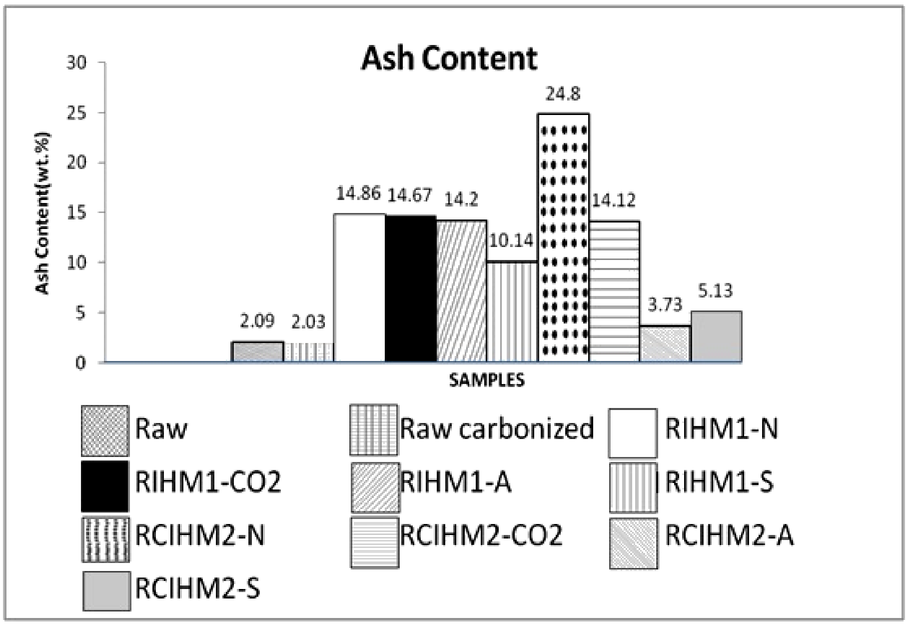

Fig.4 : Sea Mango activated carbon ash content prepared at different flowing gas.

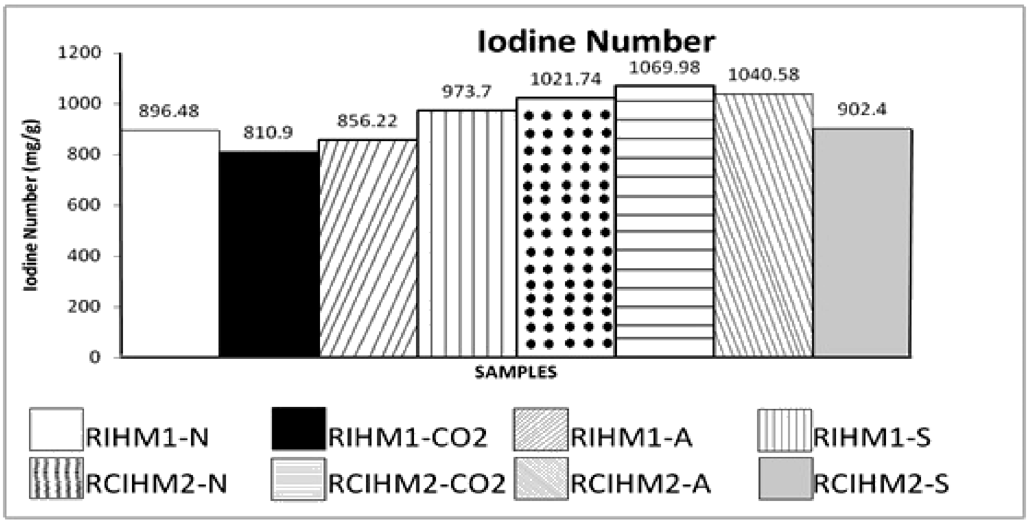

Fig.5 : Sea Mango activated carbon Iodine Number prepared at different flowing gas.

within the range of 0.008 to 0.04 N, the whole procedure should be repeated using different carbon masses for each isotherm point. A least squares fitting regression is applied for the three points. The iodine number is the X/M value when the residual concentration (C) is 0.02 N.

The highest Iodine Number indicated the highest micro porosity and approximation surface area with good precision (Saka 2012). As listed in Table 1 and Figure 5, the highest Iodine Number was shown from Method 2 samples, RCIHM2 in the range of 902.40 to 1069.98 mg/g compared to Method 1 in the range of 810.90 to 973.70 mg/g. It was proven by comparing different method with similar flowing gas, RCIHM2-N and RIHM1-N, 1021.74 and 896.48 mg/g, correspondingly. RCIHM2-CO_2 and RIHM1-CO_2 recorded at 1069.98 and 810.90 mg/g, respectively as well as RCIHM2-A and RIHM1-A measured at 1040.58 and 856.22 mg/g respectively which conclusively summarizes that the maximum iodine number was reach via Method 2 preparation using CO_2. In addition, based on the iodine number adsorption result, preparation of Sea Mango activated carbon via Method 2 has the potential to produce higher micro porosity characteristics as compared to Method 1 due to two stages of heating process.

CONCLUSION

Both methods involved in this study are the combination of chemical and physical activation seems to be promising for preparation of carbon adsorbents. Activated carbons prepared by impregnation of Sea Mango with H_3PO_4 followed by heat thermal in different methods and flowing gasses (nitrogen, carbon dioxide, steam and absent of any gasses) have been compared. The characteristics of the activated carbons were strongly dependent on the condition of the preparation and flowing gasses in the carbonization process. Samples prepared via two-stage activation process (Method 2) generated larger surface area compared to sample produced with one-stage activation (Method 1) which was in the range of 902.40 to 1069.98 mg/g; measured using iodine adsorption number test. The best iodine adsorption potential was shown by sample RCIHM2-CO_2 with iodine number of 1069.98 mg/g.

Chemical Symbols

N_2	:	Nitrogen
CO_2	:	Carbon dioxide
H_3PO_4	:	Phosphoric acid
KOH	:	Potassium hydroxide
NaOH	:	Sodium hydroxide
$ZnCl_2$	:	zinc chloride
$Na_2S_2O_3$	:	Sodium Thiosulfate

Abbreviations

RIHM1-N	:	Raw Impregnated Heat Method 1 (N_2 gas)
RIHM1-CO_2	:	Raw Impregnated Heat Method 1 (CO_2 gas)
RIHM1-A	:	Raw Impregnated Heat Method 1 (Absent of any gases)
RIHM1-S	:	Raw Impregnated Heat Method 1 (Steam gas)
RCIHM2-N	:	Raw Carbonized Impregnated Heat Method 2 (N_2 gas)
RCIHM2-CO_2	:	Raw Carbonized Impregnated Heat Method 2 (CO_2 gas)
RCIHM2-A	:	Raw Carbonized Impregnated Heat Method 2 (Absent of any gases)
RCIHM2-S	:	Raw Carbonized Impregnated Heat Method 2 (Steam gas)
ASTM	:	American Standard Test Method

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